

## IRIDOIDS. AN UPDATED REVIEW. PART I.

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**ABSTRACT.**—Iridoid structures published for the first time during 1980–1989 are listed with available physical and spectral data: mp,  $[\alpha]_D$ , uv,  $^1\text{H}$  nmr,  $^{13}\text{C}$  nmr. Also included are revisions of iridoid structures originally published prior to 1980. The compounds are indexed alphabetically and by molecular weight, and a plant source index is also included.

This review is mainly a compilation of new iridoids reported in the literature since the El-Naggar and Beal review of 1980 (1) through December 1989 (Table 1). The large number of new structures necessitated division into two parts for publication. Secoiridoids, valeriana iridoids, plumeria-type iridoids, and other miscellaneous iridoid-like structures will be published separately. This work does not include the separately recognized classes of bis-iridoid-alkaloids or pyridine monoterpene alkaloids. A few semisynthetic iridoids were included.

The main anticipated use of this review is for the rapid identification of isolated iridoids by  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr spectroscopy. It is intended to be a comprehensive list of iridoid glycoside and aglycone structures for the time period indicated but does not include references to all isolations of a particular compound from all plant sources. Because of this, it can be viewed only as a starting point for biosystematic purposes. Spectral data from first reports of a compound were not always included if later reports gave more detailed assignments, although the original references are given. When multiple papers reported nmr spectral data for a single compound, the higher resolution data obtained in  $\text{D}_2\text{O}$  or  $\text{CD}_3\text{OD}$  were usually used. Compounds reported in the earlier review (1) have been included only when the structures (including stereochemistry) were revised or when significantly better spectral data ( $^1\text{H}$  and  $^{13}\text{C}$  nmr) were reported. Papers detailing  $^{13}\text{C}$ -nmr data of several previously reported compounds have been published (2–6); these compounds were generally not included here.

No judgments were made concerning the interpretation of data in assigning structures nor in the consideration of any compounds as artifacts as opposed to legitimate natural products. Suspected errors in assignments were not corrected unless there was some ambiguity in the numbering of a particular compound. The names given to a compound by the authors of a paper were not corrected (although alternate names from other sources were reported along with the names from the referenced papers).

Structures are arranged in a fashion similar to that of the El-Naggar and Beal review (1). Group 1 contains iridoids with an eight-carbon skeleton; Group 2 contains iridoids with a nine-carbon skeleton and is further divided into subsets depending on whether the ninth carbon is attached to C-4 (Group 2a) or C-8 (Group 2b); Group 3 contains iridoids with ten-carbon skeletons; Group 4 consists of iridoid aglycones; and Group 5 contains bis-iridoids and bis-iridoid aglycones. The oxidation state of C-10 and C-11 (Figure 1) guides the arrangement of compounds in all groups except Group 5, which is ordered by increasing molecular weight. In Group 3, for example, a compound with a C-11 Me and a C-10 Me precedes one with a C-11 Me and a C-10  $\text{CH}_2\text{OH}$ , which precedes a compound with a C-11  $\text{CH}_2\text{OH}$  and a C-10 Me. The available data were listed in the following order: name; molecular formula; molecular weight; melting point ( $^\circ\text{C}$ ); optical rotation (solvent); uv ( $\lambda$  max, nm);  $^1\text{H}$ -nmr (spectrometer frequency, solvent) chemical shifts (in ppm, starting with H-1 and listed in order) with assignments, multiplicities, and coupling constants in Hz;  $^{13}\text{C}$ -nmr (solvent) chemical shifts (in ppm,

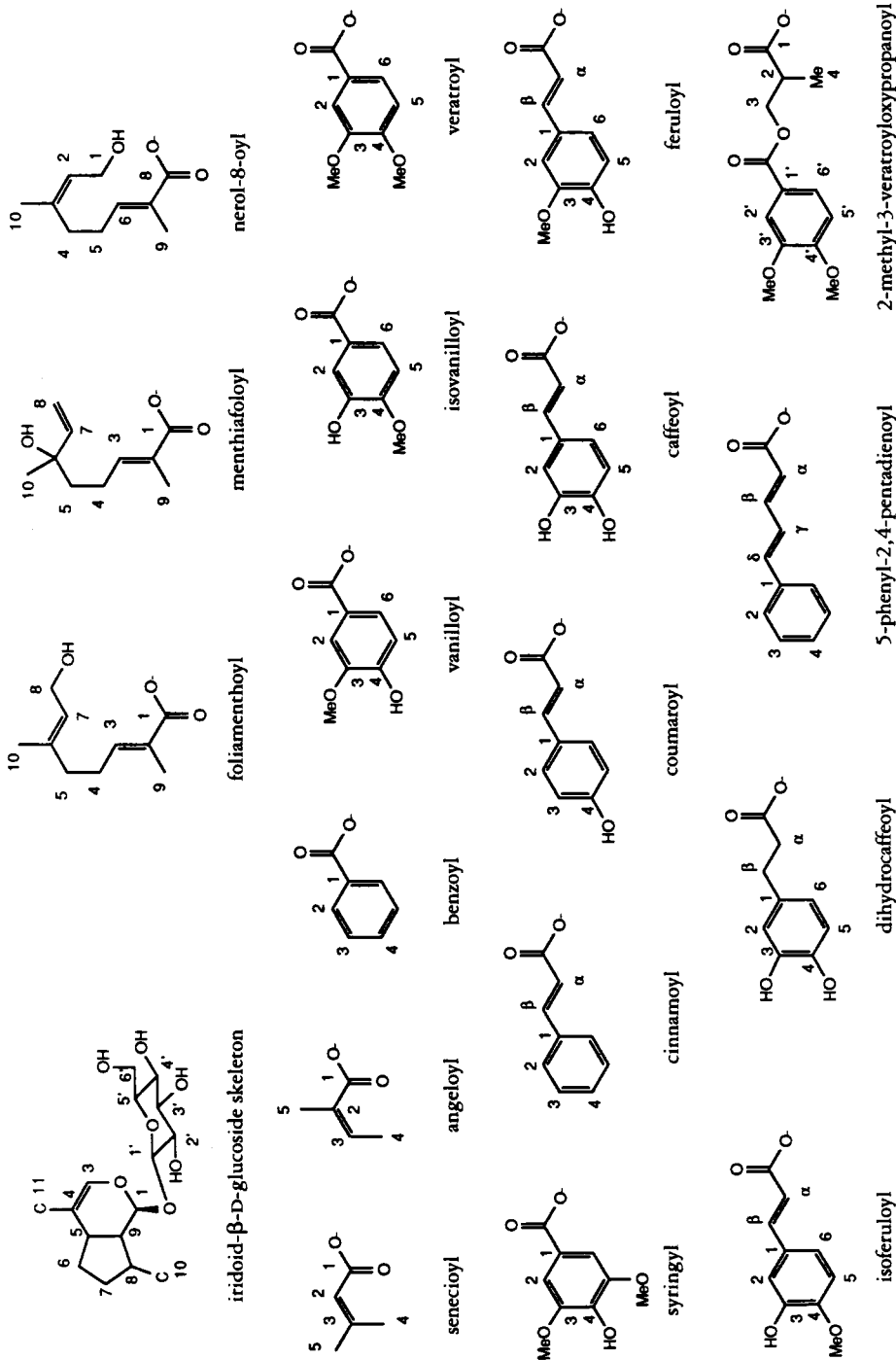


FIGURE 1. Numbering of some common substituents.

starting with C-1 and listed in order) with assignments; plant source (family); reference(s). Assignments with the same superscript may be interchanged. Space considerations required the omission of ir and ms data, but that does not necessarily mean that these data were not reported in the referenced paper. Data for derivatives were not usually listed unless the derivative, rather than the free iridoid, was isolated.

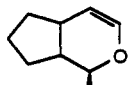
Numbering of the iridoid skeleton and of the most common functionalities is given in Figure 1. The sugar on the C-1 carbon of the aglycone portion is given the single prime (') designation, while additional substituents are designated as double prime (''), triple prime (''''), etc. according to their substitution position on the main iridoid skeleton, except in cases of substituents on other substituents. For example, the sugar portion of a *p*-O-glucosylcinnamate group would be designated as triple prime if the cinnamate bore the double prime designation. For bis-iridoids, the separate parts are designated as a and b, then numbered as above. Cinnamoyl, coumaroyl, etc. groups are in the trans configuration unless otherwise indicated.

Three indices are included: compounds listed alphabetically (Table 2), compounds listed by molecular formula (Table 3), and plant sources listed alphabetically (Table 4).

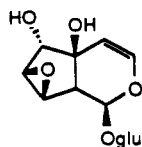
Exhaustive (and exhausting) manual and computer-aided literature searches were employed, but this review should not be used as the only source when determining the novelty of a compound or isolation source.

TABLE 1. New Iridoids

## Group 1 (8-carbon skeleton)

1. UNDULATIN (4'-O-*p*-Coumaroyl-7,8-dihydro-8-dehydroxymethylbartsioside)Oglu-4-O-*p*-coumaroyl

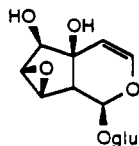
$C_{23}H_{28}O_9$  466.48 mp 227–228° [ $\alpha$ ] –177.7° (MeOH) uv 315, 230 (MeOH) (100 MHz  $CD_3OD$ ) 5.71 (H-1, d, 0.5), 6.38 (H-3, dd, 6.5, 1), 5.16 (H-4, dd, 6.5), 2.95 (H-5, bm), 2.52–2.3 (H-6), 2.3–2.1 (H-7), 1.6–1.8 (H-8), 3.2 (H-9, bm), 4.96 (H-1', d, 7.5), 6.36/7.7 (H $\alpha$ , H $\beta$ , d's, 16), 7.5 (H-2'', d, 9), 6.85 (H-3'', d, 9). *Tecomella undulata* (Bignoniaceae) (7)

2. 6-*epi*-STILBERICOSIDE

Oglu

$C_{14}H_{20}O_{10}$  348.31 [ $\alpha$ ] –67° (EtOH) (500 MHz  $D_2O$ ) 5.25 (H-1, d, 9.6), 6.59 (H-3, d, 6.2), 4.96 (H-4, d, 6.2), 4.08 (H-6, s), 3.69 (H-7, d, 1.7), 3.88 (H-8, d, 1.7), 2.48 (H-9, d, 9.6), 4.85 (H-1', d, 8.1); ( $D_2O$ ) 97.1 (C-1), 144.9 (C-3), 104.3 (C-4), 79.8 (C-5), 77.1 (C-6), 58.8 (C-7)<sup>a</sup>, 59.3 (C-8)<sup>a</sup>, 49.9 (C-9), 100.1 (C-1'), 73.6 (C-2'), 76.7 (C-3'), 70.4 (C-4'), 77.2 (C-5'), 61.5 (C-6'). *Thunbergia alata* (Acanthaceae) (8)

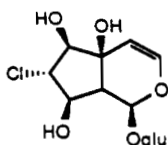
## 3. STILBERICOSIDE



Oglu

$C_{14}H_{20}O_{10}$  348.31 mp 144–146° (hexaacetate) [ $\alpha$ ] –61.5° ( $H_2O$ ) (500 MHz  $D_2O$ ) 5.33 (H-1, d, 8.2), 6.48 (H-3, d, 6.2), 5.04 (H-4, d, 6.2), 4.23 (H-6, d, 1.7), 3.75 (H-7, m), 3.79 (H-8, d, 2.5), 2.58 (H-9, d, 8.2), 4.83 (H-1', d, 8.0); ( $D_2O$ ) 96.5 (C-1), 143.1 (C-3), 107.4 (C-4), 73.4 (C-5), 77.9 (C-6), 59.4 (C-7)<sup>a</sup>, 56.3 (C-8)<sup>a</sup>, 49.7 (C-9), 99.9 (C-1'), 73.5 (C-2'), 76.6 (C-3'), 70.4 (C-4'), 77.2 (C-5'), 61.5 (C-6'). *Stilbe* (Verbenaceae), *Thunbergia* (Acanthaceae) (8,9)

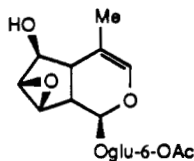
## 4. THUNBERGIOSIDE



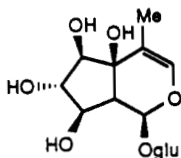
$C_{14}H_{21}ClO_{10}$  384.77 (500 MHz  $D_2O$ ) 5.54 (H-1, d, 3.5), 6.40 (H-3, d, 6.5), 5.19 (H-4, dd, 6.5, 0.5), 3.82 (H-6, d, 8.5), 3.97 (H-7, t, 8.5), 3.84 (H-8, t, 9), 2.35 (H-9, ddd, 9, 3.5, 0.5), 4.78 (H-1', d, 8.0); ( $D_2O$ ) 94.4 (C-1), 141.4 (C-3), 109.0 (C-4), 68.3 (C-5), 81.5 (C-6), 67.4 (C-7), 74.0 (C-8), 53.8 (C-9), 99.3 (C-1'), 73.3 (C-2'), 76.2 (C-3'), 70.4 (C-4'), 77.0 (C-5'), 61.5 (C-6'). *Thunbergia fragrans* (Acanthaceae) (8)

Group 2a (9-carbon skeleton; ninth carbon on C-4)

## 5. 6'-O-ACETYLDEUTZIOSIDE

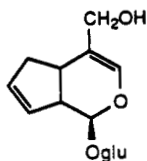


$C_{17}H_{24}O_{10}$  388.37 mp 223–225° (dec)  $[\alpha] -82^\circ$  (MeOH) (90 MHz  $D_2O$ ) 4.78 (H-1, d, 10), 6.17 (H-3, m), 2.06 (H-5), 4.12 (H-6, dd, 7.5, 1.5), 3.62 (H-7, m), 3.68 (H-8, d, 3), 2.55 (H-9, dd, 10, 8), 1.63 (H-11, s), 4.33 (H-6', m), 2.09 (OAc); ( $D_2O/Me_2CO-d_6$ ) 96.8 (C-1), 135.8 (C-3), 113.3 (C-4), 41.0 (C-5), 78.5 (C-6), 59.3 (C-7), 56.2 (C-8), 42.5 (C-9), 16.1 (C-11), 100.1 (C-1'), 73.5 (C-2'), 76.4 (C-3'), 70.2 (C-4'), 74.5 (C-5'), 63.8 (C-6'). *Mentzelia albescens* (Loasaceae) (10)

6. SCABROSIDOL (5 $\beta$ ,7 $\alpha$ -Dihydroxydeutzioside)

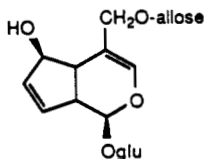
$C_{15}H_{24}O_{11}$  380.35  $[\alpha] -109^\circ$  (MeOH) uv 218 (MeOH) (90 MHz  $D_2O$ ) 5.56 (H-1, d, 1.5), 6.15 (H-3, d, 1.5), 4.0–3.4 (H-6, H-7, H-8), 2.28 (H-9, dd, 11.5, 1.5), 1.58 (H-11, d, 1.5); ( $D_2O$ ) 93.1 (C-1), 135.7 (C-3), 116.0 (C-4), 68.0 (C-5), 81.3 (C-6), 78.3 (C-7), 72.2 (C-8), 53.2 (C-9), 11.6 (C-11), 98.9 (C-1'), 73.3 (C-2'), 77.0 (C-3'), 70.5 (C-4'), 76.2 (C-5'), 61.5 (C-6'). *Deutzia scabra* (Saxifragaceae) (11)

## 7. LYCHNITOSIDE



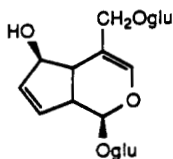
$C_{15}H_{22}O_8$  330.33 *Verbascum lychnitis* (Scrophulariaceae) (12,13)

## 8. ALLOSYLDECALOSIDE



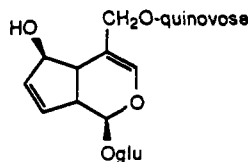
$C_{21}H_{32}O_{14}$  508.48 mp 239° (dec)  $[\alpha] -163^\circ$  ( $H_2O$ ) (90 MHz  $D_2O$ ) 5.06 (H-1, d, 6), 6.48 (H-3, m), 2.78 (H-5, m, 7.5, 4), 4.7 (H-6), 6.03 (H-7, H-8, m), 3.12 (H-9, dd, 8, 6), 4.32 (H-11, m), 4.7 (H-1''), 4.15 (H-3'', bs); ( $D_2O$ ) 98.5 (C-1), 141.6 (C-3), 113.5 (C-4), 44.7 (C-5), 81.0 (C-6), 136.1 (C-7), 134.2 (C-8), 47.7 (C-9), 70.1 (C-11), 99.7 (C-1'), 73.5 (C-2'), 76.5 (C-3'), 70.4 (C-4'), 77.1 (C-5'), 61.5 (C-6'), 99.4 (C-1''), 71.2 (C-2''), 72.0 (C-3''), 67.7 (C-4''), 74.4 (C-5''), 62.1 (C-6''). *Mentzelia albescens* (Loasaceae) (10)

## 9. GLUCOSYLDECALOSIDE



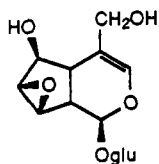
$C_{21}H_{32}O_{14}$  508.48 nonaacetate mp 177–179°  $[\alpha] -126^\circ$  ( $CHCl_3$ ) (90 MHz  $D_2O$ ) 5.06 (H-1, d, 6), 6.48 (H-3, m), 2.76 (H-5, m), 6.01 (H-7, H-8, m), 3.15 (H-9), 4.32 (H-11, m), 4.49 (H-1'', d, 7.5); ( $D_2O$ ) 98.5 (C-1), 141.6 (C-3), 113.3 (C-4), 44.6 (C-5), 80.9 (C-6), 136.1 (C-7), 134.2 (C-8), 47.7 (C-9), 70.3 (C-11), 99.4 (C-1'), 73.4 (C-2'), 76.6 (C-3'), 70.3 (C-4'), 77.1 (C-5'), 61.4 (C-6'), 101.8 (C-1''), 74.0 (C-2''), 76.4 (C-3''), 70.3 (C-4''), 76.4 (C-5''), 61.4 (C-6''). *Mentzelia lindleyi* (Loasaceae) (10)

## 10. QUINOVOSYLDECALOSIDE



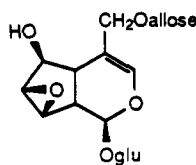
$C_{21}H_{32}O_{13}$  492.48 octaacetate mp 156–157° [ $\alpha$ ] –129° (CHCl<sub>3</sub>) (90 MHz D<sub>2</sub>O) 5.05 (H-1, d, 6), 6.49 (H-3, m), 2.80 (H-5, m), 4.7 (H-6), 6.03 (H-7, H-8, m), 3.13 (H-9, m), 4.32 (H-11, m), 4.51 (H-1", d, 7.5); (D<sub>2</sub>O) 98.7 (C-1), 141.7 (C-3), 113.6 (C-4), 44.9 (C-5), 81.2 (C-6), 136.2 (C-7), 134.2 (C-8), 47.8 (C-9), 70.5 (C-11), 99.6 (C-1'), 73.6 (C-2'), 76.6 (C-3'), 70.5 (C-4'), 77.2 (C-5'), 61.5 (C-6'), 101.9 (C-1"), 74.2 (C-2"), 76.7 (C-3"), 75.8 (C-4"), 72.6 (C-5"), 17.6 (C-6"). *Mentzelia lindleyi* (Loasaceae) (10)

## 11. EPOXYDECALOSIDE (11-Hydroxydeutzioside)



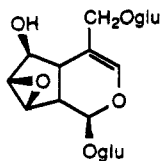
$C_{15}H_{22}O_{10}$  362.33 mp 187–188° (dec) [ $\alpha$ ] –86° (MeOH) (90 MHz D<sub>2</sub>O) 4.89 (H-1, d, 10), 6.42 (H-3, m), 2.28 (H-5, t, 7.5), 4.11 (H-6, bd, 7.5), 3.63 (H-7, m), 3.73 (H-8), 2.54 (H-9, dd, 9, 7.5), 4.05 (H-11, m); (D<sub>2</sub>O) 96.9 (C-1), 139.9 (C-3), 115.8 (C-4), 37.9 (C-5), 78.6 (C-6), 59.1 (C-7), 56.2 (C-8), 42.1 (C-9), 62.0 (C-11), 99.9 (C-1'), 73.5 (C-2'), 76.6 (C-3'), 70.3 (C-4'), 77.1 (C-5'), 61.4 (C-6'). *Mentzelia lindbeimerii* (Loasaceae) (10)

## 12. ALLOSYLEPOXYDECALOSIDE



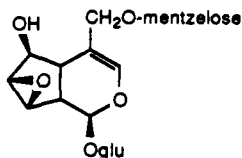
$C_{21}H_{32}O_{15}$  524.48 mp 274–275° (dec) [ $\alpha$ ] –98° (H<sub>2</sub>O) (90 MHz D<sub>2</sub>O) 4.97 (H-1, d, 9.5), 6.55 (H-3, m), 2.32 (H-5, t, 7.5), 4.2 (H-6), 3.69 (H-7, m), 3.78 (H-8, d, 3), 2.59 (H-9, dd, 9.5, 7.5), 4.29 (H-11, m), 4.7 (H-1"), 4.17 (H-3", bs); (D<sub>2</sub>O) 97.0 (C-1), 142.2 (C-3), 111.8 (C-4), 38.3 (C-5), 78.0 (C-6), 59.3 (C-7), 56.1 (C-8), 42.2 (C-9), 69.6 (C-11), 100.1 (C-1'), 73.5 (C-2'), 76.6 (C-3'), 70.3 (C-4'), 77.1 (C-5'), 61.4 (C-6'), 99.2 (C-1"), 71.2 (C-2"), 72.0 (C-3"), 67.7 (C-4"), 74.5 (C-5"), 62.1 (C-6"). *Mentzelia albescens* (Loasaceae) (10)

## 13. GLUCOSYLEPOXYDECALOSIDE



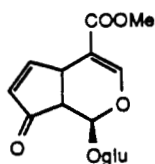
$C_{21}H_{32}O_{15}$  524.48 mp 216–217° (dec) [ $\alpha$ ] –87° (H<sub>2</sub>O) (90 MHz D<sub>2</sub>O) 4.96 (H-1, d, 9.5), 6.54 (H-3, m), 2.35 (H-5, t, 7.5), 4.22 (H-6, dd, 8, 4.5), 3.68 (H-7, m), 3.79 (H-8), 2.52 (H-9, dd, 9.5, 7.5), 4.30 (H-11, m), 4.50 (H-1", d, 7.5); (D<sub>2</sub>O) 97.0 (C-1), 142.2 (C-3), 111.9 (C-4), 38.2 (C-5), 78.1 (C-6), 59.4 (C-7), 56.2 (C-8), 42.2 (C-9), 69.7 (C-11), 100.0 (C-1'), 73.5 (C-2'), 76.7 (C-3'), 70.5 (C-4'), 77.1 (C-5'), 61.6 (C-6'), 101.5 (C-1"), 74.0 (C-2"), 76.7 (C-3"), 70.5 (C-4"), 76.7 (C-5"), 61.6 (C-6"). *Mentzelia lindbeimerii* (Loasaceae) (10)

## 14. MENTZELOSYLEPOXYDECALOSIDE



$C_{20}H_{30}O_{13}$  478.45 mp 236–237° (dec) [ $\alpha$ ] –108° (H<sub>2</sub>O) (270 MHz D<sub>2</sub>O) 4.94 (H-1, d, 9.5), 6.51 (H-3, m), 2.29 (H-5, t, 7.5), 4.15 (H-6, bd, 7.5), 3.66 (H-7, m), 3.77 (H-8, d, 3), 2.60 (H-9 dd, 9.5, 7.5), 4.23 (H-11, 11.5), 4.61 (H-1", d, 1.5), 3.81 (H-2", bt, 2), 3.89 (H-3", m, 8–12, 2.5), 1.77 (H-4", m), 3.94 (H-5" eq, m, 12), 3.48 (H-5" ax, m); (D<sub>2</sub>O) 96.9 (C-1), 141.7 (C-3), 112.2 (C-4), 38.6 (C-5), 78.1 (C-6), 59.3 (C-7), 56.1 (C-8), 42.2 (C-9), 69.8 (C-11), 100.0 (C-1'), 73.5 (C-2'), 76.5 (C-3'), 70.3 (C-4'), 77.1 (C-5'), 61.4 (C-6'), 99.8 (C-1"), 69.4 (C-2"), 68.5 (C-3"), 29.2 (C-4"), 60.2 (C-5"). *Mentzelia involucrata* (Loasaceae) (10)

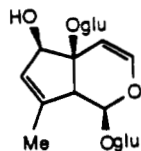
## 15. RANDIOSIDE



Group 2b (9-carbon skeleton; ninth carbon on C-8)

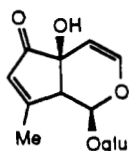
$C_{16}H_{20}O_{10}$  372.33  $[\alpha] -29.4^\circ$  (MeOH) uv 217 (MeOH) (60 MHz  $D_2O$ ) 5.68 (H-1, d, 3.0), 7.45 (H-3, d, 1.4), 8.08 (H-6, dd, 6.0, 3.0), 6.28 (H-7, dd, 6.0, 2.0), 3.80 (COOMe). *Randia canthioides* (Rubiaceae) (14)

## 16. 10-DEOXYMELITTOSIDE



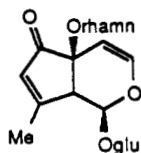
$C_{21}H_{32}O_{14}$  508.48  $[\alpha] -60.5^\circ$  (MeOH) (400 MHz  $CD_3OD$ ) 5.80 (H-1, d, 2.5), 6.39 (H-3, d, 6.5), 5.15 (H-4, dd, 6.5, 1.0), 4.28 (H-6, bd, 2.5), 5.61 (H-7, dt, 2.5, 1.2), 3.25 (H-9, m, 2.5, 1.2, 1.0), 1.89 (H-10, bs), 4.75 (H-1', d, 8), 4.65 (H-1'', d, 8), 3.96, 3.85 (H-6', H-6'', dd, 12.0, 2.1), 3.81, 3.70 (H-6', H-6'', dd, 12.0, 4.2); ( $CD_3OD$ ) 93.2 (C-1), 142.8 (C-3), 105.0 (C-4), 79.1 (C-5), 78.6 (C-6), 128.7 (C-7), 144.5 (C-8), 53.5 (C-9), 15.8 (C-10), 99.8 (C-1'), 75.2 (C-2'), 78.5 (C-3')<sup>a</sup>, 71.7 (C-4'), 78.2 (C-5')<sup>a</sup>, 62.8 (C-6'), 97.7 (C-1''), 74.9 (C-2''), 78.3 (C-3'')<sup>a</sup>, 70.6 (C-4''), 77.0 (C-5'')<sup>a</sup>, 62.1 (C-6''). *Lamiastrum galeboldon* subsp. *flavidum* (Labiatae) (15)

## 17. TEUHIRCOSIDE



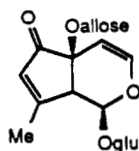
$C_{15}H_{20}O_9$  344.32 mp  $213^\circ$   $[\alpha] -400.7^\circ$  (MeOH) uv 226, 202 ( $H_2O$ ) (250 MHz  $D_2O$ ) 6.07 (H-1, d, 2.5), 6.38 (H-3, d, 6.5), 5.01 (H-4, dd, 6.5, 1.3), 6.05 (H-7, m), 3.39 (H-9, m), 2.29 (H-10, dd, 1.3, 1.0), 4.75 (H-1', d, 8.0); ( $D_2O$ ) 94.1 (C-1), 144.4 (C-3), 106.1 (C-4), 79.2 (C-5), 210.8 (C-6), 130.2 (C-7), 179.2 (C-8), 58.9 (C-9), 20.2 (C-10), 100.7 (C-1'), 74.5 (C-2'), 78.1 (C-3'), 72.5 (C-4'), 75.2 (C-5'), 63.5 (C-6'). *Teucrium bircanicum* (Labiatae) (16)

## 18. TEUCARDOSIDE



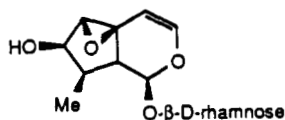
$C_{21}H_{30}O_{13}$  490.46  $[\alpha] -183.5^\circ$  (MeOH) uv 231, 206 ( $H_2O$ ) (250 MHz  $D_2O$ ) 5.98 (H-1, d, 1.8), 6.45 (H-3, d, 6.5), 5.02 (H-4, dd, 6.5, 1.3), 6.11 (H-7, m, 2.0, 1.3), 3.80 (H-9, m), 2.31 (H-10, dd, 1.3, <1), 4.75 (H-1', d, 8), 5.31 (H-1'', d, 2), 1.20 (H-6'', d, 6.5); ( $D_2O$ ) 92.8 (C-1), 144.1 (C-3), 102.6 (C-4), 77.0 (C-5), 206.4 (C-6), 128.6 (C-7), 178.2 (C-8), 53.3 (C-9), 18.3 (C-10), 99.4 (C-1'), 73.5 (C-2'), 76.4 (C-3'), 70.3 (C-4'), 77.0 (C-5'), 61.5 (C-6'), 96.9 (C-1''), 71.6 (C-2''), 70.9 (C-3''), 72.7 (C-4''), 70.3 (C-5''), 17.3 (C-6''). *Teucrium arduini* (Labiatae) (16,17)

## 19. ALLOBETONICOSIDE



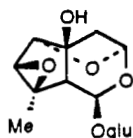
$C_{21}H_{30}O_{14}$  506.46  $[\alpha] -53.3^\circ$  (MeOH) uv 230, 211 (MeOH) (400 MHz  $D_2O$ ) 5.95 (H-1, d, 1.2), 6.45 (H-3, d, 6.4), 5.04 (H-4, dd, 6.4, 1.1), 6.13 (H-7, t, 1.5), 3.97 (H-9, m), 2.30 (H-10, s), 4.77 (H-1', d, 8.0), 3.39 (H-2', dd, 9.0, 8.0), 3.42 (H-3', t), 3.48 (H-4', t), 3.50 (H-5', m), 3.94 (H-6', dd, 12.3, 2.1), 3.72 (H-6'', dd, 12.3, 5.9), 5.29 (H-1'', d, 8.3), 3.47 (H-2'', dd, 8.3, 2.9), 4.20 (H-3'', t, 2.9), 3.60 (H-4'', dd, 10.1, 2.9), 3.72 (H-5'', m), 3.85 (H-6'', dd, 12.3, 2.1), 3.64 (H-6'', dd, 12.3, 5.4); ( $D_2O$ ) 92.3 (C-1), 144.2 (C-3), 102.8 (C-4), 77.5 (C-5), 204.9 (C-6), 127.9 (C-7), 178.5 (C-8), 55.0 (C-9), 17.7 (C-10), 98.9 (C-1'), 73.7 (C-2'), 75.7 (C-3'), 69.6 (C-4'), 76.3 (C-5'), 60.8 (C-6'), 96.7 (C-1''), 71.3 (C-2''), 70.7 (C-3''), 66.8 (C-4''), 72.4 (C-5''), 61.2 (C-6''). *Betonica officinalis* (Lamiaceae) (18)

20. 5,6- $\beta$ -EPOXY-7 $\beta$ -HYDROXY-8 $\beta$ -METHYL-1- $\beta$ -D-RHAMNOSIDAL IRIDOID



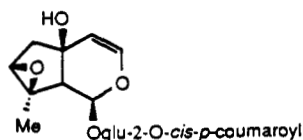
$C_{15}H_{22}O_8$  330.33 mp 265–266° uv 209 (EtOH) (tetraacetate  $^2$  MHz  $CDCl_3$ ) 5.35 (H-1, d, 9), 7.6 (H-3, d, 9), 5.2 (H-4, d, 9), 3.35 (H-6, bs), 4.6 (H-7, t, 1), 2.25 (H-9, m), 0.95 (H-10, bs), 4.75 (H-1', d, 8), 3.7 (H-5', m), 1.24 (H-6', s), 2.04, 2.0, 1.96, 1.94 (OAc); (tetraacetate  $CDCl_3$ ) 80.1 (C-1), 140.4 (C-3), 122.2 (C-4), 56.9 (C-5), 56.1 (C-6), 73.0 (C-7), 36.8 (C-8), 50.3 (C-9), 18.8 (C-10), 99.7 (C-1'), 68.7 (C-2'), 71.8 (C-3'), 62.2 (C-4'), 71.6 (C-5'), 19.4 (C-6'), 21.1, 20.7, 19.8, 19.4 (O=CMe), 170.6, 170.3, 169.4, 169.3 (O=CMe). *Barleria prionitis* (Acanthaceae) (19)

21. PROCUMBOSIDE



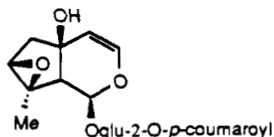
$C_{15}H_{22}O_{10}$  362.33  $[\alpha] -112^\circ$  (MeOH) (200 MHz  $D_2O$ ) 5.43 (H-1, s), 5.48 (H-3, d, 3.5), 2.09 (H-4 $\alpha$ , dd, 12, 3.5), 2.96 (H-4 $\beta$ , d, 12), 4.20 (H-6, s), 3.76 (H-7, s), 2.76 (H-9, s), 1.55 (H-10, s), 4.75 (H-1', d, 8); ( $CD_3OD$ ) 93.4 (C-1)<sup>a</sup>, 101.8 (C-3)<sup>a</sup>, 37.4 (C-4), 81.8 (C-5), 85.3 (C-6), 64.9 (C-7), 66.1 (C-8), 58.9 (C-9), 15.4 (C-10), 98.5 (C-1')<sup>a</sup>, 74.6 (C-2')<sup>a</sup>, 78.3 (C-3')<sup>a</sup>, 71.6 (C-4')<sup>a</sup>, 78.1 (C-5')<sup>a</sup>, 62.6 (C-6')<sup>a</sup>. *Harpagophytum procumbens* (Pedaliaceae) (20)

22. DECUMBESIDE B



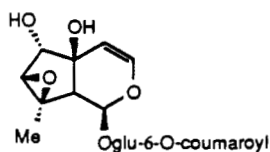
$C_{24}H_{28}O_{11}$  492.48  $[\alpha] -13^\circ$  (MeOH) uv 312, 225 (MeOH) (200 MHz  $CD_3OD$ ) 5.42 (H-1, d, 6), 6.25 (H-3, d, 6.5), 1.99 (H-6, bs), 3.26 (H-7, bs), 2.24 (H-9, d, 6), 1.47 (H-10, s), 3.94 (H-6', d, 11.5), 6.89/5.81 (H $\alpha$ , H $\beta$ , d's, 13), 7.65 (H-2'', d, 8.5), 6.75 (H-3'', d, 8.5); ( $CD_3OD$ ) 95.3 (C-1), 141.4 (C-3), 110.1 (C-4), 76.7 (C-5), 43.7 (C-6), 64.0 (C-7), 67.0 (C-8), 54.5 (C-9), 17.3 (C-10), 97.9 (C-1'), 75.6 (C-2')<sup>a</sup>, 74.8 (C-3')<sup>a</sup>, 71.8 (C-4')<sup>a</sup>, 78.4 (C-5')<sup>a</sup>, 62.7 (C-6')<sup>a</sup>, 167.0 (C=O), 115.8 (C $\alpha$ ), 145.5 (C $\beta$ ), 127.7 (C-1''), 133.8 (C-2''), 115.8 (C-3''), 160.0 (C-4''). *Ajuga decumbens* (Labiatae) (21)

23. DECUMBESIDE A



$C_{24}H_{28}O_{11}$  492.48  $[\alpha] -60^\circ$  (MeOH) uv 315, 228 (MeOH) (200 MHz  $CD_3OD$ ) 5.50 (H-1, d, 5), 6.21 (H-3, d, 6.5), 1.97 (H-6, bs), 3.21 (H-7, bs), 2.27 (H-9, d, 5), 1.43 (H-10, s), 3.94 (H-6', d, 11.5), 6.36/7.65 (H $\alpha$ , H $\beta$ , d's, 16), 7.48 (H-2''), 6.81 (H-3''), 3.70 (m, 2H's); ( $CD_3OD$ ) 94.9 (C-1), 141.2 (C-3), 110.6 (C-4), 76.9 (C-5), 43.7 (C-6), 64.1 (C-7), 67.1 (C-8), 54.6 (C-9), 17.1 (C-10), 97.9 (C-1'), 75.7 (C-2')<sup>a</sup>, 75.1 (C-3')<sup>a</sup>, 71.7 (C-4')<sup>a</sup>, 78.5 (C-5')<sup>a</sup>, 62.8 (C-6')<sup>a</sup>, 169.2 (C=O), 115.3 (C $\alpha$ ), 147.3 (C $\beta$ ), 127.1 (C-1''), 131.2 (C-2''), 116.9 (C-3''), 161.3 (C-4''). *Ajuga decumbens* (Labiatae) (21)

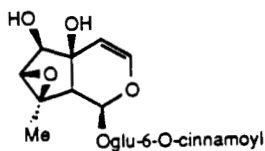
24. 6'-O-*p*-COUMAROYLPRO-CUMBIDE



$C_{24}H_{28}O_{12}$  508.48  $[\alpha] -58.2^\circ$  (MeOH) uv 313, 228 (MeOH) (200 MHz  $D_2O$ ) 5.30 (H-1, d, 8), 6.53 (H-3, d, 6.5), 4.93 (H-4, d, 6.5), 3.93 (H-6, s), 3.38 (H-7, s), 2.43 (H-9, d, 8), 1.43 (H-10, s), 4.46 (H-6', dd, 12, 4.5), 4.60 (H-6', d, 12), 6.44/7.72 (H $\alpha$ , H $\beta$ , d's, 16), 6.95 (H-2'', d, 8.5), 7.95 (H-3'', d, 8.5); ( $CD_3OD$ ) 96.1 (C-1), 144.1 (C-3), 104.2 (C-4), 80.1 (C-5), 77.6 (C-6), 65.8 (C-7), 66.9 (C-8), 52.9 (C-9), 17.6 (C-10), 100.0 (C-1'), 74.7 (C-2'), 78.1 (C-3'), 71.5 (C-4'), 75.6 (C-5'), 64.2 (C-6'), 169.0 (C=O),

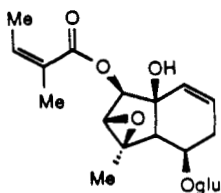
146.8 (C $\alpha$ ), 114.9 (C $\beta$ ), 127.0 (C-1'), 131.2 (C-2''), 116.8 (C-3''), 161.2 (C-4'). *Harpagophytum procumbens* (Pedaliaceae) (20)

25. 6'-O-CINNAMOYLANTIRRINOSIDE



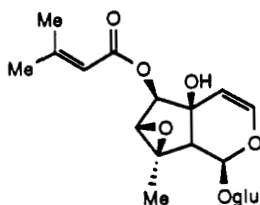
C<sub>25</sub>H<sub>28</sub>O<sub>11</sub> 504.49 [ $\alpha$ ] -67.3° (MeOH) (400 MHz CDCl<sub>3</sub>/CD<sub>3</sub>OD) 5.22 (H-1, d, 5), 6.26 (H-3, d, 6.2), 4.72 (H-4, bd, 6.2), 3.70 (H-6, d, 2.5), 3.30 (H-7, bd, 2.5), 2.32 (H-9, bd, 5), 1.30 (H-10, s), 4.53 (H-1', d, 8), 3.34 (H-2', H-4', m), 3.20 (H-3', m), 3.44 (H-5', m), 4.41 (H-6', dd, 12.5, 2.5), 4.34 (H-6'', dd, 12.5, 4.5), 6.35/7.58 (H $\alpha$ , H $\beta$ , d's, 16), 7.41 (H-2'', H-4'', m), 7.27 (H-3'', m); (CDCl<sub>3</sub>) 92.6 (C-1), 142.5 (C-3), 105.8 (C-4), 73.7 (C-5), 74.2 (C-6), 65.0 (C-7), 64.4 (C-8), 51.0 (C-9), 16.5 (C-10), 98.2 (C-1'), 72.7 (C-2'), 75.9 (C-3'), 69.7 (C-4'), 75.5 (C-5'), 63.1 (C-6'), 167.2 (C=O), 117.3 (C $\alpha$ ), 145.5 (C $\beta$ ), 134.0 (C-1''), 128.8 (C-2''), 128.0 (C-3''), 117.3 (C-4''). *Anarrbinum orientale* (Scrophulariaceae) (22)

26. 6-O-ANGELOYLANTIRRINOSIDE  
(mixed with 6-O-Seneciolyantirrinoside)



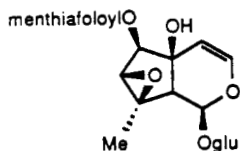
C<sub>20</sub>H<sub>28</sub>O<sub>11</sub> 444.44 uv 225.5 (MeOH) (90 MHz CD<sub>3</sub>OD) 5.46 (H-1, d, 6), 6.40 (H-3, d, 6), 4.90 (H-4, dd, 6, 2), 4.96 (H-6, d, 3), 3.50 (H-7, t, 3), 2.46 (H-9, d, 6), 1.49 (H-10, s), 6.16 (H-3''), 1.93 (H-4''), 2.00 (H-5''); (CD<sub>3</sub>OD) 94.9 (C-1), 143.0 (C-3), 107.4 (C-4), 74.5 (C-5), 79.4 (C-6), 64.3 (C-7, C-8), 53.3 (C-9), 17.3 (C-10), 99.6 (C-1'), 74.5 (C-2'), 78.1 (C-3'), 71.6 (C-4'), 77.5 (C-5'), 62.8 (C-6'), 167.2 (C-1''), 128.7 (C-2''), 139.3 (C-3''), 20.6 (C-4''), 27.4 (C-5''). *Linaria clementei* (Scrophulariaceae) (23)

27. 6-O-SENECIOYLANTIRRINOSIDE  
(mixed with 6-O-Angeloylantirrinoside)



C<sub>20</sub>H<sub>28</sub>O<sub>11</sub> 444.44 uv 225.5 (MeOH) (90 MHz CD<sub>3</sub>OD) 5.46 (H-1, d, 6), 6.40 (H-3, d, 6), 4.90 (H-4, dd, 6, 2), 5.05 (H-6, d, 3), 3.50 (H-7, t, 3), 2.46 (H-9, d, 6), 1.50 (H-10, s), 5.83 (H-2''), 2.16 (H-4''), 1.93 (H-5''); (CD<sub>3</sub>OD) 94.9 (C-1), 143.0 (C-3), 107.4 (C-4), 74.5 (C-5), 78.6 (C-6), 64.3 (C-7, C-8), 53.3 (C-9), 17.3 (C-10), 99.6 (C-1'), 74.5 (C-2'), 78.1 (C-3'), 71.6 (C-4'), 77.5 (C-5'), 62.8 (C-6'), 169.3 (C-1''), 116.3 (C-2''), 159.2 (C-3''), 20.6 (C-4''), 27.4 (C-5''). *Linaria clementei* (Scrophulariaceae) (23)

28. KICKXIOSIDE

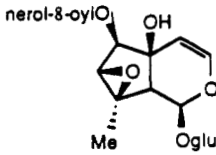


C<sub>25</sub>H<sub>36</sub>O<sub>12</sub> 528.55 [ $\alpha$ ] -63.2° (MeOH) uv 230 (MeOH) (400 MHz CD<sub>3</sub>OD/CDCl<sub>3</sub> 3/7) 5.38 (H-1, d, 6.3), 6.36 (H-3, d, 6.3), 4.90 (H-4, d, 6.3), 4.96 (H-6, d, 1.8), 3.53 (H-7, bd, 1.8), 2.50 (H-9, d, 6.3), 1.50 (H-10, s), 4.68 (H-1', d, 8), 3.26 (H-2', dd, 9.1, 8), 3.35 (H-3', t, 9.1), 3.41 (H-4', t, 9.1), 3.32 (H-5', m), 3.89 (H-6', dd, 12.1, 2.4), 3.70 (H-6'', dd, 12.1, 5), 6.90 (H-3'', dt, 7.2, 1.3), 2.23 (H-4'', m), 1.62 (H-5'', m), 5.86 (H-7'', dd, 17.2, 10.5), 5.19 (H-8'', dd, 17.2, 1.1), 5.05 (H-8'', dd, 10.5, 1.1), 1.83 (H-9'', bs), 1.26 (H-10'', s); (CD<sub>3</sub>OD/CDCl<sub>3</sub> 3/7) 94.5 (C-1), 142.8 (C-3), 106.8 (C-4), 71.2 (C-5), 79.0 (C-6), 64.4 (C-7), 64.5 (C-8), 51.3 (C-9), 17.7 (C-10), 99.4 (C-1'), 75.3 (C-2'), 77.5 (C-3''), 72.4 (C-4''), 77.2 (C-5''), 62.5 (C-6'), 169.0 (C-1''), 145.5 (C-2''), 127.2 (C-3''), 24.5 (C-



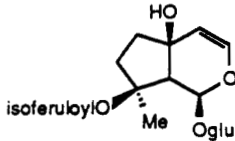
4<sup>n</sup>), 41.3 (C-5<sup>n</sup>), 71.2 (C-6<sup>n</sup>), 144.7 (C-7<sup>n</sup>), 112.8 (C-8<sup>n</sup>), 13.2 (C-9<sup>n</sup>), 28.0 (C-10<sup>n</sup>). *Kickxia spuria* (Scrophulariaceae) (24)

29. 6-O-NEROL-8-OYLANTIR-RINOSIDE



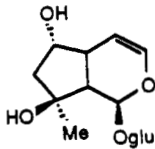
C<sub>25</sub>H<sub>36</sub>O<sub>12</sub> 528.55 [α] -88.8° (MeOH) uv 224 (?) (400 MHz CDCl<sub>3</sub>/CD<sub>3</sub>OD) 5.42 (H-1, d, 5.8), 6.37 (H-3, d, 6.2), 4.90 (H-4, bd, 6.2), 4.83 (H-6, d, 2.2), 3.50 (H-7, d, 2.2), 2.55 (H-9, bd, 5.8), 1.44 (H-10, s), 4.62 (H-1', d, 8), 3.32 (H-2', H-5', m), 3.48 (H-3', H-4', m), 3.84 (H-6', dd, 12.5, 2.5), 3.78 (H-6', dd, 12.5, 4), 4.06 (H-1'', bd, 7), 5.41 (H-2'', bt, 7), 2.20 (H-4'', bt, 7), 2.32 (H-5'', bdt, 7, 7), 6.84 (H-6'', tq, 7, 1.5), 1.83 (H-9'', dt, 1.5, 1), 1.71 (H-10'', dt, 1, 1); (CDCl<sub>3</sub>) 93.1 (C-1), 142.2 (C-3), 105.5 (C-4), 73.4 (C-5), 77.6 (C-6), 63.1 (C-7), 63.4 (C-8), 51.3 (C-9), 16.5 (C-10), 98.2 (C-1'), 72.8 (C-2'), 76.2 (C-3'), 69.8 (C-4'), 75.9 (C-5'), 63.1 (C-6'), 58.2 (C-1''), 125.3 (C-2''), 137.1 (C-3''), 30.0 (C-4''), 26.5 (C-5''), 142.9 (C-6''), 127.1 (C-7''), 167.6 (C-8''), 12.0 (C-9''), 22.7 (C-10''). *Anarrhinum orientale* (Scrophulariaceae) (22)

30. 6-DESOXY-8-O-ISOFERULOYL-HARPAGIDE



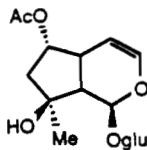
C<sub>25</sub>H<sub>32</sub>O<sub>12</sub> 524.52 mp 139–141° uv 320, 289, 234, 216 (MeOH) (60 MHz CD<sub>3</sub>OD) 5.44 (H-1, bs), 6.20 (H-3, m), 5.82 (H-4, d, 13), 2.62–2.30 (H-6, m), 2.22–1.99 (H-7, m), 2.87 (H-9, bs), 1.38 (H-10, s), 6.38/7.60 (H<sub>α</sub>, H<sub>β</sub>, d's, 16), 3.83 (OMe), 7.82 (OH, s); (CD<sub>3</sub>OD) 93.2 (C-1), 140.8 (C-3), 104.2 (C-4), 74.1 (C-5), 47.8 (C-6), 38.7 (C-7), 84.8 (C-8), 50.2 (C-9), 25.6 (C-10), 98.9 (C-1'), 74.2 (C-2'), 78.8 (C-3'), 71.2 (C-4'), 77.2 (C-5'), 62.2 (C-6'), 168.4 (C=O), 123.6 (C<sub>α</sub>), 146.1 (C<sub>β</sub>), 129.4 (C-1''), 112.8 (C-2''), 149.5 (C-3''), 150.8 (C-4''), 111.5 (C-5''), 112.8 (C-6''), 56.1 (OMe). *Veronicastrum sibiricum* (Scrophulariaceae) (25)

31. MYOPOROSIDE (revision of stereochemistry at C-6)



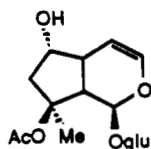
C<sub>15</sub>H<sub>24</sub>O<sub>9</sub> 348.35 [α] -175° (MeOH) uv 204 (MeOH) (250 MHz D<sub>2</sub>O) 5.5 (H-1, d, 2.4), 6.34 (H-3, dd, 6.5, 2.0), 4.96 (H-4, bdd, 6.5, 2.2), 2.90 (H-5, m), 4.46 (H-6, dr, 10.3, 6.5), 1.76 (H-7<sub>α</sub>, dd, 13.4, 10.4), 1.94 (H-7<sub>β</sub>, bd, 13.4, 6.5), 2.30 (H-9, bd, 8.0), 1.33 (H-10, s), 4.73 (H-1', d); (D<sub>2</sub>O) 93.6 (C-1), 141.0 (C-3), 101.7 (C-4), 36.1 (C-5), 72.0 (C-6), 47.3 (C-7), 77.7 (C-8), 50.8 (C-9), 25.9 (C-10), 98.8 (C-1'), 73.5 (C-2'), 76.4 (C-3'), 70.4 (C-4'), 77.0 (C-5'), 61.5 (C-6'). *Myoporum* (Myoporaceae), *Physostegia virginiana* (Lamiaceae) (26–28)

32. 6-O-ACETYLMIOPOROSIDE



C<sub>17</sub>H<sub>26</sub>O<sub>10</sub> 390.39 [α] -165.3 (MeOH) uv 232, 207 (MeOH) (400 MHz D<sub>2</sub>O) 5.55 (H-1, d, 2.9), 6.40 (H-3, dd, 6.4, 2.0), 4.95 (H-4, dd, 6.4, 2.9), 3.21 (H-5, dddd, 8.5, 6.8, 2.9, 2.0), 5.33 (H-6, q), 2.16 (H-7, dd, 13.8, 6.8), 1.99 (H-7, dd, 13.8, 8.6), 2.40 (H-9, dd, 8.5, 2.9), 1.45 (H-10, s), 2.14 (OAc), 4.82 (H-1', d, 8.0), 3.33 (H-2', dd, 9.1, 8.0), 3.43 (H-3', t, 9.1), 3.53 (H-4', dd, 9.1), 3.50 (H-5', m), 3.96 (H-6', dd, 12.3, 2.0), 3.76 (H-6', dd, 12.3, 5.9); (D<sub>2</sub>O) 95.5 (C-1), 142.9 (C-3), 103.3 (C-4), 36.6 (C-5), 77.4 (C-6), 47.2 (C-7), 79.5 (C-8), 52.4 (C-9), 27.4 (C-10), 100.6 (C-1'), 75.3 (C-2'), 78.3 (C-3'), 72.3 (C-

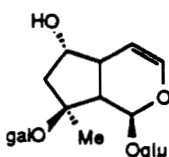
## 33. 8-O-ACETYLMIOPOROSIDE



4'), 78.8 (C-5'), 63.3 (C-6'), 176.7 (O=CMe), 23.1 (O=CMe). *Betonica officinalis* (Lamiaceae) (18)

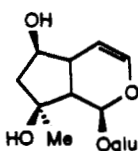
$C_{17}H_{26}O_{10}$  390.39  $[\alpha] -151.8^\circ$  (MeOH) uv 188 (H<sub>2</sub>O) (250 MHz D<sub>2</sub>O) 5.83 (H-1, d, 1.5), 6.32 (H-3, dd, 6.5, 2), 5.00 (H-4, dd, 6.5, 1.5), 2.89 (H-5, m, 7, 6, 2, 1.5), 4.47 (H-6, m, 11.2, 6, 5.8), 2.30 (H-7 $\alpha$ , dd, 13.5, 5.8), 1.84 (H-7 $\beta$ , dd, 13.5, 11.2), 2.69 (H-9, dd, 7, 1.5), 1.53 (H-10, s), 2.03 (OAc), 4.76 (H-1', d, 7.5); (CD<sub>3</sub>OD) 94.1 (C-1), 142.0 (C-3), 101.3 (C-4), 37.1 (C-5), 71.9 (C-6), 47.4 (C-7), 88.0 (C-8), 49.3 (C-9), 22.4 (C-10), 100.0 (C-1'), 74.8 (C-2'), 78.0 (C-3'), 71.6 (C-4'), 78.0 (C-5'), 62.9 (C-6'), 173.3 (O=CMe), 22.2 (O=CMe). *Clerodendrum tobomsonae* (Verbenaceae) (29,30)

## 34. REHMANNIOSIDE C



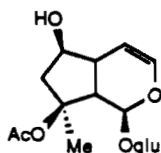
$C_{21}H_{34}O_{14}$  510.49  $[\alpha] -11.3^\circ$  (MeOH) (90 MHz D<sub>2</sub>O) 5.71 (H-1, bs), 6.38 (H-3, q, 6, 1), 1.56 (H-10, s); (D<sub>2</sub>O) 94.1 (C-1), 139.6 (C-3), 105.8 (C-4), 39.7 (C-5), 77.0 (C-6)<sup>a</sup>, 45.8 (C-7), 86.2 (C-8), 49.1 (C-9), 24.1 (C-10), 98.7 (C-1'), 73.6 (C-2'), 76.9 (C-3')<sup>a</sup>, 70.5 (C-4'), 76.5 (C-5'), 61.6 (C-6'), 94.6 (C-1''), 69.3 (C-2''), 70.5 (C-3''), 70.2 (C-4''), 71.8 (C-5''), 62.1 (C-6''). *Rebmannia glutinosa* (Scrophulariaceae) (31)

## 35. AJUGOL (revision of stereochemistry at C-6)

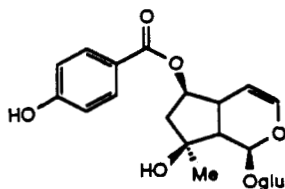


$C_{15}H_{24}O_9$  348.35  $[\alpha] -172.1^\circ$  (MeOH) (500 MHz CD<sub>3</sub>OD) 5.46 (H-1, d, 2.3), 6.16 (H-3, ddd, 6.3, 2.1, 0.5), 4.85 (H-4, ddd, 6.3, 3.2, 0.7), 2.72 (H-5, m), 3.92 (H-6, dt, 5.2, 2.9), 2.04 (H-7, dd, 13.4, 5.7), 1.79 (dd, 13.4, 4.7), 2.54 (H-9, dd, 9.6, 2.3), 1.31 (H-10, s), 4.54 (H-1', d, 7.9), 3.20 (H-2', dd, 9.2, 8.0), 3.37 (H-3', dd, 9.2, 8.0), 3.27 (H-4', dd, 9.7, 8.3), 3.30 (H-5', m), 3.89 (H-6', dd, 11.9, 2.0), 3.66 (H-6', dd, 11.9, 5.7); (CD<sub>3</sub>OD) 93.8 (C-1), 140.4 (C-3), 105.9 (C-4), 41.3 (C-5), 78.2 (C-6), 50.0 (C-7), 79.5 (C-8), 51.8 (C-9), 25.2 (C-10), 99.4 (C-1'), 74.8 (C-2'), 77.8 (C-3'), 71.7 (C-4'), 78.0 (C-5'), 62.9 (C-6'). *Ajuga reptans* (Labiatae) (32-34)

## 36. AJUGOSIDE (Leonuride) (revision of stereochemistry at C-6)

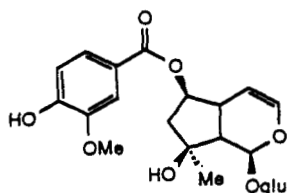


$C_{17}H_{26}O_{10}$  390.39 (D<sub>2</sub>O) 94.5 (C-1), 140.5 (C-3), 104.3 (C-4), 40.6 (C-5), 76.4 (C-6), 47.7 (C-7), 90.1 (C-8), 48.4 (C-9), 22.5 (C-10)<sup>a</sup>, 99.1 (C-1'), 73.6 (C-2'), 76.6 (C-3'), 70.5 (C-4'), 77.1 (C-5'), 61.6 (C-6'), 174.8 (O=CMe), 22.4 (O=CMe)<sup>a</sup>. *Ajuga reptans* (Labiatae) (32,34)

37. 6-O-*p*-HYDROXYBENZOYL-AJUGOL

$C_{22}H_{28}O_{11}$  468.46  $[\alpha] -138.8^\circ$  (MeOH) (200 MHz CD<sub>3</sub>OD) 5.51 (H-1, d, 2.4), 6.23 (H-3, dd, 6.2, 2.3), 5.02 (H-4, m), 2.98 (H-5, dd, 9.2, 2.2), 5.02 (H-6, m), 2.28 (H-7, dd, 14.2, 6.4), 2.05 (H-7, dd, 14.2, 4.0), 2.61 (H-9, dd, 9.2, 2.4), 1.40 (H-10, s), 4.67 (H-1', d, 7.8), 4.0-3.2 (H-2'-H-6', m), 7.90 (H-2'', d, 9), 6.82 (H-3'', d, 9); (CD<sub>3</sub>OD) 93.5 (C-1), 141.1 (C-3), 104.6 (C-4), 39.4 (C-5), 80.5 (C-6), 47.9 (C-7), 79.1 (C-8), 51.7 (C-9), 26.1 (C-10), 99.4 (C-1'), 74.8 (C-2'), 78.0 (C-3'), 71.7 (C-4'), 78.2 (C-5'), 62.9 (C-6'),

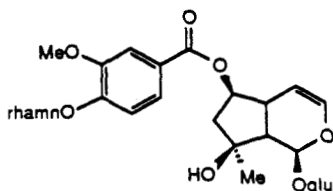
## 38. 6-O-VANILLOYLAJUGOL



168.0 (C=O), 122.5 (C-1<sup>n</sup>), 132.8 (C-2<sup>n</sup>), 116.1 (C-3<sup>n</sup>), 163.5 (C-4<sup>n</sup>). *Rebmannia glutinosa* var. *purpurea* (Scrophulariaceae) (33)

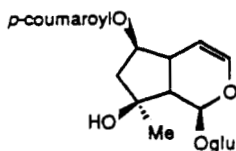
C<sub>23</sub>H<sub>30</sub>O<sub>12</sub> 498.48 [α] -135.2° (MeOH) (200 MHz CD<sub>3</sub>OD) 5.52 (H-1, d, 2.4), 6.23 (H-3, dd, 6.2, 2.3), 5.02 (H-4, m), 2.99 (H-5, dd, 9.3, 2.2), 5.02 (H-6, m), 2.28 (H-7, dd, 14.2, 6.4), 2.06 (H-7, dd, 14.2, 3.9), 2.62 (H-9, dd, 9.2, 2.4), 1.41 (H-10, s), 4.68 (H-1', d, 7.8), 4.0-3.2 (H-2', H-6', m), 7.57 (H-2'', d, 2), 6.84 (H-5'', d, 8.8), 7.58 (H-6'', dd, 8.8, 2), 3.89 (OMe); (CD<sub>3</sub>OD) 93.5 (C-1), 141.1 (C-3), 104.6 (C-4), 39.4 (C-5), 80.7 (C-6), 47.9 (C-7), 79.2 (C-8), 51.7 (C-9), 26.2 (C-10), 99.5 (C-1'), 74.8 (C-2'), 78.0 (C-3'), 71.7 (C-4'), 78.2 (C-5'), 62.9 (C-6'), 168.0 (C=O), 122.9 (C-1<sup>n</sup>), 113.8 (C-2<sup>n</sup>), 152.9 (C-3<sup>n</sup>), 148.7 (C-4<sup>n</sup>), 115.9 (C-5<sup>n</sup>), 125.2 (C-6<sup>n</sup>), 56.5 (OMe). *Rebmannia glutinosa* var. *purpurea* (Scrophulariaceae) (33)

## 39. 6-O-(4''-O-α-L-RHAMNOPYRANOSYLVANILLOYL)AJUGOL



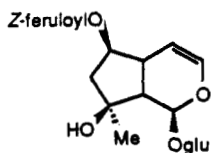
C<sub>29</sub>H<sub>40</sub>O<sub>16</sub> 644.63 [α] -156.0° (MeOH) (200 MHz CD<sub>3</sub>OD) 5.53 (H-1, d, 2.4), 6.24 (H-3, dd, 6.3, 2.2), 5.01 (H-4, H-6, m), 3.01 (H-5, dd, 9.2, 2.2), 2.29 (H-7, dd, 14.2, 6.1), 2.07 (H-7, dd, 14.2, 3.7), 2.63 (H-9, dd, 9.2, 2.4), 1.41 (H-10, s), 4.69 (H-1', d, 7.6), 4.1-3.2 (H-2'-H-6', H-2''-H-5'', m), 7.61 (H-2'', d, 2), 7.19 (H-5'', d, 8.6), 7.63 (H-6'', dd, 8.6, 2), 5.51 (H-1''', d, 1.7), 1.22 (H-6''', d, 6.1), 3.88 (OMe); (CD<sub>3</sub>OD) 93.5 (C-1), 141.1 (C-3), 104.5 (C-4), 39.4 (C-5), 80.9 (C-6), 47.8 (C-7), 79.1 (C-8), 51.7 (C-9), 26.2 (C-10), 99.4 (C-1'), 74.7 (C-2'), 77.9 (C-3'), 71.7 (C-4')<sup>a</sup>, 78.1 (C-5'), 62.9 (C-6'), 167.5 (O=C), 125.9 (C-1<sup>n</sup>), 117.5 (C-2<sup>n</sup>), 151.1 (C-3<sup>n</sup>), 151.2 (C-4<sup>n</sup>), 114.4 (C-5<sup>n</sup>), 124.4 (C-6<sup>n</sup>), 56.6 (OMe), 100.5 (C-1'''), 71.8 (C-2''')<sup>a</sup>, 72.2 (C-3''')<sup>a</sup>, 73.7 (C-4''')<sup>a</sup>, 71.0 (C-5''')<sup>a</sup>, 18.0 (C-6'''). *Rebmannia glutinosa* var. *purpurea* (Scrophulariaceae) (33)

## 40. 6-O-p-COUMAROYL AJUGOL



C<sub>24</sub>H<sub>30</sub>O<sub>11</sub> 494.49 [α] -144.9° (MeOH) (200 MHz CD<sub>3</sub>OD) 5.50 (H-1, d, 2.4), 6.22 (H-3, dd, 6.4, 2.2), 4.95 (H-4, m), 2.93 (H-5, dd, 9.3, 2.4), 4.95 (H-6, m), 2.24 (H-7, dd, 14.2, 6.4), 1.99 (H-7, dd, 14.2, 3.9), 2.58 (H-9, dd, 9.3, 2.4), 1.39 (H-10, s), 4.67 (H-1', d, 7.8), 4.0-3.2 (H-2'-H-6', m), 6.34/7.63 (H<sub>α</sub>, H<sub>β</sub>, d's, 15.9), 7.45 (H-2'', d, 8.7), 6.81 (H-3'', d, 8.7); (CD<sub>3</sub>OD) 93.5 (C-1), 141.0 (C-3), 104.6 (C-4), 39.3 (C-5), 80.3 (C-6), 47.9 (C-7), 79.1 (C-8), 51.6 (C-9), 26.0 (C-10), 99.4 (C-1'), 74.8 (C-2'), 78.0 (C-3'), 71.7 (C-4'), 78.1 (C-5'), 62.9 (C-6'), 169.0 (C=O), 115.4 (C<sub>α</sub>), 146.6 (C<sub>β</sub>), 127.2 (C-1<sup>n</sup>), 131.1 (C-2<sup>n</sup>), 116.8 (C-3<sup>n</sup>), 161.2 (C-4<sup>n</sup>). *Rebmannia glutinosa* var. *purpurea* (Scrophulariaceae) (33)

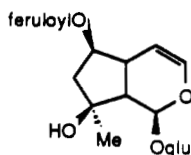
## 41. 6-O-cis-FERULOYL AJUGOL



C<sub>25</sub>H<sub>32</sub>O<sub>12</sub> 524.52 [α] -84.5° (MeOH) (200 MHz CD<sub>3</sub>OD) 5.48 (H-1, d, 2.4), 6.20 (H-3, dd, 6.4, 2.2), 4.98 (H-4, dd, 6.4, 2.4), 2.87 (H-5, dd, 9.3, 2.4), 5.0-4.9 (H-6, m), 2.23 (H-7, dd, 13.9, 6.6), 1.94 (H-7, dd, 13.9, 4.6), 2.52 (H-9, dd, 9.3, 2.4), 1.37 (H-10, s), 4.66 (H-1', d, 7.8), 4.0-3.2 (H-2'-H-6', m), 5.81/6.85 (H<sub>α</sub>, H<sub>β</sub>, d's, 13.1), 7.76 (H-2'', d, 2), 6.77 (H-5'', d, 8.3), 7.13 (H-6'', dd, 8.3, 2), 3.87 (OMe); (CD<sub>3</sub>OD) 93.4 (C-1), 140.9 (C-3), 104.7 (C-4), 39.1

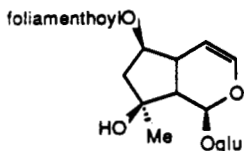
(C-5), 80.1 (C-6), 47.9 (C-7), 79.0 (C-8), 51.5 (C-9), 25.8 (C-10), 99.4 (C-1'), 74.8 (C-2'), 78.0 (C-3'), 71.7 (C-4'), 78.2 (C-5'), 62.9 (C-6'), 168.0 (C=O), 115.7 (C $\alpha$ ), 145.4 (C $\beta$ ), 128.2 (C-1''), 115.1 (C-2''), 148.3 (C-3''), 149.4 (C-4''), 117.0 (C-5''), 126.5 (C-6''), 56.5 (OMe). *Rebmannia glutinosa* var. *purpurea* (Scrophulariaceae) (33)

42. 6-O-*trans*-FERULOYLALJUGOL



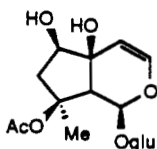
C<sub>25</sub>H<sub>32</sub>O<sub>12</sub> 524.52 [ $\alpha$ ] -147.0° (MeOH) (200 MHz CD<sub>3</sub>OD) 5.52 (H-1, d, 2.2), 6.22 (H-3, dd, 6.3, 2.2), 4.95 (H-4, m), 2.94 (H-5, dd, 9.3, 2.2), 4.95 (H-6, m), 2.24 (H-7, dd, 14.2, 6.3), 2.01 (H-7, dd, 14.2, 3.9), 2.60 (H-9, dd, 9.3, 2.2), 1.39 (H-10, s), 4.70 (H-1', d, 7.6), 4.0-3.2 (H-2'-H-6', m), 6.36/7.61 (H $\alpha$ , H $\beta$ , d's, 16), 7.15 (H-2'', d, 1.7), 6.82 (H-5'', d, 8.1), 7.05 (H-6'', dd, 8.1, 1.7), 3.88 (OMe); (CD<sub>3</sub>OD) 93.4 (C-1), 140.9 (C-3), 104.5 (C-4), 39.2 (C-5), 80.2 (C-6), 47.7 (C-7), 79.0 (C-8), 51.5 (C-9), 26.0 (C-10), 99.3 (C-1'), 74.6 (C-2'), 77.8 (C-3'), 71.6 (C-4'), 78.0 (C-5'), 62.8 (C-6'), 168.8 (C=O), 115.6 (C $\alpha$ ), 146.7 (C $\beta$ ), 127.6 (C-1''), 111.7 (C-2''), 150.4 (C-3''), 149.2 (C-4''), 116.4 (C-5''), 124.0 (C-6''), 56.4 (OMe). *Rebmannia glutinosa* var. *purpurea* (Scrophulariaceae) (33)

43. NEMOROSOSIDE (6-O-Folia-menthoylajugol)



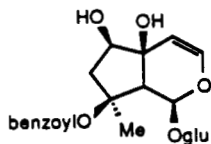
C<sub>25</sub>H<sub>38</sub>O<sub>11</sub> 514.57 mp 72-75° (400 MHz CDCl<sub>3</sub>) 5.42 (H-1, bs), 6.15 (H-3, dd, 6, 2), 4.87 (H-4, H-6, m), 2.82 (H-5, bd, 9), 1.90-2.30 (H-7, H-4'', H-5''), 2.55 (H-9, bd, 9), 1.32 (H-10, s), 4.77 (H-1', d, 8), 3.38 (H-3', dd, 9.3, 8.7), 3.92 (H-6', dd, 12.2, 6.6), 3.63 (H-6'', dd, 12.2, 2.2), 6.83 (H-3'', qt, 7.4, 1.4), 5.40 (H-7'', qt, 7.5, 1.4), 4.08 (H-8'', d, 7.5), 1.85 (H-9'', d, 1.4), 1.69 (H-10'', d, 1.4); (D<sub>2</sub>O) 93.7 (C-1), 140.3 (C-3), 104.4 (C-4), 38.1 (C-5), 80.3 (C-6), 46.7 (C-7), 79.1 (C-8), 50.6 (C-9), 25.6 (C-10), 98.9 (C-1'), 73.6 (C-2'), 77.0 (C-3'), 70.5 (C-4'), 76.4 (C-5'), 61.6 (C-6'), 170.9 (C-1''), 128.3 (C-2''), 145.0 (C-3''), 27.2 (C-4''), 38.1 (C-5''), 140.7 (C-6''), 123.5 (C-7''), 58.7 (C-8''), 12.4 (C-9''), 16.0 (C-10''). *Penstemon nemorosus* (Scrophulariaceae) (35)

44. 8-O-ACETHYLHARPAGIDE



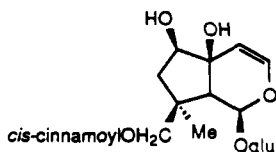
C<sub>17</sub>H<sub>26</sub>O<sub>11</sub> 406.39 [ $\alpha$ ] -117° (MeOH) (200 MHz CD<sub>3</sub>OD) 6.07 (H-1, d, 1), 6.38 (H-3, d, 6.5), 4.91 (H-4, dd, 6.5, 1), 3.71 (H-6, d, 4.5), 1.95 (H-7 $\alpha$ , dd, 15, 4.5), 2.17 (H-7 $\beta$ , d, 15), 2.85 (H-9, bs), 1.45 (H-10, s), 2.01 (OAc), 4.59 (H-1', d, 8), 3.89 (H-6', dd, 12, 1.5); (CD<sub>3</sub>OD) 94.5 (C-1), 143.7 (C-3), 106.8 (C-4), 73.2 (C-5), 78.0 (C-6), 46.0 (C-7), 88.5 (C-8), 55.5 (C-9), 22.5 (C-10), 173.2 (O=CMe), 22.2 (O=CMe), 99.8 (C-1'), 74.5 (C-2'), 77.6 (C-3'), 71.6 (C-4'), 77.6 (C-5'), 62.8 (C-6'). *Ajuga decumbens* (Labiatae) (21,36)

45. CAPRARIOSIDE (8-O-Benzoylharpagide)

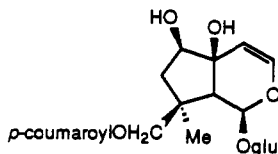


C<sub>21</sub>H<sub>28</sub>O<sub>11</sub> 456.45 (D<sub>2</sub>O) 96.5 (C-1), 145.2 (C-3), 107.6 (C-4), 74.9 (C-5), 78.9 (C-6)<sup>a</sup>, 47.1 (C-7), 91.2 (C-8), 56.0 (C-9), 24.0 (C-10), 101.4 (C-1'), 75.1 (C-2'), 78.1 (C-3'), 72.3 (C-4'), 78.8 (C-5')<sup>a</sup>, 63.4 (C-6'), 171.0 (C=O), 133.0 (C-1''), 131.9 (C-2''), 131.3 (C-3''), 136.3 (C-4''). *Capraria biflora* (Scrophulariaceae) (37)

46. 8-*O*-*cis*-CINNAMOYLHARPAGIDE  $C_{24}H_{30}O_{11}$  494.49 no data available. *Rogeria adenophylla* (Pedaliaceae) (38)

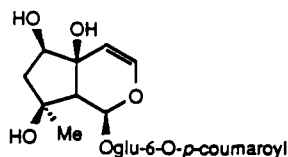


47. 8-*O*-*p*-COUMAROYLHARPAGIDE  $C_{24}H_{30}O_{12}$  510.49  $[\alpha] -30.5^\circ$  (MeOH) uv 313, 224 (MeOH) (200 MHz D<sub>2</sub>O) 6.18 (H-1, bs), 6.49 (H-3, d, 6.5), 5.04 (H-4, d, 6.5), 3.88 (H-6, d, 4), 2.28 (H-7 $\alpha$ , d, 15), 2.08 (H-7 $\beta$ , dd, 15, 4), 2.95 (H-9, s), 1.50 (H-10, s), 6.40/7.65 (H $\alpha$ , H $\beta$ , d's, 16), 5.98 (H-2'', d, 8.5), 6.94 (H-3'', d, 8.5); (CD<sub>3</sub>OD) 94.6 (C-1), 143.9 (C-3), 106.7 (C-4), 73.3 (C-5), 77.5 (C-6)<sup>a</sup>, 46.2 (C-7), 88.4 (C-8), 55.5 (C-9), 22.7 (C-10), 99.9 (C-1'), 74.4 (C-2'), 78.0 (C-3')<sup>a</sup>, 71.6 (C-4'), 78.0 (C-5')<sup>a</sup>, 62.8 (C-6'), 169.3 (C=O), 116.3 (C $\alpha$ ), 146.5 (C $\beta$ ), 127.0 (C-1''), 131.0 (C-2''), 116.7 (C-3''), 161.1 (C-4''). *Harpagophytum procumbens* (Pedaliaceae) (20)

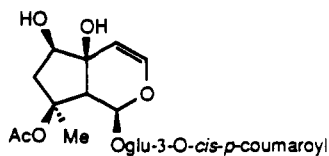


48. 6'-*O*-*p*-COUMAROYL-HARPAGIDE

$C_{24}H_{30}O_{12}$  510.49 *cis/trans* mixture, no data available. *Rogeria adenophylla* (Pedaliaceae) (38)

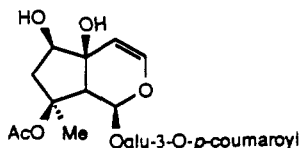


49. DECUMBESIDE D



$C_{26}H_{32}O_{13}$  552.53  $[\alpha] -158^\circ$  (MeOH) uv 307, 224 (MeOH) (200 MHz CD<sub>3</sub>OD) 6.08 (H-1, d, 1), 6.39 (H-3, d, 6.5), 4.91 (H-4, dd, 6.5, 1.5), 3.70-3.76 (H-6, m), 1.94 (H-7 $\alpha$ , dd, 15, 4.5), 2.17 (H-7 $\beta$ , d, 15), 2.86 (H-9, bs), 1.46 (H-10, s), 4.70 (H-1', d, 8), 5.06 (H-3', dd, 9, 9), 3.90 (H-6', dd, 12, 2), 5.83/6.86 (H $\alpha$ , H $\beta$ , d's, 13), 7.64 (H-2'', d, 8.5), 6.74 (H-3'', d, 8.5); (CD<sub>3</sub>OD) 94.4 (C-1), 143.7 (C-3), 106.8 (C-4), 73.2 (C-5), 77.9 (C-6)<sup>a</sup>, 46.0 (C-7), 88.4 (C-8), 55.4 (C-9), 22.4 (C-10), 173.1 (O=CMe), 22.1 (O=CMe), 99.7 (C-1'), 72.8 (C-2'), 78.0 (C-3')<sup>a</sup>, 69.7 (C-4'), 77.5 (C-5'), 62.4 (C-6'), 167.9 (O=C), 116.9 (C $\alpha$ ), 144.4 (C $\beta$ ), 127.5 (C-1''), 133.4 (C-2''), 115.7 (C-3''), 159.7 (C-4''). *Ajuga decumbens* (Labiatae) (21)

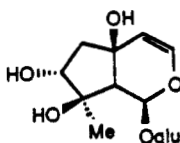
50. DECUMBESIDE C



$C_{26}H_{32}O_{13}$  552.53  $[\alpha] -108^\circ$  (MeOH) uv 312, 227 (MeOH) (200 MHz CD<sub>3</sub>OD) 6.09 (H-1, bs), 6.39 (H-3, d, 6.5), 4.91 (H-4, dd, 6.5, 1.5), 3.72 (H-6, d, 4.5), 1.94 (H-7 $\alpha$ , dd, 15, 4.5), 2.18 (H-7 $\beta$ , d, 15), 3.65-3.77 (H-8, m), 2.86 (H-9, bs), 1.46 (H-10, s), 2.02 (OAc), 4.72 (H-1', d, 8), 3.41 (H-2', dd, 10, 8), 5.07 (H-3', dd, 10, 9), 3.54 (H-4', dd, 10, 9), 3.91 (H-6', dd, 12, 2), 6.39/7.66 (H $\alpha$ , H $\beta$ , d's, 16), 7.47 (H-2'', d, 8.5), 6.80 (H-3'', d, 8.5); (CD<sub>3</sub>OD) 94.5 (C-1), 143.7 (C-3), 106.8 (C-4), 73.2 (C-5), 77.9 (C-6), 46.0 (C-7), 88.4 (C-8), 55.4 (C-9), 22.5 (C-10), 99.7 (C-1'), 72.9 (C-2'), 78.4 (C-3')<sup>a</sup>, 69.8 (C-4'), 77.5 (C-5'), 62.5 (C-6'), 168.9 (O=C), 115.4 (C $\alpha$ ), 146.5

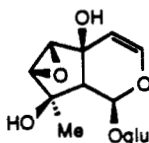
(C $\beta$ ), 127.1 (C-1 $^{\alpha}$ ), 131.0 (C-2 $^{\alpha}$ ), 116.7 (C-3 $^{\alpha}$ ), 161.0 (C-4 $^{\alpha}$ ), 173.1 (O=CMe), 22.2 (O=CMe). *Ajuga decumbens* (Labiatae) (21)

## 51. DAUNOSIDE



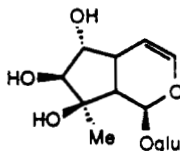
C<sub>15</sub>H<sub>24</sub>O<sub>10</sub> 364.35 [α] -174.2° (MeOH) uv 193.5 (H<sub>2</sub>O) (100 MHz D<sub>2</sub>O) 6.11 (H-1, bs), 6.74 (H-3, d, 6.6), 5.66 (H-4, d, 6.6), 2.71 (H-6, dd, 14.4, 8.6), 2.19 (H-6, dd, 14.4, 11.0), 4.68 (H-7, dd, 11.0, 8.6), 2.88 (H-9, bs), 1.58 (H-10, s); (CD<sub>3</sub>OD) 92.3 (C-1), 139.3 (C-3), 111.5 (C-4), 65.6 (C-5), 46.6 (C-6), 78.2 (C-7)<sup>a</sup>, 80.5 (C-8), 58.8 (C-9), 15.9 (C-10), 99.0 (C-1'), 74.6 (C-2'), 78.1 (C-3')<sup>a</sup>, 71.8 (C-4'), 77.6 (C-5')<sup>a</sup>, 62.9 (C-6'). Hydrolysis of galiridoside (4,39)

## 52. VIRGINIOSIDE



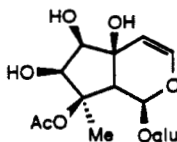
C<sub>15</sub>H<sub>22</sub>O<sub>10</sub> 362.33 [α] -170° (EtOH) (250 MHz D<sub>2</sub>O) 5.68 (H-1, bs), 6.39 (H-3, d, 6.6), 5.09 (H-4, dd, 6.5, 1.6), 3.51 (H-6, d, 2.9), 3.41 (H-7, d, 2.9), 2.16 (H-9, m), 1.18 (H-10, s), 4.70 (H-1', d, 8); (D<sub>2</sub>O) 93.3 (C-1), 143.4 (C-3), 102.6 (C-4), 69.3 (C-5), 61.7 (C-6)<sup>a</sup>, 62.3 (C-7)<sup>a</sup>, 77.3 (C-8), 52.1 (C-9), 20.2 (C-10), 99.5 (C-1'), 73.4 (C-2'), 76.3 (C-3'), 70.6 (C-4'), 77.2 (C-5'), 61.5 (C-6'). *Physostegia virginiana* var. *speciosa* (Lamiaceae) (27)

## 53. PHYSOSIDE

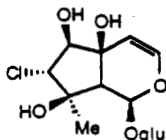


C<sub>15</sub>H<sub>24</sub>O<sub>10</sub> 364.35 mp 222° [α] -232° (H<sub>2</sub>O) (250 MHz D<sub>2</sub>O) 5.57 (H-1, d, 1.9), 6.29 (H-3, dd, 6.5, 1.9), 5.02 (H-4, bdd, 6.5, 2.1), 2.78 (H-5, m), 4.08 (H-6, dd, 9.5, 7.0), 3.53 (H-7, d, 9.5), 2.36 (H-9, bd, 9), 1.27 (H-10, s), 4.72 (H-1', d, 8); (D<sub>2</sub>O) 93.4 (C-1), 140.3 (C-3), 102.6 (C-4), 30.3 (C-5), 75.5 (C-6)<sup>a</sup>, 80.6 (C-7)<sup>a</sup>, 74.9 (C-8), 47.6 (C-9), 23.2 (C-10), 98.7 (C-1'), 73.5 (C-2'), 76.4 (C-3'), 70.4 (C-4'), 77.0 (C-5'), 61.5 (C-6'). *Physostegia virginiana* var. *speciosa* (Lamiaceae) (27)

## 54. JARANIDOSIDE

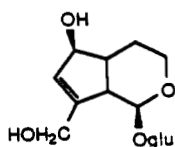


C<sub>17</sub>H<sub>26</sub>O<sub>12</sub> 422.39 mp 128-130° (90 MHz D<sub>2</sub>O) 6.42 (H-1, s), 6.95 (H-3, d, 6), 5.55 (H-4, dd, 6, 1.5), 4.6-3.7 (H-6, H-7, m), 3.17 (H-9, s), 1.95 (H-10, s), 2.55 (OAc), 5.2 (H-1'). *Ajuga spectabilis* (Labiatae) (40)

55. LINARIOSIDE (revision of *Avicennioside*)

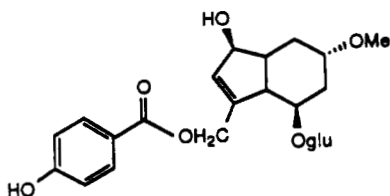
C<sub>15</sub>H<sub>23</sub>ClO<sub>10</sub> 380.35 uv 203 (H<sub>2</sub>O) (250 MHz CD<sub>3</sub>CN/D<sub>2</sub>O) 5.64 (H-1, bs), 6.32 (H-3, d, 6.5), 5.11 (H-4, dd, 6.5, 1.5), 3.63 (H-6, d, 10), 4.03 (H-7, d, 10), 2.41 (H-9, bs), 1.15 (H-10, s), 4.64 (H-1', d, 8), 3.24 (H-2', dd, 9, 8), 3.42 (H-3', dd, 9, 8), 3.22 (H-4', dd, 9, 8), 3.39 (H-5', ddd, 9, 5.5, 2), 3.9 (H-6', dd, 13, 2), 3.65 (H-6', dd, 13, 5.5); (D<sub>2</sub>O) 93.1 (C-1), 141.3 (C-3), 110.2 (C-4), 66.6 (C-5), 81.3 (C-6), 72.9 (C-7), 76.0 (C-8), 58.4 (C-9), 19.3 (C-10), 100.0 (C-1'), 74.5 (C-2'), 77.4 (C-3'), 71.7 (C-4'), 78.2 (C-5'), 62.8 (C-6'). *Avicennia officinalis* (Verbenaceae) (41-43)

## 56. 3,4-DIHYDROAUCUBIN



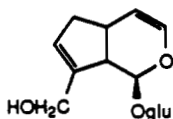
$C_{15}H_{24}O_9$  348.35  $[\alpha] -146.4^\circ$  ( $H_2O$ ) (90 MHz  $D_2O$ ) 5.20 (H-1, d, 4.5), 1.85 (H-4, m), 2.60 (H-5, m), 5.99 (H-7, m), 3.00 (H-9, m), 4.40 (H-10, s); ( $D_2O$ ) 98.0 (C-1), 61.0 (C-3), 24.5 (C-4), 44.1 (C-5), 79.1 (C-6), 129.1 (C-7), 147.9 (C-8), 47.2 (C-9), 60.4 (C-10), 98.5 (C-1'), 73.8 (C-2'), 77.0 (C-3'), 70.5 (C-4'), 76.7 (C-5'), 61.6 (C-6'). *Plantago asiatica* (Plantaginaceae) (44)

## 57. NISHINDASIDE

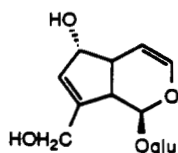


$C_{23}H_{30}O_{12}$  498.48  $[\alpha] -83.5$  (MeOH) (100 MHz  $DMSO-d_6$ ) 4.96 (H-1, d, 6), 5.76 (H-7, bs), 4.84 (H-10, bs), 4.52 (H-1', d, 8), 7.86 (H-2', d, 8), 6.86 (H-3', d, 8), 3.40 (OMe); ( $CD_3OD$ ) 98.4 (C-1), 100.0 (C-3), 30.2 (C-4), 44.6 (C-5), 80.8 (C-6), 131.4 (C-7), 142.5 (C-8), 49.2 (C-9), 63.0 (C-10), 56.1 (OMe), 100.0 (C-1'), 74.6 (C-2'), 77.9 (C-3'), 71.2 (C-4'), 77.9 (C-5'), 62.6 (C-6'), 167.6 (C=O), 121.8 (C-1''), 132.7 (C-2''), 116.1 (C-3''), 163.3 (C-4'') (Verbenaceae) (45)

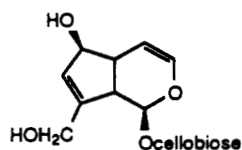
## 58. BARTSIOSIDE



$C_{15}H_{22}O_8$  330.33 (360 MHz  $D_2O$ ) 5.33 (H-1, d, 3.5), 6.23 (H-3, d, 6.3), 4.92 (H-4, dt), 2.92 (H-5, bs), 2.62, 2.07 (H-6, bd's, 15), 5.61 (H-7, bs), 2.92 (H-9, bs), 4.23, 4.16 (H-10, d's, 14.2), 4.73 (H-1'), 3.5-3.25 (H-2'-H-5'), 3.87 (H-6', dd, 12.3, 1.9), 3.68 (H-6', dd, 12.3, 5.5); ( $CD_3OD$ ) 96.2 (C-1), 140.4 (C-3), 107.9 (C-4), 35.4 (C-5)<sup>a</sup>, 39.7 (C-6)<sup>a</sup>, 127.4 (C-7), 144.3 (C-8), 48.4 (C-9), 61.1 (C-10)<sup>b</sup>, 99.5 (C-1'), 74.5 (C-2'), 77.8 (C-3')<sup>c</sup>, 71.2 (C-4'), 77.5 (C-5')<sup>c</sup>, 62.4 (C-6')<sup>b</sup>. *Penstemon cardwellii* (Scrophulariaceae) (46, 47, personal communication of M. Roby and F. Stermitz)

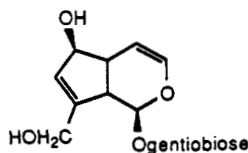
59. 6-*epi*-AUCUBIN

$C_{15}H_{22}O_9$  346.33  $[\alpha] -58.9^\circ$  (MeOH) uv 204 ( $H_2O$ ) (100 MHz  $CD_3OD$ ) 4.95 (H-1, d, 7.0), 6.45 (H-3, dd, 6.0, 1.5), 4.92 (H-4, dd, 6.0, 4.0), 2.4-2.9 (H-5), 4.70 (H-6, m), 5.90 (H-7, bs), 2.4-2.9 (H-9), 4.40, 4.15 (H-10, 15.0), 4.65 (H-1', d, 7.0); ( $CD_3OD$ ) 99.1 (C-1), 143.2 (C-3), 102.7 (C-4), 41.9 (C-5), 76.2 (C-6), 129.6 (C-7), 150.6 (C-8), 47.7 (C-9), 61.5 (C-10), 99.9 (C-1'), 74.7 (C-2'), 78.0 (C-3')<sup>a</sup>, 71.4 (C-4'), 77.6 (C-5')<sup>a</sup>, 62.6 (C-6'). *Tecoma chrysantha* (Bignoniaceae) (48)

60. AUCUBIGENIN-1-O- $\beta$ -CELLOBIOSIDE

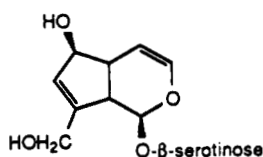
$C_{21}H_{32}O_{14}$  508.48  $[\alpha] -92.0^\circ$  (MeOH) uv 204 (MeOH) (60 MHz  $D_2O$ ) 5.14 (H-1, d, 5), 6.21 (H-3, dd, 6, 2), 5.01 (H-4, dd, 6, 4), 2.74 (H-5, m), 4.44 (H-6, m), 5.75 (H-7, m), 3.03 (H-9, m), 4.23 (H-10, bs), 4.70 (H-1', d, 7), 4.47 (H-1'', d, 7); ( $D_2O$ ) 96.3 (C-1), 140.4 (C-3), 106.1 (C-4), 43.3 (C-5), 81.4 (C-6), 129.4 (C-7), 147.6 (C-8), 47.2 (C-9), 60.3 (C-10), 99.0 (C-1'), 73.4 (C-2')<sup>a</sup>, 76.3 (C-3')<sup>b</sup>, 79.4 (C-4')<sup>a</sup>, 75.8 (C-5'), 60.8 (C-6'), 103.3 (C-1''), 73.9 (C-2'')<sup>a</sup>, 76.8 (C-3'')<sup>b</sup>, 70.3 (C-4'')<sup>b</sup>, 76.5 (C-5'')<sup>b</sup>, 61.4 (C-6''). *Odontites verna* subsp. *serotina* (Scrophulariaceae) (49)

61. 6'-O-GLUCOSYLAUCUBIN (Aucubigenin-1-O- $\beta$ -gentiobioside)



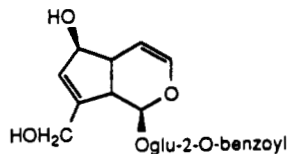
$C_{21}H_{32}O_{14}$  508.48 mp 180–181°  $[\alpha] -45^\circ$  (MeOH) uv 204 (MeOH) (60 MHz  $D_2O$ ) 5.14 (H-1, d, 5), 6.24 (H-3, dd, 6, 2), 5.04 (H-4, dd, 6, 4), 2.75 (H-5, m), 4.47 (H-6, m), 5.77 (H-7, m), 3.07 (H-9, m), 4.24 (H-10, bs), 4.70 (H-1', d, 7), 4.44 (H-1'', d, 7); ( $D_2O$ ) 96.4 (C-1), 140.4 (C-3), 106.0 (C-4), 43.4 (C-5), 81.4 (C-6), 129.5 (C-7), 147.5 (C-8), 47.2 (C-9), 60.3 (C-10), 99.2 (C-1'), 73.5 (C-2')<sup>a</sup>, 77.0 (C-3')<sup>b</sup>, 70.4 (C-4'), 76.2 (C-5'), 69.4 (C-6'), 103.7 (C-1''), 73.9 (C-2'')<sup>a</sup>, 76.6 (C-3'')<sup>b</sup>, 70.4 (C-4''), 76.4 (C-5'')<sup>b</sup>, 61.5 (C-6''). *Odontites verna* subsp. *serotina* (Scrophulariaceae) (49)

62. AUCUBIGENIN-1-O- $\beta$ -SEROTINOSIDE



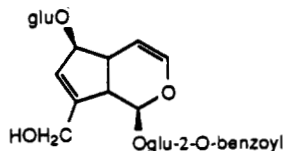
$C_{20}H_{30}O_{13}$  478.45  $[\alpha] -44.7^\circ$  (MeOH) uv 204 (MeOH) (60 MHz  $D_2O$ ) 5.12 (H-1, d, 4, 5), 6.22 (H-3, dd, 6, 2), 5.02 (H-4, dd, 6, 4), 2.71 (H-5, m), 4.45 (H-6, m), 5.76 (H-7, m), 3.02 (H-9, m), 4.20 (H-10, bs), 4.73 (H-1', d, 7), 4.83 (H-1'', d, 3); ( $D_2O$ ) 96.4 (C-1), 140.4 (C-3), 106.2 (C-4), 43.5 (C-5), 81.5 (C-6), 129.8 (C-7), 147.4 (C-8), 47.4 (C-9), 60.5 (C-10), 99.1 (C-1')<sup>a</sup>, 73.7 (C-2'), 76.8 (C-3'), 70.4 (C-4')<sup>b</sup>, 75.7 (C-5'), 67.0 (C-6'), 99.3 (C-1''), 72.4 (C-2''), 74.2 (C-3''), 70.3 (C-4'')<sup>b</sup>, 62.3 (C-5''). *Odontites verna* subsp. *serotina* (Scrophulariaceae) (50)

63. 2'-O-BENZOYLAUCUBIN



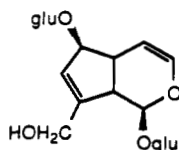
$C_{22}H_{26}O_{10}$  450.45  $[\alpha] -124.8^\circ$  (MeOH) uv 233 ( $H_2O$ ) (90 MHz  $D_2O$ ) 5.42 (H-1, d, 3), 5.62 (H-3, dd, 6, 1.5), 4.32 (H-4), 2.56 (H-5, m), 5.06 (H-6, bs), 5.79 (H-7, bs), 3.18 (H-9, m), 4.25 (H-10, bs), 5.00 (H-1', d, 2), 4.00 (H-2'), 8.2–8.0 (H-2''), 7.7–7.4 (H-3'', H-4''); ( $D_2O$ ) 94.7 (C-1), 139.3 (C-3), 105.9 (C-4), 41.5 (C-5), 80.5 (C-6), 128.7 (C-7), 147.7 (C-8), 46.9 (C-9), 59.8 (C-10), 97.3 (C-1'), 74.7 (C-2'), 74.4 (C-3'), 70.4 (C-4'), 77.2 (C-5'), 61.5 (C-6'), 168.0 (C=O), 130.1 (C-1''), 130.4 (C-2''), 129.3 (C-3''), 134.6 (C-4''). *Odontites verna* subsp. *serotina* (Scrophulariaceae) (51)

64. 6-O-GLUCOSYL-2'-O-BENZOYL-AUCUBIN



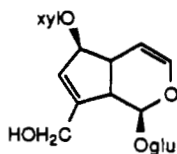
$C_{28}H_{36}O_{15}$  612.58 mp 141–143°  $[\alpha] -165.4^\circ$  (MeOH) uv 233 ( $H_2O$ ) (90 MHz  $D_2O$ ) 5.30 (H-1, d, 3), 5.65 (H-3, dd, 6, 1.5), 2.60 (H-5, m), 4.8–5.0 (H-6), 5.85 (H-7, bs), 3.00 (H-9, m), 4.4–4.0 (H-10, H-2', H-1''), 4.8–5.0 (H-1'); ( $D_2O$ ) 94.5 (C-1), 139.4 (C-3), 105.8 (C-4), 39.6 (C-5), 89.3 (C-6), 126.2 (C-7), 149.9 (C-8), 47.1 (C-9), 59.8 (C-10), 97.1 (C-1'), 74.7 (C-2'), 74.4 (C-3'), 70.2 (C-4')<sup>a</sup>, 77.2 (C-5')<sup>b</sup>, 61.4 (C-6'), 168.2 (O=C), 129.9 (C-1''), 130.4 (C-2''), 129.4 (C-3''), 134.7 (C-4''), 102.4 (C-1'''), 73.9 (C-2'''), 76.6 (C-3''')<sup>b</sup>, 70.3 (C-4''')<sup>a</sup>, 76.6 (C-5''')<sup>b</sup>, 61.4 (C-6'''). *Odontites verna* subsp. *serotina* (Scrophulariaceae) (52)

65. 6-O-GLUCOPYRANOSYLAUCUBIN



$C_{21}H_{32}O_{14}$  508.48  $[\alpha] -94.4^\circ$  (MeOH) uv 204 (MeOH) (90 MHz  $D_2O$ ) 5.23 (H-1, d, 5.0), 6.32 (H-3, dd, 6.0, 1.5), 5.18 (H-4, dd, 6.0, 3.5), 3.2–3.0 (H-5), 4.64 (H-6, m), 5.96 (H-7, bs), 3.2–3.0 (H-9), 4.64 (H-6, m), 5.96 (H-7, bs), 3.2–3.0 (H-9), 4.34 (H-10, bs), 4.78 (H-1', d, 7), 4.60 (H-1'', d, 7); ( $D_2O$ ) 96.4 (C-1), 140.6 (C-3), 105.8 (C-4), 41.7 (C-5), 90.4 (C-6),

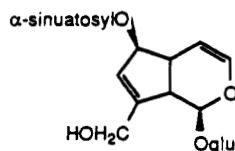


66. 6-O- $\beta$ -D-XYLOPYRANOSYL-AUCUBIN

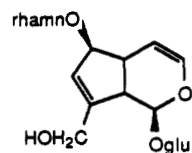
127.0 (C-7), 149.3 (C-8), 47.4 (C-9), 60.3 (C-10), 99.2 (C-1'), 73.6 (C-2')<sup>a</sup>, 76.9 (C-3')<sup>b</sup>, 70.4 (C-4'), 76.4 (C-5')<sup>b</sup>, 61.5 (C-6'), 102.5 (C-1''), 74.0 (C-2''), 76.7 (C-3'')<sup>b</sup>, 70.4 (C-4''), 76.7 (C-5'')<sup>b</sup>, 61.5 (C-6''). *Odontites verna* subsp. *serotina* (Scrophulariaceae) (53)

$C_{20}H_{30}O_{13}$  478.45 mp 192–193° [ $\alpha$ ] –85° (H<sub>2</sub>O) uv 204 (MeOH) (90 MHz D<sub>2</sub>O) 5.22 (H-1, d, 5), 6.38 (H-3, dd, 6, 1.5), 5.17 (H-4, dd, 6, 3.7), 3.2–2.9 (H-5), 4.60 (H-6, bs), 5.98 (H-7, bs), 3.2–2.9 (H-9), 4.38 (H-10, bs); (D<sub>2</sub>O) 94.7 (C-1), 139.0 (C-3), 103.9 (C-4), 40.0 (C-5), 88.6 (C-6), 125.3 (C-7), 147.7 (C-8), 45.7 (C-9), 59.8 (C-10), 97.5 (C-1'), 73.6 (C-2'), 77.1 (C-3'), 70.5 (C-4'), 76.5 (C-5'), 61.7 (C-6'), 101.6 (C-1''), 74.0 (C-2''), 76.7 (C-3''), 70.1 (C-4''), 64.0 (C-5''). *Verbascum sinuatum* (Scrophulariaceae) (54)

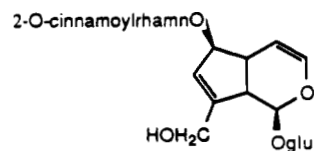
## 67. SINUATOSIDE (6-O-Sinuatosyl-aucubin)



$C_{26}H_{40}O_{18}$  640.59 [ $\alpha$ ] –55.7° (H<sub>2</sub>O) uv 204 (MeOH) (90 MHz D<sub>2</sub>O) 5.36 (H-1, d, 4.5), 6.34 (H-3, dd, 6.3, 1.7), 5.17 (H-4, dd, 3), 4.58 (H-6, bs), 5.97 (H-7, bs), 4.36 (H-10, bs), 4.76 (H-1', d), 5.20 (H-1'', bs); (D<sub>2</sub>O) 96.0 (C-1), 140.5 (C-3), 106.2 (C-4), 40.6 (C-5), 88.0 (C-6), 128.1 (C-7), 148.8 (C-8), 47.1 (C-9), 60.3 (C-10), 99.2 (C-1'), 73.6 (C-2'), 77.0 (C-3')<sup>a</sup>, 70.4 (C-4'), 76.6 (C-5')<sup>a</sup>, 61.6 (C-6'), 98.7 (C-1''), 68.2 (C-2''), 79.9 (C-3''), 69.9 (C-4''), 71.6 (C-5''), 61.9 (C-6''), 105.2 (C-1'''), 74.0 (C-2'''), 76.4 (C-3'''), 69.9 (C-4'''), 65.9 (C-5'''). *Verbascum sinuatum* (Scrophulariaceae) (55)

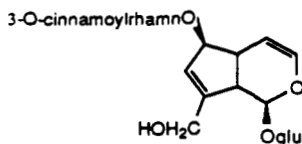
68. SINUATOL (6-O- $\alpha$ -L-Rhamnopyranosylaucubin)

$C_{21}H_{32}O_{13}$  492.48 [ $\alpha$ ] –158° (H<sub>2</sub>O) uv 204 (MeOH) (90 MHz D<sub>2</sub>O) 5.20 (H-1, d, 5.0), 6.38 (H-3, dd, 6.0, 1.6), 5.16 (H-4, dd, 6.0, 3.7), 2.98 (H-5, bs), 4.60 (H-6, bs), 5.98 (H-7, bs), 3.10 (H-9, bd), 4.36 (H-10, bs); (D<sub>2</sub>O) 96.7 (C-1), 140.8 (C-3), 105.8 (C-4), 41.6 (C-5), 88.3 (C-6), 126.9 (C-7), 149.2 (C-8), 47.4 (C-9), 60.4 (C-10), 99.3 (C-1'), 73.6 (C-2'), 77.0 (C-3'), 70.4 (C-4'), 76.5 (C-5'), 61.4 (C-6'), 100.4 (C-1''), 71.2 (C-2''), 71.0 (C-3''), 72.9 (C-4''), 69.8 (C-5''), 17.4 (C-6''). *Verbascum sinuatum* (Scrophulariaceae) (56)

69. NIGROSIDE 2 [6-O-(2''-O-Cinnamoyl- $\alpha$ -L-rhamnopyranosyl)aucubin]

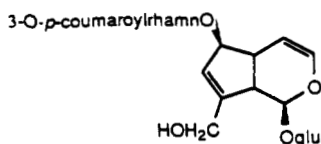
$C_{30}H_{38}O_{14}$  622.62 [ $\alpha$ ] –142° (MeOH) uv 281, 217 (MeOH) (200 MHz CD<sub>3</sub>OD) 4.90 (H-1), 6.32 (H-3, dd, 6, 1.5), 5.11 (H-4, dd, 6, 3.5), 2.90–2.80 (H-5, H-9, m), 4.46 (H-6, m), 5.87 (H-7, bs), 4.65 (H-1', d, 7.6), 4.87 (H-1'', d, 1.6), 5.05 (H-2'', dd, 3.4, 1.6), 3.45 (H-4'', t, 9.3), 1.28 (H-6'', d, 6.1), 6.57/7.72 (H $\alpha$ , H $\beta$ , d's, 16), 7.60, 7.38 (H-2'''–H-4'''); (CD<sub>3</sub>OD) 98.0 (C-1), 141.9 (C-3), 105.4 (C-4), 44.4 (C-5), 89.3 (C-6), 127.0 (C-7), 149.7 (C-8), — (C-9), 61.5 (C-10), 99.9 (C-1'), 74.9 (C-2'), 78.3 (C-3'), 71.6 (C-4'), 77.9 (C-5'), 62.7 (C-6'), 98.3 (C-1''), 74.6 (C-2''), 70.6 (C-3''), 74.3 (C-4''), 70.3 (C-5''), 18.1 (C-6''), 167.9 (O=C), 118.6 (C $\alpha$ ), 146.7 (C $\beta$ ), 135.6 (C-1'''), 129.9 (C-2''')<sup>a</sup>, 129.2 (C-3''')<sup>a</sup>, 131.5 (C-4'''). *Verbascum nigrum* (Scrophulariaceae) (57)

70. NIGROSIDE 1 [6-*O*-(3''-*O*-Cinnamoyl- $\alpha$ -L-rhamnopyranosyl)aucubin]



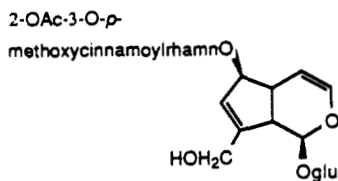
C<sub>30</sub>H<sub>38</sub>O<sub>14</sub> 622.62 [ $\alpha$ ] -140° (MeOH) uv 280, 217 (MeOH) (200 MHz CD<sub>3</sub>OD) 4.93 (H-1, d, 6.6), 6.36 (H-3, dd, 6, 1.5), 5.18 (H-4, dd, 6, 3.5), 2.96-2.84 (H-5, H-9, m), 4.50 (H-6, m), 5.90 (H-7, bs), 4.69 (H-1', d, 7.6), 4.89 (H-1'', 4.01 (H-2'', dd, 3.4, 1.6), 5.08 (H-3'', dd, 9.3, 3.4), 1.33 (H-6'', d, 6.1), 6.60/7.77 (H $\alpha$ , H $\beta$ , d's, 16), 7.60, 7.41 (H-2''-H-4''); (CD<sub>3</sub>OD) 98.0 (C-1), 141.9 (C-3), 105.5 (C-4), 44.3 (C-5), 89.0 (C-6), 127.0 (C-7), 149.5 (C-8), — (C-9), 61.5 (C-10), 99.9 (C-1'), 74.9 (C-2'), 78.3 (C-3'), 71.5 (C-4'), 77.9 (C-5'), 62.7 (C-6'), 101.0 (C-1''), 70.4 (C-2''), 75.7 (C-3''), 71.4 (C-4''), 70.4 (C-5''), 18.1 (C-6''), 168.1 (O=C), 119.0 (C $\alpha$ ), 146.3 (C $\beta$ ), 135.7 (C-1'''), 129.9 (C-2'''), 129.1 (C-3'''), 131.4 (C-4'''). *Verbascum nigrum* (Scrophulariaceae) (57)

71. 3''-*O*-*p*-COUMAROYLSINUATOL [6-*O*-(3''-*O*-*p*-Coumaroyl- $\alpha$ -L-rhamnopyranosyl)aucubin]



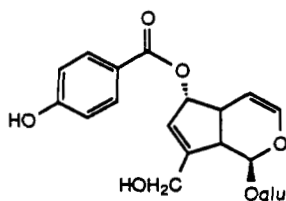
C<sub>30</sub>H<sub>38</sub>O<sub>15</sub> 638.62 [ $\alpha$ ] -174.2° (MeOH) uv 312, 225, 213, 205 (MeOH) (DMSO-*d*<sub>6</sub>) 95.1 (C-1), 139.9 (C-3), 103.8 (C-4), 42.3 (C-5), 86.4 (C-6), 132.1 (C-7), 148.6 (C-8), 46.6 (C-9), 59.4 (C-10), 97.7 (C-1'), 73.0 (C-2'), 77.0 (C-3'), 69.8 (C-4'), 76.2 (C-5'), 60.9 (C-6'), 99.2 (C-1''), 66.3 (C-2''), 73.4 (C-3''), 67.9 (C-4''), 68.7 (C-5''), 17.7 (C-6''), 166.2 (O=C), 114.4 (C $\alpha$ ), 143.9 (C $\beta$ ), 124.6 (C-1'''), 130.0 (C-2'''), 115.4 (C-3'''), 159.6 (C-4'''). *Verbascum laxum* (Scrophulariaceae) (58)

72. 6-*O*-(2''-*O*-ACETYL-3''-*O*-*p*-METHOXY-*trans*-CINNAMOYL)-RHAMNOPYRANOSYLAUCUBIN

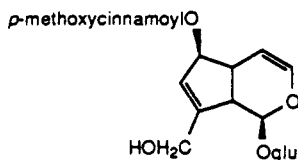


C<sub>33</sub>H<sub>42</sub>O<sub>16</sub> 694.69 [M]<sub>546</sub> -130° (MeOH) uv 320, 288, 225, 209 (MeOH) (250 MHz CD<sub>3</sub>OD) 6.20 (H-3, d, 6), 2.9-2.7 (H-5, m), 5.75 (H-7, bs), 2.9-2.7 (H-9, m), 1.97 (OAc), 1.37 (H-6'', d, 16), 3.65 (OMe), 6.22/7.45 (H $\alpha$ , H $\beta$ , d's, 15.8), 6.77 (H-2'', d, 9), 7.35 (H-3'', d, 9); (CD<sub>3</sub>OD) 98.0 (C-1), 142.0 (C-3), 105.4 (C-4), 44.1 (C-5), 89.4 (C-6), 127.1 (C-7), 149.9 (C-8), 48.2 (C-9), 61.4 (C-10), 172.2 (O=CMe), 20.9 (O=CMe), 100.1 (C-1'), 74.9 (C-2'), 78.2 (C-3'), 71.6 (C-4'), 77.9 (C-5'), 62.7 (C-6'), 98.4 (C-1''), 71.6 (C-2''), 73.3 (C-3''), 71.6 (C-4''), 70.3 (C-5''), 18.1 (C-6''), 167.9 (O=C), 115.5 (C $\alpha$ ), 147.0 (C $\beta$ ), 128.2 (C-1'''), 131.1 (C-2'''), 115.5 (C-3'''), 163.3 (C-4'''), 55.9 (ArOMe). *Verbascum laxum* (Scrophulariaceae) (58)

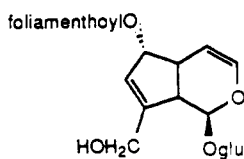
73. 6-*O*-*p*-HYDROXYBENZOYL-6-*epi*-AUCUBIN



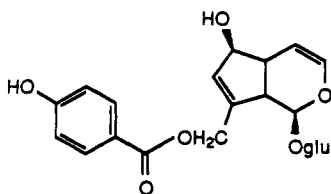
C<sub>22</sub>H<sub>26</sub>O<sub>11</sub> 466.44 [ $\alpha$ ] -87.6° (MeOH) uv 236 (H<sub>2</sub>O) (100 MHz D<sub>2</sub>O) 4.98 (H-1, d, 7), 6.30 (H-3, dd, 6, 1.5), 4.93 (H-4, dd, 6, 4), 3.1-2.5 (H-5, m), 5.65 (H-6, bd), 5.95 (H-7, m), 3.1-2.5 (H-9, m), 4.35 (H-10, bs), 4.70 (H-1', d, 7), 7.66 (H-2'', d, 8), 6.78 (H-3'', d, 8); (D<sub>2</sub>O) 98.7 (C-1), 142.7 (C-3), 102.0 (C-4), 40.1 (C-5), 79.7 (C-6), 125.9 (C-7), 152.4 (C-8), 46.9 (C-9), 60.7 (C-10), 99.2 (C-1'), 73.6 (C-2'), 76.4 (C-3')<sup>a</sup>, 70.0 (C-4'), 76.7 (C-5')<sup>a</sup>, 61.1 (C-6'), 167.6 (C=O), 121.7 (C-1''), 132.2 (C-2''), 115.8 (C-3''), 161.3 (C-4''). *Tecoma chrysantha* (Bignoniaceae) (59)

74. 6-*O*-*p*-METHOXYCINNAMOYL-AUCUBIN

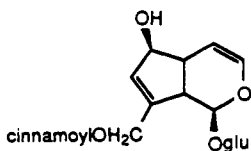
$C_{25}H_{30}O_{11}$  506.51 uv 310, 224 (MeOH) (pentaacetate 250 MHz  $CDCl_3$ ) 5.50–4.70 (H-1), 6.23 (H-3, d, 6.1), 5.50–4.70 (H-4), 2.37 (H-5, m), 5.50–4.70 (H-6), 5.72 (H-7, d, 8.2), 2.91 (H-9, m), 4.65, 3.97 (H-10, dd's, 11, 1.8), 5.50–4.70 (H-1'-H-4'), 3.70 (H-5', m), 4.35–4.01 (H-6', m), 6.26/7.49 (H $\alpha$ , H $\beta$ , d's, 16), 7.49 (H-2'', d, 8.8), 6.92 (H-3'', d, 8.8), 3.84 (OMe), 2.18–2.01 (OAc). *Buddleja globosa* (Loganiaceae) (60)

75. AMARELOSIDE (6-*O*-Foliamenthoyl-6-*epi*-aucubin)

$C_{25}H_{36}O_{11}$  512.55 [ $\alpha$ ] -50.7° (MeOH) uv 233 (H<sub>2</sub>O) (100 MHz  $CD_3OD$ ) 4.6–5.0 (H-1), 6.42 (H-3, dd, 6, 1.5), 4.6–5.0 (H-4), 2.4–2.9 (H-5), 5.62 (H-6, m), 5.92 (H-7, bs), 2.4–2.9 (H-9), 4.52, 4.24 (H-10, 15), 4.6–5.0 (H-1'), 6.73 (H-3'', m), 2.0–2.4 (H-4'', H-5''), 5.38 (H-7'', t, 7.5), 4.20, 3.95 (H-8'', 15), 1.80 (H-9'', bs), 1.70 (H-10'', bs); ( $CD_3OD$ ) 100.8 (C-1), 143.7 (C-3)<sup>a</sup>, 102.3 (C-4), 39.7 (C-5), 79.9 (C-6), 126.1 (C-7)<sup>b</sup>, 155.0 (C-8), 48.4 (C-9), 62.2 (C-10)<sup>c</sup>, 100.0 (C-1'), 75.4 (C-2'), 78.5 (C-3')<sup>d</sup>, 71.7 (C-4'), 78.3 (C-5')<sup>d</sup>, 62.8 (C-6')<sup>c</sup>, 169.6 (C-1''), 129.5 (C-2'')<sup>b</sup>, 144.1 (C-3'')<sup>a</sup>, 28.6 (C-4''), 42.0 (C-5''), 138.8 (C-6''), 126.3 (C-7''), 59.9 (C-8''), 13.2 (C-9''), 17.2 (C-10''). *Tecoma chrysantha* (Bignoniaceae) (61)

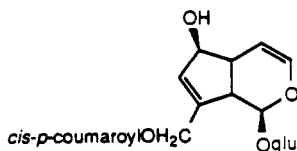
76. AGNUSIDE (10-*O*-*p*-Hydroxybenzoylaucubin)

$C_{22}H_{26}O_{11}$  466.44 mp 148–152° (100 MHz  $DMSO-d_6$ ) 6.36 (H-3, dd, 7, 2), 5.10 (H-4, dd, 7, 4), 2.90 (H-5, m), 4.38 (H-6, m), 5.80 (H-7, bs), 2.90 (H-9, m), 4.90 (H-10, bs), 4.54 (H-1', d, 8), 3.7 (H-6', m), 7.90 (H-2'', d, 8), 6.90 (H-3'', d, 8); ( $CD_3OD$ ) 97.9 (C-1), 141.7 (C-3), 105.5 (C-4), 46.2 (C-5), 82.8 (C-6), 132.8 (C-7), 142.8 (C-8), 48.7 (C-9), 63.6 (C-11), 100.1 (C-1'), 74.8 (C-2'), 77.8 (C-3'), 71.3 (C-4'), 78.1 (C-5'), 62.6 (C-6'), 167.8 (C=O), 122.0 (C-1''), 132.3 (C-2''), 116.2 (C-3''), 163.6 (C-4''). *Vitex agnus-castus* (Verbenaceae) (45, 62, 63)

77. ISOSCROPHULARIOSIDE (10-*O*-Cinnamoylaucubin, Lytanthosalin)

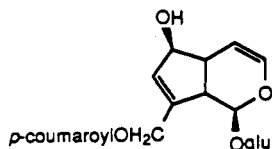
$C_{24}H_{28}O_{10}$  476.48 mp 98–101° uv 277, 222, 216, 204 (MeOH) (100 MHz  $CD_3OD$ ) 4.95 (H-1, d, 7.4), 6.32 (H-3, dd, 6, 1.8), 5.10 (H-4, dd, 6, 3.8), 2.62 (H-5, m), 4.44 (H-6, m), 5.80 (H-7, tdd), 2.95 (H-9, ddd, 7.4), 4.94 (H-10), 4.68 (H-1', d, 7.1), 3.74 (H-6', m), 6.55/7.71 (H $\alpha$ , H $\beta$ , d's, 16), 7.62 (H-2'', m), 7.43 (H-3'', H-4'', m); ( $CD_3OD$ ) 97.9 (C-1), 141.6 (C-3), 105.5 (C-4), 46.0 (C-5), 82.6 (C-6), 132.5 (C-7), 142.3 (C-8), 48.1 (C-9), 63.5 (C-10), 100.0 (C-1'), 74.6 (C-2'), 77.9 (C-3')<sup>a</sup>, 71.4 (C-4'), 77.6 (C-5')<sup>a</sup>, 62.6 (C-6'), 168.4 (C=O), 118.4 (C $\alpha$ ), 146.5 (C $\beta$ ), 135.4 (C-1''), 129.9 (C-2'')<sup>b</sup>, 129.2 (C-3'')<sup>b</sup>, 131.5 (C-4''). *Penstemon eriantherus* (Scrophulariaceae) (64)

78. *cis*-EUROSTOSIDE (10-*O*-*cis*-*p*-Coumaroylaucubin)



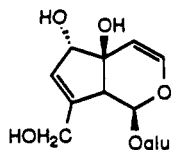
C<sub>24</sub>H<sub>28</sub>O<sub>11</sub> 492.48 [α] -49.6° (EtOH *cis/trans* mix) (90 MHz CD<sub>3</sub>OD) 5.00 (H-1, d, 7.4), 6.39 (H-3, dd, 6.3, 2.0), 5.11 (H-4, dd, 6.3, 3.8), 2.70 (H-5, m), 4.45 (H-6, m), 5.80 (H-7, bs), 2.96 (H-9, bt, 7.4), 4.70 (H-10, d, 7.1), 4.69 (H-1', d, 7.1), 5.81/6.90 (H<sub>α</sub>, H<sub>β</sub>, d's, 12.6), 7.63 (H-2'', d, 8.9), 6.75 (H-3'', d, 8.9); (CD<sub>3</sub>OD) 100.3 (C-1'), 74.9 (C-2'), 78.2 (C-3'), 71.5 (C-4'), 78.0 (C-5'), 62.8 (C-6'). *Vitex rotundifolia* (Verbenaceae) (65)

79. *trans*-EUROSTOSIDE (10-*O*-*trans*-*p*-Coumaroylaucubin)



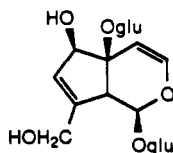
C<sub>24</sub>H<sub>28</sub>O<sub>11</sub> 492.48 [α] -128.1° (MeOH) uv 303, 292 sh, 218 (MeOH) (360 MHz D<sub>2</sub>O) 5.46 (H-1, d, 5), 6.49 (H-3, dd, 6, 1.5), 5.28 (H-4, dd, 6, 3.5), 2.92 (H-5, m), 4.70 (H-6, s), 6.10 (H-7, tdd, 1.6, 1), 3.36 (H-9, m), 5.10-4.98 (H-10), 4.92 (H-1', d, 7.5), 3.90 (H-6'), 6.54/7.82 (H<sub>α</sub>, H<sub>β</sub>, d's, 16), 7.69 (H-2'', d, 9), 7.08 (H-3'', d, 9); (CD<sub>3</sub>OD) 97.9 (C-1), 141.6 (C-3), 105.5 (C-4), 46.1 (C-5), 82.7 (C-6), 132.3 (C-7), 142.6 (C-8), 48.2 (C-9), 63.3 (C-10), 100.1 (C-1'), 74.7 (C-2'), 77.7 (C-3'), 71.3 (C-4'), 77.9 (C-5'), 62.6 (C-6'), 168.8 (C=O), 114.8 (C<sub>α</sub>), 146.9 (C<sub>β</sub>), 127.0 (C-1''), 131.3 (C-2''), 116.8 (C-3''), 161.1 (C-4''). *Euphrasia rostkoviana* (Scrophulariaceae) (66)

80. 6-*epi*-MONOMELITTOSIDE



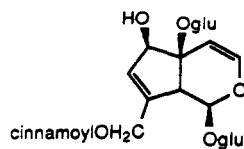
C<sub>15</sub>H<sub>22</sub>O<sub>10</sub> 362.33 [α] -47° (MeOH) (100 MHz D<sub>2</sub>O) 5.51 (H-1, d, 4.7), 6.45 (H-3, d, 6.5), 5.12 (H-4, d, 6.5), 4.57 (H-6, m), 5.72 (H-7, bs), 3.00 (H-9, m, 4.7), 4.24 (H-10, bs); (CD<sub>3</sub>OD) 95.2 (C-1), 142.8 (C-3), 105.7 (C-4), 78.3 (C-5), 83.9 (C-6), 129.2 (C-7), 145.4 (C-8), 55.1 (C-9), 60.9 (C-10), 99.6 (C-1'), 74.7 (C-2'), 78.3 (C-3'), 71.7 (C-4'), 77.7 (C-5'), 62.8 (C-6'). *Tecoma heptaphylla* (Bignoniaceae) (67)

81. MELITTOSIDE



C<sub>21</sub>H<sub>32</sub>O<sub>15</sub> 524.47 mp 157-159° [α] -41.9° (MeOH) (360 MHz D<sub>2</sub>O) 5.44 (H-1, d, 5.4), 6.51 (H-3, d, 6.5), 5.16 (H-4, d, 6.5), 4.58 (H-6, bs), 5.86 (H-7, dd, 2.0, 1.8), 3.35 (H-9, d, 5.4), 4.28, 4.25 (H-10, d's, 15.2); (CD<sub>3</sub>OD) 94.2 (C-1), 143.4 (C-3), 105.3 (C-4), 80.1 (C-5), 79.9 (C-6), 128.2 (C-7), 147.3 (C-8), 50.5 (C-9), 60.9 (C-10), 99.7 (C-1'), 74.9 (C-2'), 78.2 (C-3')<sup>a</sup>, 70.8 (C-4')<sup>a</sup>, 77.2 (C-5')<sup>a</sup>, 62.1 (C-6')<sup>a</sup>, 98.1 (C-1''), 75.1 (C-2''), 78.4 (C-3'')<sup>a</sup>, 71.7 (C-4''), 78.1 (C-5'')<sup>a</sup>, 62.7 (C-6''). *Plantago media* (Plantaginaceae) (68, 69)

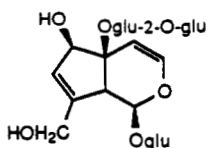
82. 10-*O*-*trans*-CINNAMOYLMELIT-TOSIDE



C<sub>30</sub>H<sub>38</sub>O<sub>16</sub> 654.62 [α] -8.3° (MeOH) uv 276 (MeOH) (500 MHz CD<sub>3</sub>OD) 5.63 (H-1, d, 4.4), 6.42 (H-3, d, 6.4), 5.15 (H-4, d, 6.4), 4.43 (H-6, bs), 5.91 (H-7, bs), 3.43-3.27 (H-9), 4.87 (H-10), 4.69 (H-1', d, 7.7), 3.43-3.27 (H-2''-H-5', H-2''-H-5''), 3.89-3.64 (H-6', H-6''), 4.64 (H-1'', d, 7.7), 6.58/7.74 (H<sub>α</sub>, H<sub>β</sub>, d's, 16.1), 7.43 (H-2''', H-4''', m), 7.62 (H-3''', m); (CD<sub>3</sub>OD) 94.9 (C-1), 143.8 (C-3), 105.5 (C-4), 80.5 (C-5), 80.4 (C-6), 131.6 (C-7), 142.1 (C-8), 52.6 (C-9), 63.1 (C-10), 100.0, 98.8 (C-1', C-1''), 75.4, 75.1 (C-2', C-2''), 78.3, 77.5 (C-3', C-3''), 71.9, 71.2 (C-4', C-4''), 78.6, 78.4 (C-5', C-5''), 63.0, 62.4 (C-6',

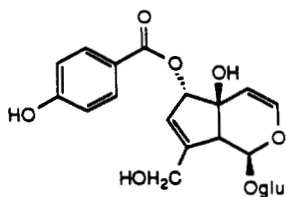
C-6<sup>m</sup>), 168.2 (O=C), 118.7 (C $\alpha$ ), 147.1 (C $\beta$ ), 135.9 (C-1<sup>m</sup>), 130.2 (C-2<sup>m</sup>), 129.5 (C-3<sup>m</sup>), 131.8 (C-4<sup>m</sup>). *Castilleja wightii* (Scrophulariaceae) (70)

**83. REHMANNIOSIDE D (Sophorosylmonomelittoside)**



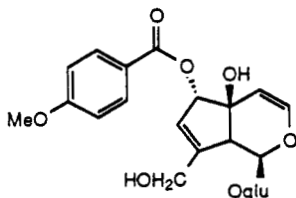
C<sub>27</sub>H<sub>42</sub>O<sub>20</sub> 686.62 [α] -27.1° (H<sub>2</sub>O) (90 MHz D<sub>2</sub>O) 5.30 (H-1, d, 6), 6.57 (H-3, d, 6), 5.43 (H-4, d, 6), 5.90 (H-7, bs); (D<sub>2</sub>O) 96.5 (C-1), 145.4 (C-3), 104.9 (C-4), 82.0 (C-5), 81.0 (C-6)<sup>a</sup>, 128.5 (C-7), 144.6 (C-8), 52.1 (C-9), 60.5 (C-10), 99.0 (C-1'), 73.7 (C-2'), 77.1 (C-3')<sup>b</sup>, 70.2 (C-4')<sup>c</sup>, 76.5 (C-5')<sup>d</sup>, 61.3 (C-6')<sup>e</sup>, 97.2 (C-1<sup>m</sup>), 80.8 (C-2<sup>m</sup>)<sup>a</sup>, 76.8 (C-3<sup>m</sup>)<sup>d</sup>, 70.2 (C-4<sup>m</sup>)<sup>c</sup>, 76.4 (C-5<sup>m</sup>)<sup>d</sup>, 61.7 (C-6<sup>m</sup>)<sup>e</sup>, 103.8 (C-1<sup>m</sup>), 74.8 (C-2<sup>m</sup>), 77.2 (C-3<sup>m</sup>)<sup>b</sup>, 70.5 (C-4<sup>m</sup>)<sup>c</sup>, 76.4 (C-5<sup>m</sup>)<sup>d</sup>, 61.4 (C-6<sup>m</sup>)<sup>e</sup>. *Rehmannia glutinosa* (Scrophulariaceae) (31)

**84. 6-O-*p*-HYDROXYBENZOYL-6-*epi*-MONOMELITTOSIDE**



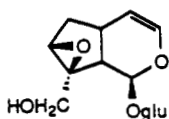
C<sub>22</sub>H<sub>26</sub>O<sub>12</sub> 482.44 [α] -121° (MeOH) uv 259 (?) (100 MHz D<sub>2</sub>O) 5.45 (H-1, d, 5), 6.45 (H-3, d, 6.5), 5.10 (H-4, d, 6.5), 5.84 (H-6, bs), 5.70 (H-7, bs), 3.02 (H-9, bd), 4.28 (H-10, bs), 7.76 (H-2<sup>m</sup>), 6.82 (H-3<sup>m</sup>); (CD<sub>3</sub>OD) 96.6 (C-1), 143.4 (C-3), 105.7 (C-4), 78.1 (C-5), 85.7 (C-6), 125.2 (C-7), 149.9 (C-8), 55.5 (C-9), 61.1 (C-10), 99.8 (C-1'), 74.7 (C-2'), 78.1 (C-3')<sup>a</sup>, 71.4 (C-4')<sup>a</sup>, 77.7 (C-5')<sup>a</sup>, 62.5 (C-6'), 167.6 (C=O), 122.2 (C-1<sup>m</sup>), 132.8 (C-2<sup>m</sup>), 116.2 (C-3<sup>m</sup>), 163.5 (C-4<sup>m</sup>). *Tecoma heptaphylla* (Bignoniaceae) (71)

**85. 6-O-*p*-METHOXYBENZOYL-6-*epi*-MONOMELITTOSIDE**



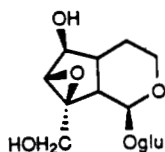
C<sub>23</sub>H<sub>28</sub>O<sub>12</sub> 496.47 mp 116-118° [α] -109° (MeOH) uv 255 (?) (100 MHz D<sub>2</sub>O) 5.44 (H-1, d, 5), 6.45 (H-3, d, 6.5), 5.12 (H-4, d, 6.5), 5.82 (H-6, bs), 5.75 (H-7, bs), 3.00 (H-9, bd), 4.20 (H-10, bs), 7.80 (H-2<sup>m</sup>), 6.84 (H-3<sup>m</sup>), 3.85 (OMe); (CD<sub>3</sub>OD) 96.6 (C-1), 143.4 (C-3), 105.7 (C-4), 78.1 (C-5), 85.7 (C-6), 125.2 (C-7), 150.0 (C-8), 55.5 (C-9), 61.1 (C-10), 99.8 (C-1'), 74.7 (C-2'), 78.1 (C-3')<sup>a</sup>, 71.5 (C-4')<sup>a</sup>, 77.6 (C-5')<sup>a</sup>, 62.6 (C-6'), 167.3 (C=O), 123.4 (C-1<sup>m</sup>), 132.6 (C-2<sup>m</sup>), 114.9 (C-3<sup>m</sup>), 165.2 (C-4<sup>m</sup>), 56.0 (OMe). *Tecoma heptaphylla* (Bignoniaceae) (71)

**86. 6-DEOXYCATALPOL**

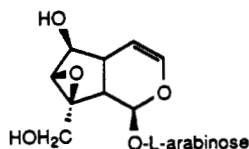


C<sub>15</sub>H<sub>22</sub>O<sub>9</sub> 346.33 mp 212.5-214° [α] -34° (EtOH) [α] -47° (MeOH) (360 MHz D<sub>2</sub>O) 5.08 (H-1, d, 9.1), 6.33 (H-3, dd, 5.8, 1.8), 5.06 (H-4, dd, 5.8, 4.2), 2.47 (H-5, m), 2.33 (H-6, dd, 14.1, 7.9), 1.56 (H-6, dd, 14.1, 9.9), 3.63 (H-7, bs), 2.49 (H-9, dd, 9.1, 7.4), 4.33, 3.76 (H-10, d's, 13.3), 4.87 (H-1', d, 7.9), 3.52-3.35 (H-2', H-5', m), 3.89 (H-6', bd, 12.2), 3.73 (H-6', dd, 12.2, 4.0); (CD<sub>3</sub>OD) 95.2 (C-1), 141.1 (C-3), 105.9 (C-4), 32.5 (C-5), 36.1 (C-6), 61.0 (C-7), 69.2 (C-8), 44.4 (C-9), 62.1 (C-10)<sup>a</sup>, 100.2 (C-1'), 75.1 (C-2'), 78.6 (C-3')<sup>b</sup>, 72.0 (C-4'), 78.0 (C-5')<sup>b</sup>, 63.1 (C-6')<sup>a</sup>. *Castilleja rhexifolia* aff. *miniata* (Scrophulariaceae), *Utricularia australis* (Lentibulariaceae) (72, 73)

## 87. DIHYDROCATALPOL

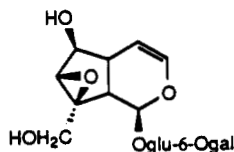


$C_{15}H_{24}O_{10}$  364.35 mp 223–224° [ $\alpha$ ] –99.2° (MeOH) (100 MHz  $CD_3OD$ ) 4.8 (H-1), 4.12 (H-3), 1.9–1.6 (H-4), 2.05 (H-5, m), 3.83 (H-6), 3.42 (H-7, s), 2.27 (H-9, dd, 8.8, 8.0), 4.05, 3.75 (H-10, d's, 13), 4.65 (H-1', d, 7.2); ( $CD_3OD$ ) 97.8 (C-1), 62.9 (C-3), 23.9 (C-4), 38.2 (C-5), 73.2 (C-6), 62.0 (C-7), 66.0 (C-8), 43.5 (C-9), 61.2 (C-10), 99.3 (C-1'), 74.8 (C-2'), 78.3 (C-3')<sup>a</sup>, 71.7 (C-4'), 77.7 (C-5')<sup>a</sup>, 62.9 (C-6'). Hydrolysis of globularidin (74)

88. JIOGLUTOSIDE A (Catalpogenin-1- $O$ - $\alpha$ -L-arabinofuranoside)

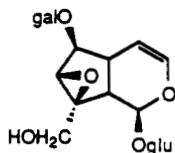
$C_{14}H_{20}O_9$  332.31 [ $\alpha$ ] –158.8° (MeOH) (500 MHz  $CD_3OD$ ) 4.83 (H-1, d, 9.7), 6.34 (H-3, dd, 6.0, 1.9), 5.07 (H-4, dd, 6.0, 4.5), 2.25 (H-5, dddd, 8.2, 7.7, 4.5, 1.9), 3.87 (H-6, dd, 8.2, 1.2), 3.39 (H-7, d, 1.2), 2.53 (H-9, dd, 9.7, 7.7), 4.18, 3.57 (H-10, d's, 13.2), 5.44 (H-1', d, 1.1), 4.08 (H-2', dd, 2.3, 1.1), 3.95 (H-3', dd, 3.8, 2.3), 4.11 (H-4', dt, 5.5, 3.9), 3.71 (H-5', dd, 11.6, 4.1), 3.65 (H-5'', dd, 11.6, 5.5); ( $CD_3OD$ ) 95.8 (C-1), 141.7 (C-3), 104.1 (C-4), 39.0 (C-5), 79.7 (C-6), 62.2 (C-7), 66.1 (C-8), 43.4 (C-9), 63.5 (C-10), 106.4 (C-1'), 82.5 (C-2'), 78.5 (C-3'), 88.7 (C-4'), 62.0 (C-5'). *Rebmannia glutinosa* var. *bueichingensis* (Scrophulariaceae) (75)

## 89. REHMANNIOSIDE A

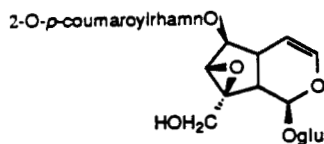


$C_{21}H_{32}O_{15}$  524.47 [ $\alpha$ ] –0.1° (MeOH) (90 MHz  $D_2O$ ) 5.11 (H-1, s), 5.56 (H-3, q, 6, 1), 5.27 (H-4, q, 6, 1); ( $D_2O$ ) 95.7 (C-1), 141.4 (C-3), 104.0 (C-4), 38.1 (C-5), 78.5 (C-6), 62.8 (C-7), 66.6 (C-8), 42.6 (C-9), 61.0 (C-10), 99.5 (C-1')<sup>a</sup>, 73.5 (C-2'), 76.6 (C-3'), 70.4 (C-4'), 75.6 (C-5'), 66.8 (C-6'), 99.1 (C-1'')<sup>a</sup>, 69.2 (C-2''), 70.4 (C-4''), 71.9 (C-5''), 61.9 (C-6''). *Rebmannia glutinosa* (Scrophulariaceae) (31)

## 90. REHMANNIOSIDE B



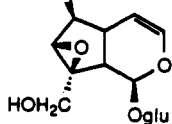
$C_{21}H_{32}O_{15}$  524.47 [ $\alpha$ ] –8.8° (MeOH) (90 MHz  $D_2O$ ) 6.53 (H-3, q, 6, 1); (nonacetate 90 MHz  $CDCl_3$ ) 5.44 (H-1, bs), 6.27 (H-3, q, 6, 2), 2.41–2.77 (H-5, H-9, m); ( $D_2O$ ) 95.5 (C-1), 141.4 (C-3), 104.2 (C-4), 36.8 (C-5), 86.5 (C-6), 62.0 (C-7), 66.4 (C-8), 41.8 (C-9), 60.9 (C-10), 99.4 (C-1'), 73.6 (C-2'), 77.1 (C-3'), 70.1 (C-4'), 76.5 (C-5'), 61.5 (C-6'), 100.9 (C-1''), 69.2 (C-2''), 70.4 (C-3''), 70.1 (C-4''), 72.0 (C-5''), 62.4 (C-6''). *Rebmannia glutinosa* (Scrophulariaceae) (31)

91. SACCATOSIDE [6- $O$ -(2''- $O$ -*p*-Coumaroyl- $\alpha$ -L-rhamnopyranosyl)catalpol]

$C_{30}H_{38}O_{16}$  654.62 [ $\alpha$ ] –200° (MeOH) uv 312, 222, 206 (EtOH) ( $DMSO-d_6$ ) 92.6 (C-1), 139.9 (C-3), 104.2 (C-4), 35.4 (C-5), 81.4 (C-6), 57.1 (C-7), 65.3 (C-8), 41.7 (C-9), 58.6 (C-10), 97.7 (C-1'), 73.3 (C-2'), 77.3 (C-3'), 70.0 (C-4'), 76.2 (C-5'), 61.2 (C-6'), 95.4 (C-1''), 72.3 (C-2''), 68.4 (C-3''), 72.0 (C-4''), 68.7 (C-5''), 17.7 (C-6''), 166.1 (O=C), 115.7 (C $\alpha$ ), 145.2 (C $\beta$ ), 124.9 (C-1'''), 130.3 (C-2'''), 115.1 (C-3'''), 159.1 (C-4'''). *Verbascum saccatum* (Scrophulariaceae) (76)

92. 6-O-(3''-O-p-COUMAROYL- $\alpha$ -L-RHAMNOPYRANOSYL)CATALPOL

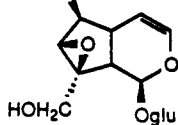
3-O-p-coumaroylrhamno



$C_{30}H_{38}O_{16}$  654.62 mp 266–266.5° [ $\alpha$ ] –178.5° (pyridine/MeOH) uv 312, 222, 206 (EtOH) (60 MHz DMSO- $d_6$ ) 5.29 (H-1, d, 5.5), 6.46 (H-3, dd, 6, 1.5), 5.01 (H-4, dd, 6, 3), 4.67 (H-1', d, 7.5), 4.85 (H-1'', d, 2), 1.2 (H-6'', d, 6.2), 6.43/7.56 (H $\alpha$ , H $\beta$ , d's, 16), 7.56 (H-2''', dd, 9, 1), 6.82 (H-3''', dd, 9, 1); (DMSO- $d_6$ ) 93.2 (C-1), 140.9 (C-3), 102.3 (C-4), 35.6 (C-5), 84.8 (C-6), 57.5 (C-7), 65.3 (C-8), 41.9 (C-9), 58.9 (C-10), 97.9 (C-1'), 73.9 (C-2'), 77.3 (C-3'), 70.2 (C-4'), 76.3 (C-5'), 61.3 (C-6'), 166.3 (O=C), 114 (C $\alpha$ ), 144.4 (C $\beta$ ), 125.2 (C-1'''), 130.1 (C-2'''), 115.8 (C-3'''), 159.6 (C-4'''), 98.9 (C-1''), 68.2 (C-2''), 73.3 (C-3''), 69.1 (C-4''), 68.9 (C-5''), 17.7 (C-6''). *Verbascum sinuatum* (Scrophulariaceae) (77)

## 93. VERBASCOSIDE A

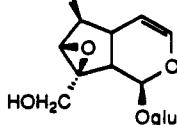
4-p-methoxycinnamoylrhamno



$C_{31}H_{40}O_{16}$  668.65 [ $\alpha$ ] –215° (EtOH) uv 312, 222, 206 (MeOH) (60 MHz DMSO/CDCl<sub>3</sub>) 4.98 (H-1, d, 8.5), 6.36 (H-3, dd, 6, 1.6), 5.01 (H-4, dd, 6, 4.5), 2.30 (H-5, m, 8, 7.5, 4.5, 1.6), 3.9 (H-6, bd), 3.64 (H-7, bs), 2.45 (H-9, dd, 8.5, 8.0), 4.08–3.85 (H-10), 4.97 (H-1', d, 7.5), 4.1–3.2 (H-2'–H-5'), 4.96 (H-1'', d, 1), 4.1–3.2 (H-2'', H-3''), 5.15–4.97 (H-4''), 4.1–3.8 (H-5''), 1.16 (H-6'', d, 6.2), 6.40/7.68 (H $\alpha$ , H $\beta$ , d's, 15.5), 7.63 (H-2''', dd, 9, 2), 7.00 (H-3''', dd, 9, 2), 3.83 (ArOMe); (DMSO/CDCl<sub>3</sub>) 93.3 (C-1), 140.8 (C-3), 102.3 (C-4), 35.6 (C-5), 82.1 (C-6), 57.6 (C-7), 65.3 (C-8), 41.9 (C-9), 59.4 (C-10), 98.0 (C-1'), 73.5 (C-2') 77.2 (C-3'), 70.8 (C-4'), 76.4 (C-5'), 61.4 (C-6'), 98.9 (C-1''), 70.2 (C-2''), 68.4 (C-3''), 73.7 (C-4''), 66.6 (C-5''), 17.4 (C-6''), 196.2 (O=C), 115.5 (C $\alpha$ ), 144.3 (C $\beta$ ), 126.7 (C-1'''), 129.8 (C-2'''), 114.3 (C-3'''), 161.2 (C-4'''). *Verbascum georgicum* (Scrophulariaceae) (78)

## 94. 6-O-(2''-O-CAFFEYOYL-RHAMNOPYRANOSYL)CATALPOL

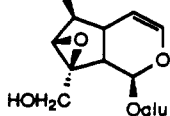
2-O-p-caffeoylrhamno



$C_{30}H_{38}O_{17}$  670.62 [ $\alpha$ ] –120° (MeOH) uv 332, 304, 245, 222 (MeOH) (100 MHz CD<sub>3</sub>OD) 6.38 (H-3, d, 6), 2.65–2.35 (H-5, H-9, m), 1.31 (H-6'', d, 6), 6.33/7.60 (H $\alpha$ , H $\beta$ , d's, 16), 7.07 (H-2''', d, 2), 6.78 (H-5''', d, 8), 6.97 (H-6''', dd, 8, 2); (CD<sub>3</sub>OD) 95.2 (C-1), 142.3 (C-3), 103.5 (C-4), 37.2 (C-5), 84.4 (C-6), 59.6 (C-7), 66.5 (C-8), 43.3 (C-9), 61.5 (C-10), 99.7 (C-1'), 74.8 (C-2'), 77.6 (C-3'), 71.7 (C-4'), 78.6 (C-5'), 62.9 (C-6'), 97.8 (C-1''), 74.1 (C-2''), 70.5 (C-3''), 74.2 (C-4''), 70.3 (C-5''), 18.1 (C-6''), 168.7 (O=C), 115.3 (C $\alpha$ ), 147.6 (C $\beta$ ), 127.7 (C-1'''), 114.9 (C-2'''), 149.6 (C-3'''), 146.7 (C-4'''), 116.5 (C-5'''), 123.2 (C-6'''). *Premna odorata* (Verbenaceae) (79)

## 95. 6-O-(3''-O-CAFFEYOYL-RHAMNOPYRANOSYL)CATALPOL

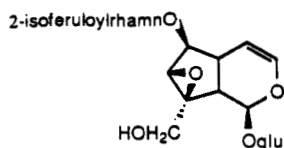
3-O-p-caffeoylrhamno



$C_{30}H_{38}O_{17}$  670.62 [ $\alpha$ ] –121° (MeOH) uv 330, 303, 245, 220 (MeOH) (100 MHz CD<sub>3</sub>OD) 6.38 (H-3, d, 6), 2.65–2.35 (H-5, H-9, m), 1.31 (H-6'', d, 6), 6.36/7.64 (H $\alpha$ , H $\beta$ , d's, 16), 7.06 (H-2''', d, 2), 6.78 (H-5''', d, 8), 6.97 (H-6''', dd, 8, 2); (CD<sub>3</sub>OD) 95.2 (C-1), 142.2 (C-3), 103.6 (C-4), 37.2 (C-5), 83.8 (C-6), 59.3 (C-7), 66.6 (C-8), 43.2 (C-9), 61.5 (C-10), 99.7 (C-1'), 74.8 (C-2'), 77.6 (C-3'), 71.7 (C-4'), 78.5 (C-5'), 62.9 (C-6'), 100.2 (C-1''), 70.3 (C-2''), 75.3 (C-3''), 71.7 (C-4''), 70.3 (C-5''), 18.0 (C-6''), 168.9

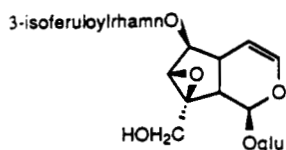
(O=C), 115.3 (C $\alpha$ ), 147.1 (C $\beta$ ), 127.5 (C-1 $''$ ), 115.2 (C-2 $''$ ), 149.5 (C-3 $''$ ), 146.7 (C-4 $''$ ), 116.5 (C-5 $''$ ), 123.0 (C-6 $''$ ). *Premna odorata* (Verbenaceae) (79)

96. 6-O-(2''-O-ISOFERULOYL)RHAMNOPYRANOSYL)CATAPOL



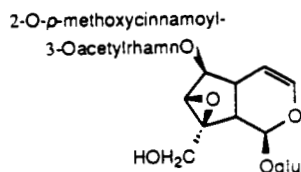
C<sub>31</sub>H<sub>40</sub>O<sub>17</sub> 684.65 [ $\alpha$ ] -115.5° (MeOH) uv 326, 310, 298, 243, 235, 217 (MeOH) (400 MHz CD<sub>3</sub>OD) 5.09 (H-1, d, 2), 6.37 (H-3, dd, 6, 2), 5.07 (H-4, dd, 6, 4), 2.42 (H-5, m), 4.02 (H-6, dd, 8, 1), 2.57 (H-9, dd, 10, 8), 4.15, 3.79 (H-10, d's, 13), 4.77 (H-1', d, 8), 5.02 (H-1'', d, 2), 5.15 (H-2'', dd, 4, 2), 1.30 (H-6'', d, 6), 6.39/7.62 (H $\alpha$ , H $\beta$ , d's, 16), 7.10 (H-2 $''''$ , d, 2), 6.94 (H-5 $''''$ , d, 8), 7.06 (H-6 $''''$ , dd, 8, 2), 3.89 (ArOMe); (CD<sub>3</sub>OD) 95.3 (C-1), 142.3 (C-3), 103.5 (C-4), 37.3 (C-5), 84.5 (C-6), 59.6 (C-7), 66.6 (C-8), 43.4 (C-9), 61.5 (C-10), 99.8 (C-1'), 74.9 (C-2'), 78.7 (C-3'), 71.8 (C-4'), 77.8 (C-5'), 63.0 (C-6'), 97.9 (C-1''), 74.3 (C-2''), 70.6 (C-3''), 74.3 (C-4''), 70.4 (C-5''), 18.1 (C-6''), 168.5 (O=C), 116.0 (C $\alpha$ ), 147.2 (C $\beta$ ), 129.0 (C-1 $''''$ ), 112.7 (C-2 $''''$ ), 151.7 (C-3 $''''$ ), 148.1 (C-4 $''''$ ), 115.0 (C-5 $''''$ ), 122.9 (C-6 $''''$ ), 56.5 (ArOMe). *Premna japonica* (Verbenaceae) (80)

97. 6-O-(3''-O-ISOFERULOYL)RHAMNOPYRANOSYL)CATAPOL



C<sub>31</sub>H<sub>40</sub>O<sub>17</sub> 684.65 [ $\alpha$ ] -117.9° (MeOH) uv 325, 311, 296, 242, 234, 217 (MeOH) (400 MHz CD<sub>3</sub>OD) 5.10 (H-1, d, 10), 6.38 (H-3, dd, 6, 1), 5.12 (H-4, dd, 6, 4), 2.45 (H-5, m), 4.04 (H-6, dd, 8, 1), 2.57 (H-9, dd, 10, 8), 4.15, 3.81 (H-10, d's, 13), 4.78 (H-1', d, 8), 4.97 (H-1'', d, 2), 4.09 (H-2'', dd, 3, 2), 1.31 (H-6'', d, 6), 6.41/7.66 (H $\alpha$ , H $\beta$ , d's, 16), 7.10 (H-2 $''''$ , d, 2), 6.94 (H-5 $''''$ , d, 8), 7.06 (H-6 $''''$ , dd, 8, 2), 3.89 (ArOMe); (CD<sub>3</sub>OD) 95.2 (C-1), 142.2 (C-3), 103.6 (C-4), 37.2 (C-5), 83.8 (C-6), 59.4 (C-7), 66.6 (C-8), 43.3 (C-9), 61.5 (C-10), 99.7 (C-1'), 74.8 (C-2'), 78.6 (C-3'), 71.7 (C-4'), 77.7 (C-5'), 62.9 (C-6'), 100.2 (C-1''), 70.3 (C-2''), 75.4 (C-3''), 71.4 (C-4''), 70.3 (C-5''), 18.0 (C-6''), 168.7 (O=C), 116.4 (C $\alpha$ ), 146.7 (C $\beta$ ), 129.0 (C-1 $''''$ ), 112.5 (C-2 $''''$ ), 151.5 (C-3 $''''$ ), 147.9 (C-4 $''''$ ), 114.8 (C-5 $''''$ ), 122.8 (C-6 $''''$ ), 56.4 (ArOMe). *Premna japonica* (Verbenaceae) (80)

98. PULVERULENTOSIDE I



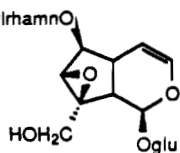
C<sub>33</sub>H<sub>42</sub>O<sub>17</sub> 710.68 [ $\alpha$ ] -86° (MeOH) uv 312, 300, 225, 208 (MeOH) (200 MHz CD<sub>3</sub>OD/CDCl<sub>3</sub>) 5.02 (H-1, d, 9.4), 6.34 (H-3, dd, 6.2, 1.8), 5.12 (H-4, dd, 6.2, 4.4), 2.67-2.47 (H-5, H-9, m), 4.09, 3.84 (H-10, d's, 13.1), 4.80 (H-1', d, 8), 5.03 (H-1'', d, 1.8), 5.41 (H-2'', dd, 3.6, 1.8), 5.17 (H-3'', dd, 9.2, 3.6), 1.38 (H-6'', d, 6.5), 7.55 (H-2 $''''$ , d, 8.8), 6.97 (H-3 $''''$ , d, 8.8), 6.40/7.69 (H $\alpha$ , H $\beta$ , d's, 15.4), 3.87 (OMe), 2.05 (OAc); (CD<sub>3</sub>OD/CDCl<sub>3</sub>) 95.3 (C-1), 142.4 (C-3), 103.4 (C-4), 37.3 (C-5), 84.5 (C-6), 59.5 (C-7), 66.6 (C-8), 43.4 (C-9), 61.5 (C-10), 99.8 (C-1'), 74.9 (C-2'), 78.6 (C-3'), 71.8 (C-4'), 77.8 (C-5'), 63.0 (C-6'), 97.9 (C-1''), 71.4 (C-2''), 73.3 (C-3''), 71.5 (C-4''), 70.3 (C-5''), 18.0 (C-6''), 168.0 (O=C), 115.4 (C $\alpha$ ), 147.2 (C $\beta$ ), 128.3 (C-1 $''''$ ), 131.2 (C-2 $''''$ ), 115.5 (C-3 $''''$ ), 163.4 (C-4 $''''$ ), 56.0 (OMe), 172.3 (O=CMe), 20.9 (O=CMe). *Verbascum sinuatum*, *Verbascum pulverulentum* (Scrophulariaceae) (81, 82)



## 99. PULVERULENTOSIDE II

2-OAc- 3-O-

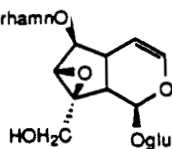
isoferylulrhamnO



$C_{33}H_{42}O_{18}$  726.68  $[\alpha] -84^\circ$  (MeOH) uv 315, 300, 222, 208 (MeOH) (200 MHz  $CD_3OD/CDCl_3$ ) 5.00 (H-1, d, 9.4), 6.36 (H-3, dd, 6.2, 1.8), 5.12 (H-4, dd, 6.2, 4.4), 2.68-2.47 (H-5, H-9, m), 4.05, 3.85 (H-10, d, 13), 4.81 (H-1', d, 8), 5.03 (H-1'', d, 1.8), 5.41 (H-2'', dd, 3.6, 1.8), 5.18 (H-3'', dd, 9.2, 3.6), 1.38 (H-6'', d, 6), 7.12 (H-2''', d, 1.9), 6.90 (H-5''', d, 8.2), 7.06 (H-6''', dd, 8.2, 1.9), 6.35/7.61 (H $\alpha$ , H $\beta$ , d's, 15.6), 3.92 (OMe), 2.05 (OAc); ( $CD_3OD/CDCl_3$ ) 95.2 (C-1), 142.3 (C-3), 103.4 (C-4), 37.2 (C-5), 84.5 (C-6), 59.5 (C-7), 66.6 (C-8), 43.4 (C-9), 61.5 (C-10), 99.8 (C-1'), 74.9 (C-2'), 78.6 (C-3'), 71.8 (C-4'), 77.8 (C-5'), 63.0 (C-6'), 97.9 (C-1''), 71.4 (C-2''), 73.3 (C-3''), 71.5 (C-4''), 70.3 (C-5''), 18.0 (C-6''), 167.9 (O=C), 115.4 (C $\alpha$ ), 147.6 (C $\beta$ ), 128.8 (C-1'''), 114.9 (C-2'''), 148.1 (C-3'''), 151.7 (C-4'''), 112.7 (C-5'''), 123.0 (C-6'''), 56.5 (OMe), 172.3 (O=CMe), 20.9 (O=CMe). *Verbascum pulverulentum* (Scrophulariaceae) (82)

## 100. PREMNSIDE A

2,3-di-O-caffeoylrhamnO

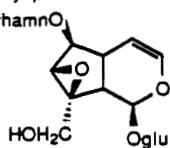


$C_{39}H_{44}O_{20}$  832.76  $[\alpha] +24.8^\circ$  (MeOH) uv 328, 303, 245, 219 (MeOH) (100 MHz  $CD_3OD$ ) 6.39 (H-3, d, 6), 2.5 (H-5, H-9, m), 1.37 (H-6'', d, 6), 6.34, 6.23 (H $\alpha$ , H $\alpha'$ , d's, 16), 7.59, 7.54 (H $\beta$ , H $\beta'$ , d's, 16), 7.0-6.6 (H-2''-H-6''', H-2'''-H-6'''); ( $CD_3OD$ ) 95.2 (C-1), 142.3 (C-3), 103.4 (C-4), 37.2 (C-5), 84.4 (C-6), 59.5 (C-7), 66.5 (C-8), 43.3 (C-9), 99.7 (C-1'), 74.8 (C-2'), 78.6 (C-3'), 71.7 (C-4'), 77.6 (C-5'), 62.9 (C-6'), 97.9 (C-1''), 71.4 (C-2''), 73.1 (C-3''), 71.7 (C-4''), 70.3 (C-5''), 18.1 (C-6''), 168.0, 168.5 (O=C), 115.0, 115.3 (C $\alpha$ , C $\alpha'$ ), 147.4, 148.1 (C $\beta$ , C $\beta'$ ), 127.5, 127.6 (C-1''', C-1'''), 114.3, 114.8 (C-2''', C-2'''), 149.6, 149.8 (C-3''', C-3'''), 146.7 (C-4''', C-4'''), 116.5, 116.6 (C-5''', C-5'''), 123.0 (C-6''', C-6'''). *Premna odorata* (Verbenaceae) (83)

## 101. PREMNSIDE B

2,3-O-caffeoyl-p-

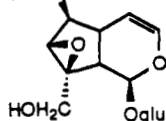
coumaroylrhamnO



$C_{39}H_{44}O_{19}$  816.77  $[\alpha] +19.4^\circ$  (MeOH) uv 321, 309, 236, 222 (MeOH) (100 MHz  $CD_3OD$ ) 5.43 (H-1, bs), 6.40 (H-3, d, 6), 2.5 (H-5, H-9, m), 1.38 (H-6'', d, 5), 6.23, 6.40 (H $\alpha$ , H $\alpha'$ , d's, 16), 7.59, 7.69 (H $\beta$ , H $\beta'$ , d's, 16), 7.56 (H-2''', d, 8), 6.81 (H-3''', d, 8), 7.00 (H-2''', bs), 6.65 (H-5'''), 6.79 (H-6''', d, 8); ( $CD_3OD$ ) 95.2 (C-1), 142.3 (C-3), 103.4 (C-4), 37.2 (C-5), 84.4 (C-6), 59.5 (C-7), 66.5 (C-8), 43.3 (C-9), 61.5 (C-10), 99.7 (C-1'), 74.8 (C-2'), 78.6 (C-3'), 71.7 (C-4'), 77.6 (C-5'), 62.9 (C-6'), 97.9 (C-1''), 71.4 (C-2''), 73.1 (C-3''), 71.7 (C-4''), 70.3 (C-5''), 18.0 (C-6''), 168.0, 168.4 (O=C), 115.1, 114.8 (C $\alpha$ , C $\alpha'$ ), 147.4, 147.7 (C $\beta$ , C $\beta'$ ), 127.6 (C-1'''), 131.4 (C-2'''), 116.9 (C-3'''), 161.4 (C-4'''), 127.0 (C-1'''), 114.3 (C-2'''), 149.5 (C-3'''), 146.7 (C-4'''), 116.5 (C-5'''), 123.2 (C-6'''). *Premna odorata* (Verbenaceae) (83)

## 102. PREMNSIDE C

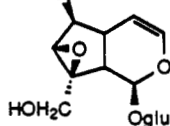
2,3-O-caffeoyl-feruloylirhamnol



$C_{40}H_{46}O_{20}$  846.79  $[\alpha] +25.9^\circ$  (MeOH) uv 336, 315, 245, 222 (MeOH) (100 MHz  $CD_3OD$ ) 5.43 (H-1, bs), 6.40 (H-3, d, 5), 2.5 (H-5, H-9, m), 1.38 (H-6", d, 5), 6.35, 6.31 (H $\alpha$ , H $\alpha'$ , d's, 16), 7.58 (H $\beta$ , H $\beta'$ , d, 16), 7.0-6.9 (H-2", H-2"', H-6"', H-6'''), 6.75 (H-5", d, 8), 6.78 (H-5"', d, 8), 3.76 (ArOMe); ( $CD_3OD$ ) 95.2 (C-1), 142.4 (C-3), 103.5 (C-4), 37.2 (C-5), 84.5 (C-6), 59.5 (C-7), 66.6 (C-8), 43.3 (C-9), 61.6 (C-10), 99.8 (C-1'), 74.9 (C-2'), 78.6 (C-3'), 71.8 (C-4'), 77.7 (C-5'), 63.0 (C-6'), 97.9 (C-1''), 71.5 (C-2''), 73.1 (C-3''), 71.8 (C-4''), 70.3 (C-5''), 18.1 (C-6''), 168.1, 168.4 (O=C), 115.2, 115.4 (C $\alpha$ , C $\alpha'$ ), 148.1, 147.3 (C $\beta$ , C $\beta'$ ), 127.6 (C-1''', C-1'''), 111.9, 114.3 (C-2''', C-2'''), 150.6, 149.9 (C-3''', C-3'''), 116.5 (C-5''', C-5'''), 124.0, 124.3 (C-6''', C-6'''), 56.4 (OMe). *Premna odorata* (Verbenaceae) (83)

## 103. PREMNSIDE D

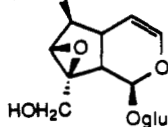
2,3-O-feruloyl-p-coumaroylirhamnol



$C_{40}H_{46}O_{19}$  830.79  $[\alpha] +14^\circ$  (MeOH) uv 336, 310, 235, 220 (MeOH) (100 MHz  $CD_3OD$ ) 6.40 (H-3, d, 5), 2.6 (H-5, H-9, m), 1.38 (H-6", d, 7), 6.40, 6.31 (H $\alpha$ , H $\alpha'$ , d's, 16), 7.64, 7.58 (H $\beta$ , H $\beta'$ , d's, 16), 6.8 (H-2", H-5", H-6''), 7.46 (H-2''', d, 8), 7.00 (H-3''', d, 8), 3.76 (OMe); ( $CD_3OD$ ) 95.2 (C-1), 142.3 (C-3), 103.4 (C-4), 37.2 (C-5), 84.4 (C-6), 59.5 (C-7), 66.5 (C-8), 43.3 (C-9), 61.5 (C-10), 99.7 (C-1'), 74.8 (C-2'), 78.5 (C-3'), 71.7 (C-4'), 77.6 (C-5'), 62.9 (C-6'), 97.8 (C-1''), 71.4 (C-2''), 73.0 (C-3''), 71.7 (C-4''), 70.3 (C-5''), 18.1 (C-6''), 168.0, 168.6 (O=C), 115.2, 114.4 (C $\alpha$ , C $\alpha'$ ), 147.3, 147.7 (C $\beta$ , C $\beta'$ ), 127.6 (C-1''', 111.8 (C-2'''), 150.6 (C-3'''), 149.2 (C-4'''), 116.4 (C-5'''), 124.0 (C-6'''), 127.0 (C-1'''), 131.4 (C-2'''), 116.9 (C-3'''), 161.5 (C-4'''). *Premna odorata* (Verbenaceae) (83)

## 104. SCROPOLIOSIDE A

2,4-di-OAc-3-p-methoxycinnamoylirhamnol

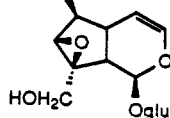


$C_{35}H_{44}O_{18}$  752.72  $[\alpha] -136.6^\circ$  (MeOH) uv 311, 300 sh, 224, 205 (MeOH) (300 MHz  $CD_3OD$ ) 5.09 (H-1, d, 9.5), 6.39 (H-3, dd, 6, 1.7), 5.1 (H-4, dd, 6, 4.4), 2.49 (H-5, m), 4.06 (H-6, dd, 8.9, 0.9), 3.67 (H-7, bs), 2.59 (H-9, dd, 9.5, 7.6), 4.15, 3.83 (H-10, d's, 13.1), 4.77 (H-1', d, 7.8), 3.44-3.23 (H-2', H-5'), 3.92 (H-6', dd, 11.8, 1.6), 3.63 (H-6', dd, 11.8, 6.2), 5.07 (H-1'', d, 1.7), 5.3 (H-2'', dd, 3.4, 1.7), 5.37 (H-3'', dd, 10.1, 3.4), 5.17 (H-4'', bt, 10), 4.07 (H-5'', dq, 10, 6.3), 1.22 (H-6'', d, 6.3), 6.36/7.67 (H $\alpha$ , H $\beta$ , d's, 15.8), 7.56 (H-2''', d, 8.8), 6.95 (H-3''', d, 8.8), 3.82 (ArOMe), 1.93, 2.16 (OAc); ( $CD_3OD$ ) 95.2 (C-1), 142.5 (C-3), 103.3 (C-4), 37.2 (C-5), 85.0 (C-6), 59.5 (C-7), 66.6 (C-8), 43.4 (C-9), 61.5 (C-10), 99.8 (C-1'), 74.9 (C-2'), 77.3 (C-3'), 71.8 (C-4'), 78.7 (C-5'), 63.0 (C-6'), 97.8 (C-1''), 71.3 (C-2''), 70.7 (C-3''), 72.1 (C-4''), 68.3 (C-5''), 17.9 (C-6''), 171.7 (O=CMe), 20.9 (O=CMe), 168.0 (O=C), 147.4 (C $\alpha$ ), 115.1 (C $\beta$ ), 128.1 (C-1'''), 131.3 (C-2'''), 115.5 (C-3'''), 163.4 (C-4'''), 56.0 (ArOMe). *Scrophularia scopolii* var. *scopolii* (Scrophulariaceae) (84)

## 105. SCROPOLIOSIDE B

2-OAc-3,4-di-

O-cinnamoylrhamno

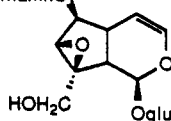


$C_{41}H_{46}O_{17}$  810.80  $[\alpha] -13.9^\circ$  (MeOH) uv 278, 222, 217, 205 (MeOH) (300 MHz  $CD_3OD$ ) 5.12 (H-1, d, 9.3), 6.41 (H-3, dd, 6, 1.3), 5.13 (H-4, dd, 6, 4.3), 2.5 (H-5, m), 4.1 (H-6, d, 7.7), 3.7 (H-7, bs), 2.62 (H-9, dd, 9.3, 7.6), 3.83, 4.19 (H-10, d's, 13.2), 4.79 (H-1', d, 8), 3.45-3.24 (H-2'-H-5'), 3.66 (H-6', dd, 12.4, 6.2), 3.93 (H-6', dd, 12.4, 1.7), 5.12 (H-1'', d, 1.7), 5.4 (H-2'', dd, 3.4, 1.7), 5.51 (H-3'', dd, 10, 3.4), 5.3 (H-4'', br, 10), 4.16 (H-5'', dq, 10, 6), 1.26 (H-6'', d, 6), 6.5/7.7 (H $\alpha$ , H $\beta$ , d's, 16), 7.52 (H-2''', H-2''', m), 7.34 (H-3''', H-3''', H-4''', H-4''', m), 6.39/7.6 (H $\alpha'$ , H $\beta'$ , d's, 16); ( $CD_3OD$ ) 95.1 (C-1), 142.5 (C-3), 103.2 (C-4), 37.1 (C-5), 85.0 (C-6), 59.4 (C-7), 66.5 (C-8), 43.3 (C-9), 61.4 (C-10), 99.7 (C-1'), 74.8 (C-2'), 77.6 (C-3'), 71.7 (C-4'), 78.6 (C-5'), 62.9 (C-6'), 97.7 (C-1''), 71.4 (C-2''), 70.8 (C-3''), 72.4 (C-4''), 68.2 (C-5''), 17.8 (C-6''), 171.6 (O=CMe), 20.7 (O=CMe), 167.6, 167.3 (O=C), 147.6, 147.4 (C $\alpha$ , C $\alpha'$ ), 117.8 (C $\beta$ , C $\beta'$ ), 135.4 (C-1''', C-1'''), 130.0 (C-2''', C-2'''), 129.3 (C-3''', C-3'''), 131.7 (C-4''', C-4'''). *Scrophularia scopolii* var. *scopolii* (Scrophulariaceae) (84)

## 106. compound not named [6-O-(2,3,4-O-ACETYLCINNAMOYL-p-METHOXYCINNAMOYL)RHAMNOSYL]CATALPOL]

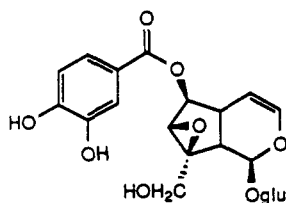
2,3,4-O-acetyl-cinnamoyl-p-

methoxycinnamoylrhamno



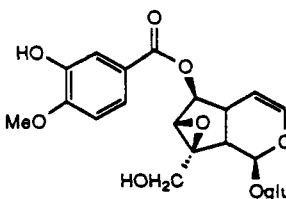
$C_{42}H_{48}O_{18}$  840.83 (pyridine- $d_5$ ) 94.7 (C-1), 141.7 (C-3), 102.6 (C-4), 36.6 (C-5), 84.7 (C-6), 58.6 (C-7), 66.4 (C-8), 43.2 (C-9), 60.1 (C-10), 100.2 (C-1'), 74.9 (C-2'), 79.0 (C-3'), 71.5 (C-4'), 78.3 (C-5'), 62.7 (C-6'), 97.2 (C-1''), 70.9 (C-2''), 70.1 (C-3''), 71.3 (C-4''), 67.5 (C-5''), 17.8 (C-6''), 170.2 (O=CMe), 20.6 (O=CMe), 166.8 (O=C), 117.9 (C $\alpha$ ), 146.2 (C $\beta$ ), 134.5 (C-1'''), 129.1 (C-2'''), 128.7 (C-3'''), 130.8 (C-4'''), 166.2 (O=C'), 114.0 (C $\alpha'$ ), 133.1 (C $\beta'$ ), 127.3 (C-1'''), 130.5 (C-2'''), 114.8 (C-3'''), 160.9 (C-4'''). *Scrophularia ningpoensis* (Scrophulariaceae) (85)

## 107. VERPROSIDE



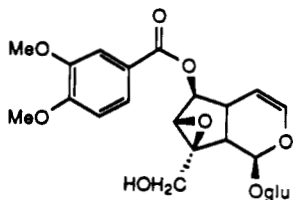
$C_{22}H_{26}O_{13}$  498.44  $[\alpha] -164.8^\circ$  (MeOH) uv 295, 263, 224, 216 (MeOH) (100 MHz  $CD_3OD$ ) 5.22-4.74 (H-1), 6.35 (H-3, d, 6), 5.22-4.74 (H-4), 2.70-2.54 (H-5, m), 5.22-4.74 (H-6), 3.74 (H-7, s), 2.70-2.54 (H-9, m), 4.18, 3.84 (H-10, 13, 2), 7.52-7.40 (H-2'', H-6''), 6.86-6.74 (H-5''); ( $CD_3OD$ ?) 95.1 (C-1), 142.2 (C-3), 102.9 (C-4), 36.5 (C-5), 81.3 (C-6), 60.2 (C-7), 66.7 (C-8), 42.9 (C-9), 61.1 (C-10), 99.5 (C-1'), 74.5 (C-2'), 78.0 (C-3'), 71.3 (C-4'), 77.3 (C-5'), 62.7 (C-6'), 167.9 (C=O), 121.8 (C-1''), 117.6 (C-2''), 145.8 (C-3''), 151.7 (C-4''), 116.0 (C-5''), 124.0 (C-6''). *Veronica officinalis* (Scrophulariaceae) (86, 87)

## 108. 6-O-ISOVANILLOYLCATALPOL

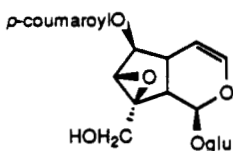


$C_{23}H_{28}O_{13}$  512.47 mp 162-166 $^\circ$   $[\alpha] -165.8^\circ$  (MeOH) uv 297, 262, 223 (MeOH) (360 MHz  $D_2O$ ) 5.12 (H-1, d, 9.6), 6.35 (H-3, dd, 6.0, 1.5), 5.03 (H-4, dd, 5.8, 4.6), 2.61 (H-5, m), 5.11 (H-6, dd, 8, 1.1), 3.83 (H-7, m), 2.68 (H-9, m), 3.78, 4.26 (H-10, d's, 13.3), 4.85 (H-1', d, 8), 3.45-3.30 (H-2'-H-5'), 3.71 (H-6', dd, 12.5, 4.8), 3.83 (H-6', m), 7.39 (H-2'', d, 2), 6.97 (H-5'', d, 8.7), 7.54 (H-6'', dd, 8.7, 2), 3.86 (OMe). *Beseya plantaginea* (Scrophulariaceae) (88)

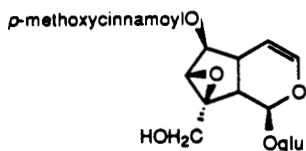
## 109. 6-O-VERATROYLCATALPOSIDE



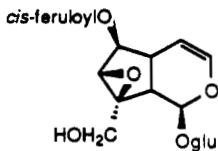
$C_{24}H_{30}O_{13}$  526.49 mp 216–218° uv 292, 263, 226 (MeOH) (60 MHz  $CD_3OD$ ) 6.36 (H-3, d, 6), 2.66–2.50 (H-5, H-9, m), 4.16, 3.60 (H-10, d's, 13), 7.62–7.13 (H-2", H-5", H-6"), 3.86 (OMe); (pyridine- $d_5$ ) 94.8 (C-1), 141.8 (C-3), 102.3 (C-4), 36.5 (C-5), 81.0 (C-6), 59.6 (C-7), 66.9 (C-8), 43.2 (C-9), 60.3 (C-10), 100.0 (C-1'), 74.8 (C-2'), 78.7 (C-3'), 71.4 (C-4'), 77.9 (C-5'), 62.6 (C-6'), 166.7 (C=O), 154.5 (C-1"), — (C-2"), 150.0 (C-3"), 150.8 (C-4"), 124.6 (C-5"), 113.6 (C-6"), 56.0 (OMe). *Veronicastrum sibiricum* (Scrophulariaceae) (25)

110. SPECIOSIDE (6-O-*p*-Coumaroyl-catalpol)

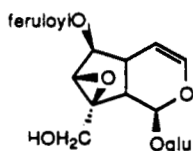
$C_{24}H_{28}O_{12}$  508.48 mp 252° (dec)  $[\alpha] -219^\circ$  (MeOH) uv 319, 229 (MeOH) (60 MHz pyridine- $d_5$ ) 5.65–5.45 (H-1, m), 6.50 (H-3, d, 7), 5.30 (H-4, dd, 7), 3.0–2.7 (H-5, m), 5.15 (H-6, dd, 6, 4), 4.8–4.0 (H-7), 3.0–2.7 (H-9, m), 4.8–4.0 (H-10), 5.65–5.45 (H-1', m), 4.8–4.0 (H-2'–H-6'), 6.55/8.01 (H $\alpha$ , H $\beta$ , d, 16.5), 7.65 (H-2"), 7.23 (H-3"); ( $CD_3OD$ ) 93.1 (C-1), 141.1 (C-3), 101.8 (C-4), 35.2 (C-5), 79.3 (C-6), 58.3 (C-7), 65.8 (C-8), 42.0 (C-9), 58.7 (C-10), 97.9 (C-1'), 73.5 (C-2'), 77.4 (C-3'), 70.3 (C-4'), 76.5 (C-5'), 61.5 (C-6'), 166.5 (C=O), 113.6 (C $\alpha$ ), 145.6 (C $\beta$ ), 125.0 (C-1"), 130.5 (C-2"), 115.8 (C-3"), 159.9 (C-4"). *Catalpa speciosa*, *Tabebuia rosea* (Bignoniaceae) (89, 90)

111. 6-O-*p*-METHOXYCINNAMOYL-CATALPOSIDE

$C_{25}H_{30}O_{12}$  522.50 uv 309, 225 (MeOH) (pentaacetate 250 MHz  $CDCl_3$ ) 5.45–4.80 (H-1), 6.33 (H-3, d, 6.1), 5.45–4.80 (H-4), 2.50 (H-5, m), 5.45–4.80 (H-6), 3.55 (H-7, bs), 2.65 (H-9, m), 4.65 (H-10, dd, 11, 1.8), 3.92 (H-10, m), 5.45–4.80 (H-1'–H-4'), 3.70 (H-5', m), 4.40–4.10 (H-6', m), 6.26/7.66 (H $\alpha$ , H $\beta$ , d's, 16), 7.49 (H-2", d, 8.8), 6.91 (H-3", d, 8.8), 3.84 (OMe), 2.2–1.95 (OAc). *Buddleja globosa* (Loganiaceae) (60)

112. 6-O-*cis*-FERULOYL-CATALPOL

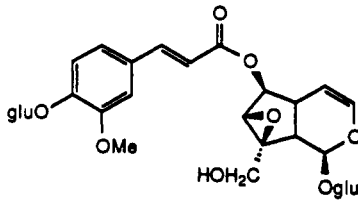
$C_{25}H_{30}O_{13}$  538.50 (300 MHz  $CD_3OD$ ) 5.23 (H-1, d, 9.5), 6.42 (H-3, dd, 6.1, 1.2), 5.01 (H-4, dd, 6.1, 3.9), 5.05 (H-6, dd, 7.8, 1.1), 4.23, 3.93 (H-10, d's, 13.2), 5.92/7.00 (H $\alpha$ , H $\beta$ , d's, 12.9), 7.83 (H-2", d, 2.1), 6.85 (H-5", d, 8.2), 7.21 (H-6", dd, 8.2, 2.1). *Picrorhiza kurroa* (Scrophulariaceae) (91)

113. 6-O-*trans*-FERULOYL-CATALPOL

$C_{25}H_{30}O_{13}$  538.50 uv 327.5, 235.8, 217.5 (MeOH) (300 MHz  $CD_3OD$ ) 5.24 (H-1, d, 9.2), 6.45 (H-3, dd, 5.9, 1.4), 5.07 (H-4, dd, 6, 4), 2.69 (H-5, m), 5.11 (H-6, dd, 7.8, 1.1), 3.79 (H-7, d, 1.1), 2.69 (H-9, dd, 9.2, 6.4), 4.25, 3.92 (H-10, d's, 13.1), 4.86 (H-1', d, 7.9), 3.5–3.2 (H-4'), 4.01 (H-6', dd, 11.9, 2.0), 3.73 (H-6', dd, 11.9, 6.3), 6.48/7.74 (H $\alpha$ , H $\beta$ , d's, 15.9), 7.28 (H-2", d, 1.8), 7.11 (H-5", dd, 8.2, 1.9), 6.88 (H-6", d, 8.2), 3.97 (OMe); ( $CD_3OD$ ) 95.1 (C-1), 142.4 (C-3), 103.0 (C-4), 36.8 (C-5), 81.3 (C-6), 60.3 (C-7), 66.9 (C-8), 43.3 (C-9), 61.3 (C-10), 99.8 (C-1'), 74.9 (C-2'), 78.6 (C-3') $\alpha$ , 71.8 (C-4'), 77.8 (C-5') $\alpha$ , 62.9 (C-6'), 169.0 (C=O), 114.7 (C $\alpha$ ), 147.6 (C $\beta$ ), 127.3 (C-1"), 111.8 (C-2"), 149.6 (C-3"), 151.6 (C-4"), 116.7 (C-5"), 124.4 (C-6"), 56.5 (OMe). *Picrorhiza kurroa* (Scrophulariaceae) (91)

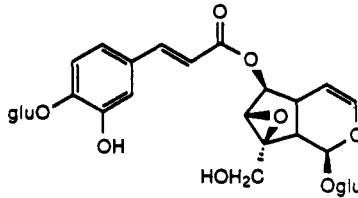
## 114. WELLOSIDE

$C_{31}H_{40}O_{18}$  700.65 no data available. *Veronica bellidoides* (Scrophulariaceae) (92)



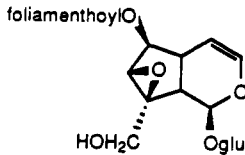
## 115. SPEEDOSIDE

$C_{30}H_{38}O_{18}$  686.62 no data available. *Veronica bellidoides* (Scrophulariaceae) (92)



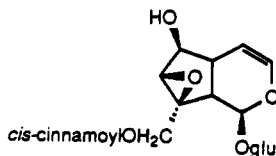
## 116. NEMOROSIDE (6-O-Foliamenthoyl-catalpol)

$C_{25}H_{36}O_{12}$  528.55 mp 68–70° (400 MHz  $CD_3OD$ ) 5.15 (H-1, d, 9.3), 6.39 (H-3, dd, 6, 1.8), 4.95 (H-4 and HDO), 2.58 (H-5, m, 7.9, 7.8, 1.8), 4.95 (H-6, dd, 7.9, 1.2), 3.66 (H-7, d, 1.2), 2.58 (H-9, m, 9.3, 7.8), 4.15, 3.81 (H-10, d's, 13.2), 4.77 (H-1', d, 8), 3.38 (H-3', dd, 9.3, 8.7), 3.92 (H-6', dd, 12.2, 6.6), 3.63 (H-6'', dd, 12.2, 2.2), 6.83 (H-3'', qt, 7.4, 1.4), 2.36 (H-4'', q, 8.2, 7.4), 2.17 (H-5'', t, 8.2), 5.40 (H-7'', qt, 7.5, 1.4), 4.08 (H-8'', d, 7.5), 1.85 (H-9'', d, 1.4), 1.69 (H-10'', d, 1.4); ( $CD_3OD$ ) 95.2 (C-1), 142.4 (C-3), 102.9 (C-4), 36.8 (C-5), 81.7 (C-6), 60.2 (C-7), 66.9 (C-8), 43.3 (C-9), 61.3 (C-10), 99.9 (C-1'), 74.9 (C-2'), 78.6 (C-3'), 71.8 (C-4'), 77.8 (C-5'), 63.0 (C-6'), 169.4 (C-1''), 128.6 (C-2''), 144.2 (C-3''), 28.0 (C-4''), 39.0 (C-5''), 138.4 (C-6''), 125.8 (C-7''), 59.4 (C-8''), 12.4 (C-9''), 16.2 (C-10''). *Penstemon nemorosus* (Scrophulariaceae) (35)

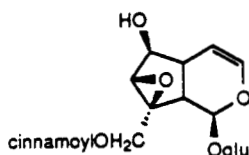


## 117. GLOBULARICISIN (10-O-cis-Cinnamoylcatalpol)

$C_{24}H_{28}O_{11}$  492.48  $[\alpha] -97.2^\circ$  (MeOH) uv 272, 215 (MeOH) (100 MHz  $CD_3OD$ ) 5.00 (H-1, d, 9.2), 6.34 (H-3, dd, 6, 1.8), 5.0 (H-4), 2.25 (H-5, m), 3.85 (H-6, s), 3.35 (H-7, s), 2.52 (H-9, dd, 9.2, 8), 4.92, 4.22 (H-10), 4.7 (H-1'), 5.98/7.01 (H $\alpha$ , H $\beta$ , d's, 13); ( $CD_3OD$ ) 95.5 (C-1), 141.5 (C-3), 103.5 (C-4), 38.6 (C-5), 79.1 (C-6), 62.4 (C-7), 63.1 (C-8), 43.2 (C-9), 63.7 (C-10), 100.0 (C-1'), 74.5 (C-2'), 77.9 (C-3')<sup>a</sup>, 71.1 (C-4')<sup>a</sup>, 77.4 (C-5')<sup>a</sup>, 62.7 (C-6'), 167.3 (C=O), 119.7 (C $\alpha$ ), 144.8 (C $\beta$ ), 135.8 (C-1''), 130.7 (C-2'')<sup>b</sup>, 128.9 (C-3'')<sup>b</sup>, 129.9 (C-4''). *Globularia atypum* (Globulariaceae), *Pinguicula vulgaris* (Lentibulariaceae) (73, 74)

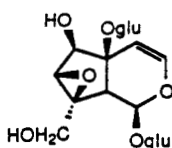


## 118. GLOBULARIN



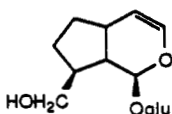
$C_{24}H_{28}O_{11}$  492.48 uv 280, 227 (MeOH) (400 MHz DMSO-*d*<sub>6</sub>) 4.97 (H-1, d, 9), 6.55 (H-3, dd, 6), 5.39 (H-4, d, 6), 2.14 (H-5, m), 4.5 (H-6, dd, 6), 2.95 (H-9, m), 4.93, 4.09 (H-10, d's, 13), 4.56 (H-1', d, 8.5), 6.62/7.63 (H $\alpha$ , H $\beta$ , d's, 16), 7.7–7.41 (H-2''–H-4'', m); (?) 98.4 (C-1), 140.5 (C-3), 103.0 (C-4), 37.3 (C-5), 77.3 (C-6), 61.4 (C-7), 62.8 (C-8), 41.9 (C-9), 61.7 (C-10), 93.6 (C-1'), 73.4 (C-2'), 77.1 (C-3'), 70.1 (C-4'), 76.5 (C-5'), 61.6 (C-6'), 165.9 (C=O), 118 (C $\alpha$ ), 144.6 (C $\beta$ ), 134.1 (C-1''), 129.0 (C-2''), 128.4 (C-3''), 130.5 (C-4''). *Globularia arabica* (Globulariaceae) (93–95)

## 119. CALYCIOSIDE (5-O-Glucosyl-macfadienoside)



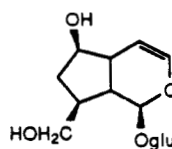
$C_{21}H_{32}O_{16}$  540.47 [ $\alpha$ ] -7.5° (MeOH) uv 204 (MeOH) (90 MHz D<sub>2</sub>O) 5.40 (H-1, d, 9.0), 6.66 (H-3, d, 6.0), 5.14 (H-4, d, 6.0), 4.41 (H-6, d, 1.5), 3.72 (H-7, d, 1.5), 3.25 (H-9, d, 9.0), 4.23, 3.80 (H-10, d's, 13.0). *Antirrhinum orontium* var. *calycinum* (Scrophulariaceae) (96)

## 120. CAPENSIOSIDE



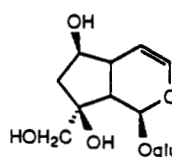
$C_{15}H_{24}O_8$  332.35 (D<sub>2</sub>O) 96.7 (C-1), 139.4 (C-3), 109.0 (C-4), 33.5 (C-5), 31.7 (C-6), 27.4 (C-7), 42.5 (C-8), 44.9 (C-9), 66.1 (C-10), 99.3 (C-1'), 73.6 (C-2'), 76.5 (C-3'), 70.4 (C-4'), 77.0 (C-5'), 61.5 (C-6'). *Retzia capensis* (Retziaceae) (2, 97)

## 121. (8S)-7,8-DIHYDROAUCUBIN



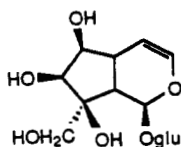
$C_{15}H_{24}O_9$  348.35 (500 MHz D<sub>2</sub>O) 5.37 (H-1, d, 3.1), 6.30 (H-3, dd, 6.2, 2.2), 4.89 (H-4, dd, 6.2, 2.5), 2.63 (H-5, m), 4.07 (H-6, m), 1.38 (H-7, m), 2.20–2.27 (H-7, H-8, H-9, m), 3.67, 3.63 (H-10, dd's, 10.5, 6.0); (D<sub>2</sub>O) 96.4 (C-1), 140.6 (C-3), 104.9 (C-4), 41.5 (C-5), 78.0 (C-6), 36.1 (C-7), 41.0 (C-8), 42.8 (C-9), 66.5 (C-10), 99.2 (C-1'), 73.5 (C-2'), 76.5 (C-3'), 70.4 (C-4'), 77.0 (C-5'), 61.5 (C-6'). *Phaulopsis imbricata* (Acanthaceae) (98)

## 122. 5,7-BISDEOXYCYNANCHOSIDE



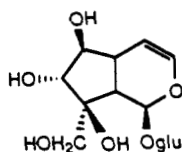
$C_{15}H_{24}O_{10}$  364.35 [ $\alpha$ ] -126° (MeOH) uv 204 (MeOH) (90 MHz D<sub>2</sub>O) 5.60 (H-1, d, 2.5), 6.24 (H-3, dd, 6.3, 3.0), 4.93 (H-4, dd, 6.3, 3.0), 2.82 (H-5, bd, 10.0), 4.02 (H-6, m), 1.95 (H-7, o, 15.0, 6.0, 3.3), 2.62 (H-9, bd, 10.0), 3.68, 3.56 (H-10, 12.5); (D<sub>2</sub>O) 93.3 (C-1), 140.1 (C-3), 105.3 (C-4), 40.8 (C-5), 76.6 (C-6), 44.1 (C-7), 82.1 (C-8), 50.4 (C-9), 67.0 (C-10), 98.9 (C-1'), 73.5 (C-2'), 76.6 (C-3'), 70.5 (C-4'), 77.0 (C-5'), 61.6 (C-6'). *Macfadyena cynanchoides* (Bignoniaceae) (99)

## 123. PAULOWNIOSIDE



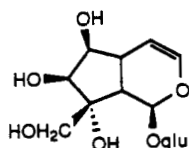
$C_{15}H_{24}O_{11}$  380.35 [ $\alpha$ ] -65° (MeOH) uv 204 (MeOH) (90 MHz D<sub>2</sub>O) 5.72 (H-1, s), 6.28 (H-3, dd, 6.0, 1.0), 5.00 (H-4, dt, 6.0, 1.5), 2.73 (H-5, bs), 3.69 (H-6, d, 4.5), 3.95 (H-7, d, 4.5), 2.73 (H-9, bs), 3.93, 3.60 (H-10, 13.0); (D<sub>2</sub>O) 93.2 (C-1), 140.1 (C-3), 105.2 (C-4), 35.5 (C-5), 74.7 (C-6), 77.0 (C-7), 79.8 (C-8), 48.2 (C-9), 65.6 (C-10), 98.8 (C-1'), 73.5 (C-2'), 76.4 (C-3'), 70.4 (C-4'), 77.0 (C-5'), 61.6 (C-6'). *Paulownia tomentosa* (Bignoniaceae) (100)

## 124. 10-DESCINNAMOYLGLLOBULARIMIN



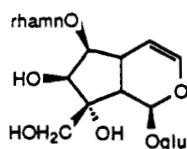
$C_{15}H_{24}O_{11}$  380.35  $[\alpha] -139.9^\circ$  (MeOH) ( $CD_3OD$ ) 93.3 (C-1), 140.4 (C-3), 106.5 (C-4), 37.3 (C-5), 83.1 (C-6), 86.4 (C-7), 80.3 (C-8), 48.0 (C-9), 64.3 (C-10), 99.5 (C-1'), 74.6 (C-2'), 77.9 (C-3')<sup>a</sup>, 71.5 (C-4'), 77.7 (C-5')<sup>a</sup>, 62.7 (C-6'). Hydrolysis of globularimin (4, 101)

## 125. 10-DESCINNAMOYLGLLOBULARININ



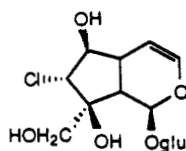
$C_{15}H_{24}O_{11}$  380.35 ( $CD_3OD$ ) 95.2 (C-1), 141.6 (C-3), 105.3 (C-4), 37.2 (C-5), 78.3 (C-6), 79.3 (C-7), 81.0 (C-8), 43.7 (C-9), 66.4 (C-10), 99.2 (C-1'), 74.6 (C-2'), 78.0 (C-3')<sup>a</sup>, 70.4 (C-4'), 78.3 (C-5')<sup>a</sup>, 62.4 (C-6'). Hydrolysis of globularinin (4, 101)

## 126. VERBASCOSIDE B



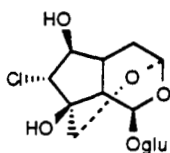
$C_{21}H_{34}O_{15}$  526.49  $[\alpha] -108^\circ$  (MeOH) (200 MHz  $CD_3OD$ ) 5.25 (H-1, d, 6), 6.32 (H-3, dd, 6.5, 2), 5.07 (H-4, dd, 6.5, 3), 2.89–2.63 (H-5, m, 10, 2), 4.03 (H-6, dd, 4, 2), 3.95 (H-7, d, 4), 2.32 (H-9, dd, 10, 6), 4.10–3.20 (H-10), 4.70 (H-1', d, 7.5), 4.03 (H-2', dd), 4.76 (H-1''), 1.22 (H-6''), d, 2.5); ( $CD_3OD$ ) 96.1 (C-1), 141.9 (C-3), 106.0 (C-4), 37.2 (C-5), 83.1 (C-6), 78.1 (C-7), 82.3 (C-8), 44.1 (C-9), 67.1 (C-10), 100.7 (C-1'), 74.6 (C-2'), 77.8 (C-3'), 71.2 (C-4'), 76.8 (C-5'), 62.3 (C-6'), 100.8 (C-1''), 72.0 (C-2''), 70.1 (C-3''), 73.9 (C-4''), 72.3 (C-5''), 18.0 (C-6''). *Verbascum georgicum* (Scrophulariaceae) (102)

## 127. ASYSTASIOSIDE E



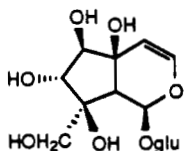
$C_{15}H_{23}ClO_{10}$  398.79  $[\alpha] -140^\circ$  (MeOH) (500 MHz  $D_2O$ ) 5.53 (H-1, d, 2.2), 6.28 (H-3, dd, 6.3, 1.7), 5.17 (H-4, dd, 6.1, 3.3), 2.67 (H-5, m), 3.88 (H-6, m), 4.10 (H-7, d, 9.0), 2.61 (H-9, bd, 11), 3.91, 3.70 (H-10, d's, 12.5); ( $D_2O$ ) 92.6 (C-1), 139.6 (C-3), 106.1 (C-4), 35.4 (C-5), 81.1 (C-6), 71.6 (C-7), 79.3 (C-8), 47.0 (C-9), 62.4 (C-10), 98.9 (C-1'), 73.4 (C-2'), 76.4 (C-3'), 70.4 (C-4'), 76.9 (C-5'), 61.5 (C-6'). *Asystasia bella* (Acanthaceae) (41)

## 128. GLUTINOSIDE



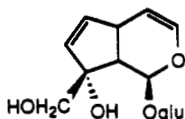
$C_{15}H_{23}ClO_{10}$  398.79  $[\alpha] -79.2^\circ$  (MeOH) mp 185–186° (pentaacetate) (pentaacetate 500 MHz  $CDCl_3$ ) 5.55 (H-1, d, 1.8), 5.33 (H-3, d, 3.4), 2.16 (H-4 $\alpha$ , dd, 14.7, 3.4), lost in acetoxy methyls (H-4 $\beta$ ), 2.22 (H-5, ddd, 10.3, 9.8, 3.1), 4.98 (H-6, dd, 7.9, 3.1), 4.28 (H-7, d, 7.9), 2.66 (H-9, bd, 9.8), 4.07 (H-10 $\alpha$ , d, 12.2), 3.67 (H-10 $\beta$ , d, 12.2), 2.01, 2.03, 2.03, 2.10, 2.11 (OAc); (pyridine- $d_5$ ) 94.6 (C-1), 92.6 (C-3), 33.9 (C-4), 35.5 (C-5), 84.3 (C-6), 75.6 (C-7), 79.3 (C-8), 47.5 (C-9), 61.9 (C-10), 98.6 (C-1'), 74.2 (C-2'), 77.9 (C-3'), 70.9 (C-4'), 77.9 (C-5'), 61.9 (C-6'). *Rebmannia glutinosa* (Scrophulariaceae) (103)

129. CYNANCHOSIDE (7 $\alpha$ , 10-Dihydroxyharpagide)



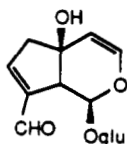
$C_{15}H_{24}O_{12}$  396.35  $[\alpha] -126^\circ$  (MeOH) uv 204 (MeOH) (90 MHz  $D_2O$ ) 5.86 (H-1, s), 6.42 (H-3, d, 6.0), 5.26 (H-4, d, 6.0), 3.97 (H-6, d, 9.0), 3.65 (H-7, d, 9.0), 2.45 (H-9, s), 3.81, 3.57 (H-10, 13.0); ( $D_2O$ ) 91.7 (C-1), 140.5 (C-3), 110.0 (C-4), 64.9 (C-5), 82.5 (C-6), 78.9 (C-7), 76.3 (C-8), 56.2 (C-9), 62.1 (C-10), 98.9 (C-1'), 73.3 (C-2'), 76.3 (C-3'), 70.6 (C-4'), 77.0 (C-5'), 61.6 (C-6'). *Macfadyena cynanchoides* (Bignoniaceae) (104)

130. ERANTHEMOSIDE



$C_{15}H_{22}O_9$  346.33  $[\alpha] -98^\circ$  (EtOH) (90 MHz  $D_2O$ ) 5.52 (H-1, d, 1.7), 6.20 (H-3, dd, 6, 2), 5.13 (H-4, dd, 6, 3), 3.3 (H-5, m), 6.11 (H-6, dd, 5.5, 3), 5.69 (H-7, dd, 5.5, 2), 2.59 (H-9, dd, 8.5, 1.7), 3.68 (H-10, s), 4.84 (H-1', d, 7); ( $D_2O$ ) 94.3 (C-1), 138.8 (C-3)<sup>a</sup>, 106.5 (C-4), 38.0 (C-5), 131.6 (C-6), 138.3 (C-7)<sup>a</sup>, 85.9 (C-8), 44.7 (C-9), 67.3 (C-10), 98.8 (C-1'), 73.6 (C-2'), 76.5 (C-3'), 70.4 (C-4'), 77.0 (C-5'), 61.5 (C-6'). *Erantthemum pulchellum* (Acanthaceae) (105)

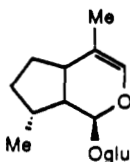
131. HYGROPHILOSIDE



$C_{15}H_{20}O_9$  344.32 (90 MHz  $D_2O$ ) 6.12 (H-1, d, 3), 6.48 (H-3, d, 6.5), 5.27 (H-4, d, 6.5), 3.05 (H-6, m), 7.32 (H-7, bd, 2), 3.5 (H-9), 9.70 (H-10, s); ( $D_2O$ ) 93.4 (C-1), 141.1 (C-3), 109.5 (C-4), 74.5 (C-5), 46.1 (C-6), 157.5 (C-7), 142.9 (C-8), 53.0 (C-9), 193.9 (C-10), 99.2 (C-1'), 73.3 (C-2'), 76.2 (C-3'), 70.5 (C-4'), 77.1 (C-5'), 61.5 (C-6'). *Hygrophila difformis* (Acanthaceae) (106)

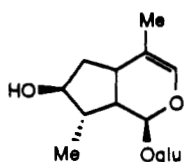
Group 3 (10-carbon skeleton)

132. BOSCHNASIDE (8-*epi*-Iridodial glucoside)



$C_{16}H_{26}O_7$  330.38 tetraacetate mp 131–132°  $[\alpha] -140.8^\circ$  ( $CHCl_3$ ) (tetraacetate 100 MHz  $CDCl_3$ ) 5.88 (H-3, bs), 0.99 (H-10, d, 7.0), 1.49 (H-11, s), 5.10–4.80 (H-4', m), 4.20 (H-6', m), 1.98–2.08 (OAc); (tetraacetate  $CDCl_3$ ) 93.4 (C-1), 133.2 (C-3), 113.9 (C-4), 35.7 (C-5)<sup>a</sup>, 28.5 (C-6)<sup>b</sup>, 33.2 (C-7)<sup>b</sup>, 34.3 (C-8)<sup>a</sup>, 42.8 (C-9), 15.9 (C-10)<sup>c</sup>, 16.3 (C-11)<sup>c</sup>, 95.0 (C-1'), 70.7 (C-2'), 71.8 (C-3'), 68.4 (C-4'), 72.6 (C-5'), 61.8 (C-6'), 170.2, 169.7, 169.0, 168.7 (O=CMe), 20.5 (O=CMe). *Boschniakia rossica* (Orobanchaceae) (107)

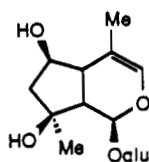
133. 7 $\beta$ -HYDROXY-8-*epi*-IRIDODIAL GLUCOSIDE



$C_{16}H_{26}O_8$  346.38  $[\alpha] -85.7^\circ$  (MeOH) (60 MHz  $D_2O$ ) 5.30 (H-1, s), 5.92 (H-3, bs), 2.60 (H-5, m), 2.1–1.1 (H-6), 4.0–3.6 (H-7), 2.1–1.1 (H-8, H-9), 0.95 (H-10, d, 7.0), 1.50 (H-11, bs), 4.80 (H-1', d, 7.5); ( $D_2O$ ) 95.3 (C-1), 133.1 (C-3), 117.3 (C-4), 33.3 (C-5), 37.1 (C-6), 79.4 (C-7), 42.9 (C-8), 41.9 (C-9), 14.1 (C-10), 15.9 (C-11), 98.8 (C-1'), 73.6 (C-2'), 76.6 (C-3')<sup>a</sup>, 70.5 (C-4'), 77.0 (C-5')<sup>a</sup>, 61.6 (C-6'). *Linaria cymbalaria* (Scrophulariaceae) (108)

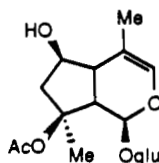


## 134. 5-DEOXYLAMIOL



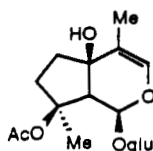
$C_{16}H_{26}O_9$  362.38 (60 MHz  $D_2O$ ) 5.45 (H-1, bs), 6.05 (H-3, m), 2.60 (H-5), 2.10 (H-7, dd, 14.0, 7.0), 1.87 (H-7, dd, 14.0, 6.0), 2.60 (H-9), 1.30 (H-10, s), 1.64 (H-11, bs); ( $D_2O$ ) 93.7 (C-1), 133.5 (C-3), 114.1 (C-4), 43.3 (C-5), 74.8 (C-6), 49.4 (C-7), 78.6 (C-8), 51.0 (C-9), 23.9 (C-10), 15.6 (C-11), 98.7 (C-1'), 73.5 (C-2'), 76.5 (C-3'), 70.5 (C-4'), 77.0 (C-5'), 61.6 (C-6'). Prepared from shanzhiside methyl ester, *Satureja vulgaris* (Labiatae) (34, 109)

## 135. 5-DEOXYLAMIOSIDE



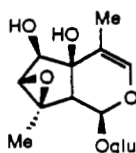
$C_{18}H_{28}O_{10}$  404.41 [ $\alpha$ ]  $-54^\circ$  (dioxane) uv 205 (MeOH) (60 MHz  $D_2O$ ) 5.80 (H-1, bs), 6.10 (H-3, m), 2.72 (H-5, bd), 3.91 (H-6, m), 2.18 (H-7, m), 2.96 (H-9, bd), 1.54 (H-10, s), 1.62 (H-11, bs), 2.09 (OAc). *Lamium amplexicaule* (Labiatae) (34)

## 136. 6-DEOXYLAMIOSIDE



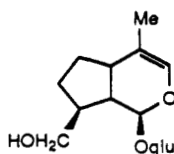
$C_{18}H_{28}O_{10}$  404.41 (60 MHz  $D_2O$ ) 5.91 (H-1, d, 1), 6.23 (H-3, q, 1.5), 2.2-1.8 (H-6, H-7, m), 2.72 (H-9, d, 1), 1.49 (H-10, s), 1.64 (H-11, d, 1.5), 2.1 (OAc). *Lamium amplexicaule* (Labiatae) (110)

## 137. 4-METHYLANTIRRINOSIDE

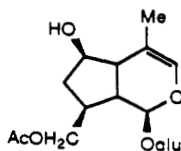


$C_{16}H_{24}O_{10}$  376.36 [ $\alpha$ ]  $-61^\circ$  (MeOH) (90 MHz  $D_2O$ ) 5.30 (H-1, d, 7.5), 6.21 (H-3, q, 1.5), 4.27 (H-6, d, 2.0), 3.61 (H-7, d, 2.0), 2.55 (H-9, d, 7.5), 1.52 (H-10, s), 1.61 (H-11, d, 1.5), 4.75 (H-1', d, 7.5); ( $D_2O$ ) 95.4 (C-1), 137.7 (C-3), 115.2 (C-4), 74.4 (C-5), 76.0 (C-6)<sup>a</sup>, 66.9 (C-7), 64.7 (C-8), 53.9 (C-9), 17.2 (C-10), 11.8 (C-11), 99.0 (C-1'), 73.5 (C-2'), 76.5 (C-3')<sup>a</sup>, 70.4 (C-4'), 77.1 (C-5')<sup>a</sup>, 61.6 (C-6'). *Satureja vulgaris* (Labiatae) (109)

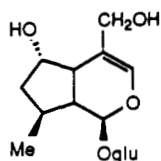
## 138. DECAPETALOSIDE



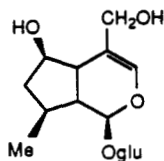
$C_{16}H_{26}O_8$  346.38 [ $\alpha$ ]  $-71^\circ$  (MeOH) (90 MHz  $D_2O$ ) 5.14 (H-1, d, 4), 6.09 (H-3, bs), 2.51 (H-5, m), 3.58 (H-10, bd, 6), 1.56 (H-11, bs); ( $D_2O$ ) 97.3 (C-1), 134.3 (C-3), 115.8 (C-4), 38.8 (C-5), 30.1 (C-6), 27.7 (C-7), 43.2 (C-8), 44.9 (C-9), 66.1 (C-10), 15.9 (C-11), 99.4 (C-1'), 73.6 (C-2'), 76.5 (C-3'), 70.3 (C-4'), 76.9 (C-5'), 61.5 (C-6'). *Viburnum betulifolium* (Caprifoliaceae) (111)

139. 10-O-ACETYL-6 $\beta$ -HYDROXY-MONGOLIOSIDE

$C_{18}H_{28}O_{10}$  404.41 ( $D_2O$ ) 95.8 (C-1), 134.9 (C-3), 112.4 (C-4), 45.5 (C-5), 75.7 (C-6), 35.8 (C-7), 38.0 (C-8), 44.0 (C-9), 69.2 (C-10), 15.4 (C-11), 99.1 (C-1'), 73.5 (C-2'), 76.4 (C-3'), 70.4 (C-4'), 76.9 (C-5'), 61.5 (C-6'). *Viburnum hupehense* (Caprifoliaceae) (112)

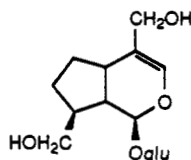
140.  $\alpha$ -DIHYDROVERBENOL

$C_{16}H_{26}O_9$  362.38  $[\alpha] -72.7^\circ$  (MeOH) uv 205 (MeOH) (90 MHz  $D_2O$ ) 5.07 (H-1, d, 8.0), 6.63 (H-3, bs), 2.88 (H-5, m), 4.49 (H-6, m), 2.5–1.4 (H-7–H-9), 1.24 (H-10, d, 6.5), 4.12 (H-11, bs), 4.86 (H-1', d, 7.5); ( $D_2O$ ) 100.8 (C-1), 142.2 (C-3), 114.4 (C-4), 43.4 (C-5), 74.2 (C-6), 42.1 (C-7), 34.5 (C-8), 47.5 (C-9), 21.3 (C-10), 62.0 (C-11)<sup>a</sup>, 99.8 (C-1'), 73.7 (C-2'), 76.7 (C-3'), 70.6 (C-4'), 77.1 (C-5'), 61.7 (C-6')<sup>a</sup>. Reduction of verbenaol (113)

141.  $\beta$ -DIHYDROVERBENOL

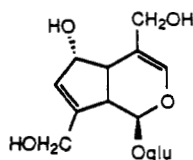
$C_{16}H_{26}O_9$  362.38  $[\alpha] -110.0^\circ$  (MeOH) uv 205 (MeOH) (90 MHz  $D_2O$ ) 5.33 (H-1, d, 2.5), 6.36 (H-3, bs), 2.72 (H-5, m), 4.17 (H-6, m), 2.5–1.7 (H-7–H-9), 1.18 (H-10, d, 6.3), 4.21, 3.98 (H-11, 13.0), 4.77 (H-1', d, 7.5); ( $D_2O$ ) 96.3 (C-1), 138.9 (C-3), 116.0 (C-4), 42.9 (C-5), 76.5 (C-6), 42.0 (C-7), 33.8 (C-8), 47.4 (C-9), 20.2 (C-10), 61.7 (C-11), 99.3 (C-1'), 73.6 (C-2'), 76.7 (C-3'), 70.5 (C-4'), 77.1 (C-5'), 61.7 (C6'). Reduction of verbenaol (113)

## 142. 11-HYDROXYDECAPETALOSIDE

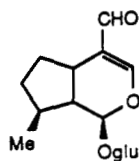


$C_{16}H_{26}O_9$  362.38  $[\alpha] -99^\circ$  (MeOH) (90 MHz  $D_2O$ ) 5.22 (H-1, d, 3.5), 6.33 (H-3, bs), 2.72 (H-5, m), 4.08, 3.89 (H-11, 12); ( $D_2O$ ) 97.4 (C-1), 138.6 (C-3), 117.9 (C-4), 35.0 (C-5), 29.7 (C-6), 27.6 (C-7), 42.7 (C-8), 44.7 (C-9), 66.1 (C-10), 61.5 (C-11), 99.5 (C-1'), 73.6 (C-2'), 76.5 (C-3'), 70.5 (C-4'), 77.0 (C-5'), 61.5 (C-6'). Prepared from adoxoside (111)

## 143. ASPERULOSIDOL

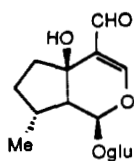


$C_{16}H_{24}O_{10}$  376.36 mp 183–184<sup>o</sup>  $[\alpha] -8^\circ$  ( $H_2O$ ) uv 206 (MeOH) (90 MHz  $D_2O$ ) 4.94 (H-1, d, 9.0), 6.66 (H-3, bs), 3.03 (H-5, br, 7.7, 6.6), 4.87 (H-6, bd), 6.07 (H-7, bs), 2.70 (H-9, br, 9.0, 7.7), 4.43 (H-10, 2d's, 15.0), 4.17 (H-11, bs); ( $D_2O$ ) 99.6 (C-1), 142.6 (C-3), 114.5 (C-4), 42.6 (C-5), 74.6 (C-6), 129.3 (C-7), 150.6 (C-8), 46.5 (C-9), 61.0 (C-10), 61.5 (C-11). Reduction of asperuloside (114)

144. 5-DEOXYSTANSIOSIDE (Stanside, 8-*epi*-Boschnaloside)

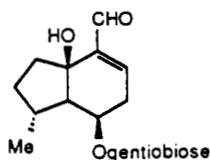
$C_{16}H_{24}O_8$  344.36 mp 146–147<sup>o</sup>  $[\alpha] -117^\circ$  (MeOH) uv 249 (MeOH) (90 MHz  $D_2O$ ) 5.54 (H-1, d, 1.5), 7.48 (H-3, s), 3.00 (H-5, m), 2.5–1.2 (H-6, H-7, H-8, H-9), 1.15 (H-10, d, 6.0), 9.18 (H-11, s), 4.88 (H-1', d, 7.5); ( $D_2O$ ) 98.8 (C-1), 164.5 (C-3), 125.2 (C-4), 31.3 (C-5), 30.8 (C-6), 33.2 (C-7), 35.4 (C-8), 48.4 (C-9), 19.9 (C-10), 192.6 (C-11), 99.7 (C-1'), 73.5 (C-2'), 76.5 (C-3'), 70.3 (C-4'), 77.2 (C-5'), 61.5 (C-6'). *Tecoma stans* (Bignoniaceae) (115)

## 145. PLANTARENALOSIDE (Yuheinoside)



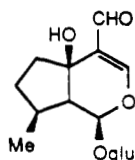
$C_{16}H_{24}O_9$  360.36  $[\alpha] -188.8^\circ$  (MeOH) uv 241 (MeOH) (90 MHz  $D_2O$ ) 5.93 (H-1, s), 7.56 (H-3, s), 0.90 (H-10, d, 7.0), 9.23 (H-11, s), 4.83 (H-1', d, 7.5); ( $D_2O$ ) 97.3 (C-1), 165.5 (C-3), 125.0 (C-4), 72.9 (C-5), 38.3 (C-6), 32.2 (C-7), 34.2 (C-8), 51.7 (C-9), 15.9 (C-10), 194.6 (C-11), 99.4 (C-1'), 73.2 (C-2'), 76.1 (C-3')<sup>a</sup>, 70.4 (C-4'), 77.2 (C-5')<sup>a</sup>, 61.5 (C-6'). *Tecoma stans* (Bignoniaceae), *Plantago arenaria* (Plantaginaceae) (116, 117)

**146. PLANTARENALOSIGENIN-1-O- $\beta$ -GENTIOBIOSIDE**



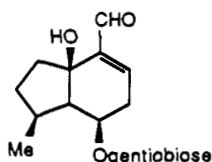
$C_{22}H_{34}O_{14}$  522.50  $[\alpha] -56.0^\circ$  (MeOH) uv 241 (MeOH) [400 MHz  $CDCl_3$ - $CD_3OD$  (8:2)] 5.93 (H-1, d, 0.5), 7.58 (H-3, s), 0.94 (H-10, d, 6.2), 9.23 (H-11, s), 4.72 (H-1', d, 7.5), 4.57 (H-1'', d, 7.5); [ $CDCl_3$ - $CD_3OD$  (6:4)] 96.3 (C-1), 165.4 (C-3), 124.9 (C-4), 72.9 (C-5), 38.2 (C-6), 32.2 (C-7), 34.2 (C-8), 51.7 (C-9), 15.9 (C-10), 194.8 (C-11), 99.4 (C-1'), 74.9 (C-2')<sup>a</sup>, 77.2 (C-3')<sup>b</sup>, 70.8 (C-4'), 76.2 (C-5')<sup>b</sup>, 69.3 (C-6'), 103.6 (C-1''), 73.1 (C-2'')<sup>a</sup>, 76.2 (C-3'')<sup>b</sup>, 70.7 (C-4''), 76.9 (C-5'')<sup>b</sup>, 61.8 (C-6''). *Campsidium valdivianum* (Bignoniaceae) (118)

**147. STANSIOSIDE**



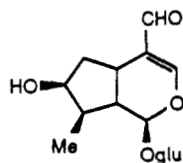
$C_{16}H_{24}O_9$  360.36  $[\alpha] -124.5^\circ$  (MeOH) uv 241 (MeOH) (400 MHz  $CD_3OD$ ) 5.70 (H-1, d, 2.8), 7.35 (H-3, s), 2.13, 1.39 (H-6, m's), 2.13, 1.71 (H-7, m's), 1.71 (H-8, m), 1.88 (H-9, dd, 9.0, 2.8), 1.13 (H-10, d, 6.3), 9.25 (H-11, s), 4.61 (H-1', d, 8.0), 3.18 (H-2', 9.1, 8.0), 3.90 (H-6', dd, 12.0, 2.0), 3.66 (H-6'', dd, 11.9, 5.8); ( $D_2O$ ) 97.6 (C-1), 164.6 (C-3), 124.6 (C-4), 73.5 (C-5), 37.9 (C-6), 31.0 (C-7), 35.1 (C-8), 56.7 (C-9), 19.9 (C-10), 193.7 (C-11), 99.7 (C-1'), 73.2 (C-2'), 76.2 (C-3'), 70.4 (C-4'), 77.2 (C-5'), 61.4 (C-6'). *Tecoma stans* (Bignoniaceae) (115, 116, 119)

**148. STANSIOSIGENIN-1-O- $\beta$ -GENTIOBIOSIDE**



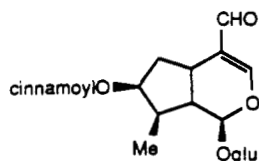
$C_{22}H_{34}O_{14}$  522.50  $[\alpha] -13.8^\circ$  (MeOH) uv 241 (MeOH) [400 MHz  $CDCl_3$ - $CD_3OD$  (8:2)] 5.80 (H-1, d, 2), 7.53 (H-3, s), 1.14 (H-10, d, 5.5), 3.37 (H-9, dd, 7, 2), 9.22 (H-11, s), 4.72 (H-1', d, 7.5), 4.57 (H-1'', d, 7.5); [ $CDCl_3$ - $CD_3OD$  (6:4)] 97.5 (C-1), 164.6 (C-3), 124.8 (C-4), 73.5 (C-5), 37.9 (C-6), 31.0 (C-7), 35.1 (C-8), 56.6 (C-9), 19.9 (C-10), 194.6 (C-11), 99.7 (C-1'), 74.9 (C-2')<sup>a</sup>, 77.2 (C-3')<sup>b</sup>, 70.8 (C-4'), 76.2 (C-5')<sup>b</sup>, 69.3 (C-6'), 103.6 (C-1''), 73.1 (C-2'')<sup>a</sup>, 76.2 (C-3'')<sup>b</sup>, 70.7 (C-4''), 76.9 (C-5'')<sup>b</sup>, 61.8 (C-6''). *Campsidium valdivianum* (Bignoniaceae) (118)

**149. CACHINESIDE I (7 $\beta$ -Hydroxystanside)**



$C_{16}H_{24}O_9$  360.36  $[\alpha] -136^\circ$  (MeOH) (200 MHz  $CD_3OD$ ) 5.46 (H-1, d, 3.0), 7.32 (H-3, d, 1.0), 3.07 (H-5, q-like, 8.0, 6.0, 1.0), 1.65 (H-6 $\alpha$ , ddd, 6.0, 6.0), 2.22 (H-6 $\beta$ , ddd, 8.0, 1.8), 4.03 (H-7, t-like, 6.0, 5.0, 1.8), 1.82 (H-8, m, 9.0, 5.0), 2.08 (H-9, m, 9.0), 1.10 (H-10, d), 9.18 (H-11, s), 4.67 (H-1', d, 7.8); ( $CD_3OD$ ) 98.2 (C-1), 162.4 (C-3), 126.4 (C-4), 29.5 (C-5), 41.2 (C-6), 74.8 (C-7), 41.4 (C-8), 45.9 (C-9), 13.0 (C-10), 192.9 (C-11), 98.8 (C-1'), 74.2 (C-2'), 77.9 (C-3')<sup>a</sup>, 71.2 (C-4'), 77.6 (C-5')<sup>a</sup>, 62.5 (C-6'). *Campsis chinensis* (Bignoniaceae) (120)

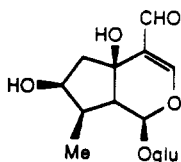
**150. CAMPENOSIDE**



$C_{25}H_{30}O_{10}$  490.51 mp 165-167 $^\circ$   $[\alpha] -59.5^\circ$  (MeOH) (200 MHz  $CD_3OD$ ) 5.46 (H-1, d, 3), 7.39 (H-3, d), 3.13 (H-5, m, 8, 4), 1.85 (H-6 $\alpha$ , m, 15, 6.5, 6), 2.32 (H-6 $\beta$ , m, 15, 8, <1), 5.24 (H-7, m, 6, 5, 1), 2.14 (H-9, m, 10, 3), 1.11 (H-10, d, 6), 9.19 (H-11, s), 4.63 (H-1', d, 7), 6.48/7.66 (H $\alpha$ , H $\beta$ , d's, 16), 7.30-7.60 (H-2''-H-4''), m); (DMSO- $d_6$ ) 96.3 (C-1), 160.6 (C-3), 123.2 (C-4), 28.5 (C-5), 37.2 (C-6), 76.3 (C-7), 38.4 (C-8), 45.2 (C-9), 12.6 (C-10), 190.2 (C-11), 98.8 (C-1'), 72.9 (C-2'), 76.9 (C-3')<sup>a</sup>, 70.0 (C-4'),

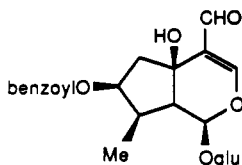
76.5 (C-5')<sup>a</sup>, 61.0 (C-6'), 165.2 (C=O), 118.0 (C $\alpha$ ), 143.8 (C $\beta$ ), 133.8 (C-1''), 128.4 (C-2'')<sup>b</sup>, 127.7 (C-3'')<sup>b</sup>, — (C-4''). *Campsis chinensis* (Bignoniaceae) (120)

**151. TECOMOSIDE**



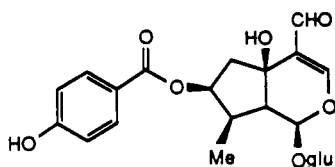
C<sub>16</sub>H<sub>24</sub>O<sub>10</sub> 376.36 mp 124–125° [ $\alpha$ ] –123.5° (MeOH) [ $\alpha$ ] –118° (MeOH) uv 241 (EtOH) (200 MHz CD<sub>3</sub>OD) 5.77 (H-1, d, 1.7), 7.35 (H-3, s), 2.50 (H-6 $\alpha$ , dd, 5.8), 2.18 (H-6 $\beta$ , dd, 2.7), 3.91 (H-7, m, 5.8, 5.8, 2.7), 1.63 (H-8, m, 12.0, 5.8), 2.32 (H-9, dd, 12, 1.7), 1.11 (H-10, d), 9.25 (H-11, s), 4.63 (H-1', d, 7.8); (CD<sub>3</sub>OD) 97.1 (C-1), 162.7 (C-3), 126.8 (C-4), 72.1 (C-5), 48.9 (C-6), 73.4 (C-7), 41.2 (C-8), 54.7 (C-9), 13.1 (C-10), 192.9 (C-11), 100.1 (C-1'), 74.4 (C-2'), 78.4 (C-3')<sup>a</sup>, 71.5 (C-4'), 77.5 (C-5')<sup>a</sup>, 62.7 (C-6'). *Campsis chinensis* (Bignoniaceae) (116, 120, 121)

**152. 7-O-BENZOYLTECOMOSIDE**



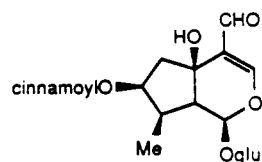
C<sub>23</sub>H<sub>28</sub>O<sub>11</sub> 480.47 no data available. *Tecoma capensis* (Bignoniaceae) (122)

**153. 7-O-p-HYDROXYBENZOYL-TECOMOSIDE**

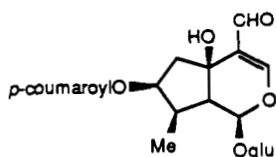


C<sub>23</sub>H<sub>28</sub>O<sub>12</sub> 496.47 [ $\alpha$ ] –64.7° (MeOH) uv 260 (MeOH) (360 MHz CD<sub>3</sub>OD) 5.80 (H-1, d, 1.5), 7.33 (H-3, s), 2.8–2.2 (H-6), 5.00 (H-7, m), 1.95 (H-8, m), 2.8–2.2 (H-9), 1.02 (H-10, d, 6.5), 9.28 (H-11, s), 7.62 (H-2'', d, 8), 6.74 (H-3'', d, 8); (CD<sub>3</sub>OD) 96.4 (C-1), 162.7 (C-3), 127.5 (C-4), 71.6 (C-5), — (C-6), 76.7 (C-7), 39.9 (C-8), 55.3 (C-9), 13.0 (C-10), 192.7 (C-11), 100.3 (C-1'), 74.5 (C-2'), 78.6 (C-3')<sup>a</sup>, 71.6 (C-4'), 77.6 (C-5')<sup>a</sup>, 62.8 (C-6'), 168.0 (C=O), 129.0 (C-1''), 133.7 (C-2''), 116.0 (C-3''), 162.7 (C-4''). *Tecoma capensis* (Bignoniaceae) (123)

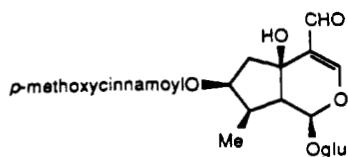
**154. 7-O-CINNAMOYLTECOMOSIDE**  
(5-Hydroxycampenoside)



C<sub>25</sub>H<sub>30</sub>O<sub>11</sub> 506.51 mp 191–192° [ $\alpha$ ] –69.8° (MeOH) uv 278, 217 (MeOH) (200 MHz CD<sub>3</sub>OD) 5.84 (H-1, d, <2), 7.40 (H-3, s), 2.67 (H-6 $\alpha$ , dd, 6, 16), 2.27 (H-6 $\beta$ , dd, 2, 16), 5.08 (H-7, m, 6, 5.5, 2), 1.88 (H-8, m, 12, 5.5), 2.46 (H-9, dd, 12, <2), 1.13 (H-10, d, 7), 9.25 (H-11, s), 4.63 (H-1', d, 7.5), 6.50/7.69 (H $\alpha$ , H $\beta$ , d's, 16), 7.30–7.60 (H-2''–H-4''); (CD<sub>3</sub>OD) 96.4 (C-1), 162.6 (C-3), 126.5 (C-4), 71.6 (C-5), — (C-6), 77.0 (C-7), 40.0 (C-8), 55.3 (C-9), 13.0 (C-10), 192.7 (C-11), 100.3 (C-1'), 74.4 (C-2'), 78.5 (C-3')<sup>a</sup>, 71.6 (C-4'), 77.5 (C-5')<sup>a</sup>, 62.7 (C-6'), 168.0 (C=O), 119.0 (C $\alpha$ ), 146.3 (C $\beta$ ), 133.3 (C-1''), 130.1 (C-2''), 129.3 (C-3''), 131.5 (C-4''). *Tecoma capensis*, *Campsis chinensis* (Bignoniaceae) (120, 123)

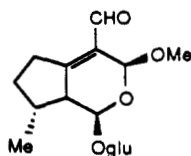
155. 7-O-*p*-COUMAROYLTECOMOSIDE

$C_{25}H_{30}O_{12}$  522.50  $[\alpha] -64.9^\circ$  (MeOH) uv 310, 266 (MeOH) (360 MHz  $CD_3OD$ ) 5.82 (H-1, d, 1.5), 7.33 (H-3, s), 2.8–2.2 (H-6), 5.08 (H-7, m), 1.95 (H-8, m), 2.8–2.2 (H-9), 1.10 (H-10, d, 6.5), 9.26 (H-11, s), 6.30/7.63 (H $\alpha$ , H $\beta$ , d, 16), 7.46 (H-2", d, 8), 6.70 (H-3", d, 8); ( $CD_3OD$ ) 96.4 (C-1), 162.6 (C-3), 126.7 (C-4), 71.6 (C-5), — (C-6), 76.7 (C-7), 40.1 (C-8), 55.3 (C-9), 13.0 (C-10), 192.6 (C-11), 100.2 (C-1'), 74.4 (C-2'), 78.5 (C-3')<sup>a</sup>, 71.6 (C-4'), 77.6 (C-5')<sup>a</sup>, 62.7 (C-6'), 168.3 (C=O), 116.7 (C $\alpha$ ), 146.8 (C $\beta$ ), 130.8 (C-1"), 131.2 (C-2"), 117.1 (C-3"), 162.6 (C-4"). *Tecoma capensis* (Bignoniaceae) (123)

156. 7-O-*p*-METHOXYCINNAMOYL-TECOMOSIDE

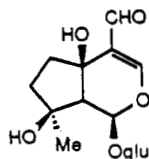
$C_{26}H_{32}O_{12}$  536.53  $[\alpha] -63.8^\circ$  (MeOH) uv 310, 228 (MeOH) (360 MHz  $CD_3OD$ ) 5.84 (H-1, d, 1.5), 7.36 (H-3, s), 2.8–2.2 (H-6, H-9), 5.08 (H-7, m), 1.95 (H-8, m), 1.12 (H-10, d, 6.5), 9.30 (H-11, s), 6.40/7.70 (H $\alpha$ , H $\beta$ , d's, 16), 7.56 (H-2", d, 8), 6.93 (H-3", d, 8), 3.83 (ArOMe); ( $CD_3OD$ ) 96.4 (C-1), 162.6 (C-3), 126.5 (C-4), 71.6 (C-5), — (C-6), 76.8 (C-7), 40.0 (C-8), 55.3 (C-9), 13.0 (C-10), 192.7 (C-11), 100.3 (C-1'), 74.4 (C-2'), 78.5 (C-3')<sup>a</sup>, 71.6 (C-4'), 77.5 (C-5')<sup>a</sup>, 62.7 (C-6'), 168.5 (O=C), 116.3 (C $\alpha$ ), 146.3 (C $\beta$ ), 128.3 (C-1"), 131.0 (C-2"), 115.5 (C-3"), 162.6 (C-4"), 55.9 (OMe). *Tecoma capensis* (Bignoniaceae) (123)

## 157. PINIFOLIN



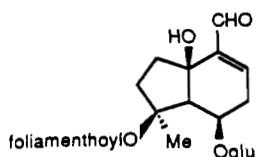
$C_{17}H_{26}O_9$  374.39 (400 MHz  $CD_3OD$ ) 5.23 (H-1, d, 8.1), 5.32 (H-3, s), 2.94 (H-6, m), 1.68 (H-7 $\alpha$ , dddd, 12, 8, 2.4), 1.94 (H-7 $\beta$ , m), 2.53 (H-8, m), 2.76 (H-9, br, 7.9), 0.84 (H-10, d, 7.1), 9.76 (H-11, s), 3.50 (OMe), 4.71 (H-1', d, 7.9), 3.84 (H-6', dd, 11.9, 2.2), 3.70 (H-6', dd, 11.9, 5.1); ( $CD_3OD$ ) 97.5 (C-1), 93.4 (C-3), 131.3 (C-4), 168.0 (C-5), 27.3 (C-6), 32.5 (C-7), 34.4 (C-8), 52.2 (C-9), 14.5 (C-10), 190.3 (C-11), 56.2 (OMe), 110.4 (C-1'), 74.7 (C-2'), 78.4 (C-3'), 71.5 (C-4'), 78.1 (C-5'), 62.7 (C-6'). *Penstemon pinifolius* (Scrophulariaceae) (124)

## 158. EUPHROSIDE



$C_{16}H_{24}O_{10}$  376.36  $[\alpha] -167.3^\circ$  (MeOH) uv 237 (EtOH) (250 MHz  $D_2O$ ) 6.00 (H-1, bs), 7.63 (H-3, s), 2.26–1.59 (H-6, H-7, m), 2.58 (H-9, bs), 1.29 (H-10, bs), 9.34 (H-11, s), 4.90 (H-1', d, 7.5), 3.35 (H-2', t, 7.5), 3.66–3.47 (H-3'–H-5', m), 4.00–3.82 (H-6', dd, 12, 6.0, dd, 12, 1.5); ( $CD_3OD$ ) 95.3 (C-1), 163.1 (C-3), 126.3 (C-4), 71.3 (C-5), 37.6 (C-6), 40.3 (C-7), 78.8 (C-8), 61.3 (C-9), 23.7 (C-10), 192.6 (C-11), 99.7 (C-1'), 74.2 (C-2'), 78.3 (C-3'), 71.5 (C-4'), 77.3 (C-5'), 62.7 (C-6'). *Euphrasia salisburgensis* (Scrophulariaceae) (125, 126)

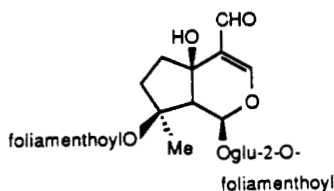
## 159. 8-O-FOLIAMENTHOYLEUPHROSIDE



$C_{26}H_{38}O_{12}$  542.58  $[\alpha] -59.2^\circ$  (MeOH) uv 245, 229 (?) (250 MHz  $D_2O$ ) 6.32 (H-1, bs), 7.69 (H-3, s), 1.61–2.42 (H-6, m), 2.82 (H-9, bs), 1.48 (H-10, bs), 9.30 (H-11, s), 4.90 (H-1', d, 7.5), 3.34 (H-2', t, 7.5), 3.42–3.61 (H-4', m), 3.79–4.02 (H-6', m, 12, 6, 1.5), 6.85 (H-3", br, 7.5, 1.5), 2.42 (H-4", m, 8), 2.18 (H-5", m), 5.48 (H-7", br, 7.2, 1.5), 4.12 (H-8", d, 7.2), 1.84 (H-9", d, 1.5), 1.72 (H-10", d, 1.5); ( $D_2O$ )

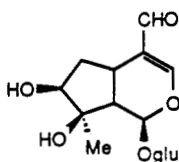
96.0 (C-1), 165.8 (C-3), 122.6 (C-4), 72.0 (C-5), 34.8 (C-6), 38.2 (C-7), 88.2 (C-8), 58.2 (C-9), 21.1 (C-10), 194.0 (C-11), 99.5 (C-1'), 73.0 (C-2'), 77.1 (C-3'), 70.3 (C-4'), 76.0 (C-5'), 61.5 (C-6'), 170.2 (C-1''), 128.9 (C-2''), 144.1 (C-3''), 27.3 (C-4''), 38.2 (C-5''), 139.9 (C-6''), 123.8 (C-7''), 58.6 (C-8''), 12.5 (C-9''), 16.1 (C-10''). *Clerodendrum incisum* (Verbenaceae) (126)

160. 2',8-DI-O-FOLIAMENTHOYL-EUPHOROSIDE



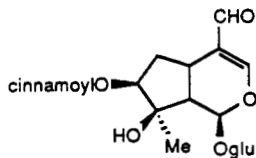
$C_{36}H_{52}O_{14}$  708.80  $[\alpha] -17.5^\circ$  (MeOH) (250 MHz  $D_2O$ ) 6.37 (H-1, bs), 7.58 (H-3, s), 1.58–2.43 (H-6, m), 2.82 (H-9, bs), 1.47 (H-10, bs), 9.16 (H-11, s), 5.18 (H-1', d, 7.5), 4.84 (H-2', t, 7.5), 3.54–3.63 (H-4', m), 3.90–4.10 (H-6', m, 12, 6, 1.5), 6.96 (H-3'', br, 7.5, 1.5), 2.43 (H-4'', m, 8, 7.5), 2.24 (H-5'', m, 8), 5.56 (H-7'', br, 7.2, 1.5), 4.19 (H-8'', d, 7.2), 1.85 (H-9'', d, 1.5), 1.77 (H-10'', d, 1.5), 6.87 (H-3''', br, 7.5, 1.5), 2.43 (H-4''', m, 8, 7.5), 2.24 (H-5''', m, 8), 5.48 (H-7''', br, 7.2, 1.5), 4.14 (H-8''', d, 7.2), 1.82 (H-9''', d, 1.5), 1.74 (H-10''', d, 1.5); ( $CDCl_3$ ) 95.4 (C-1), 159.5 (C-3), 122.4 (C-4), 72.0 (C-5), 33.2 (C-6), 37.8 (C-7), 86.5 (C-8), 57.8 (C-9), 21.1 (C-10), 188.8 (C-11), 96.9 (C-1'), 73.6 (C-2'), 75.8 (C-3'), 70.2 (C-4'), 74.2 (C-5'), 61.5 (C-6'), 167.5 (C-1''), 126.8 (C-2''), 141.8 (C-3''), 25.9 (C-4''), 37.3 (C-5''), 136.8 (C-6''), 124.6 (C-7''), 58.7 (C-8''), 11.8 (C-9''), 15.5 (C-10''), 168.2 (C-1'''), 128.0 (C-2'''), 143.5 (C-3'''), 26.0 (C-4'''), 37.4 (C-5'''), 137.0 (C-6'''), 124.7 (C-7'''), 58.7 (C-8'''), 11.8 (C-9'''), 15.6 (C-10'''). *Clerodendrum incisum* (Verbenaceae) (126)

161. CACHINESIDE V



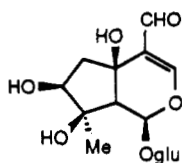
$C_{16}H_{24}O_{10}$  376.36 pentaacetate mp 197–199°  $[\alpha] -113^\circ$  ( $CHCl_3$ ) (pentaacetate 200 MHz  $CDCl_3$ ) 5.60 (H-1, d, 1.5), 7.08 (H-3, s), 3.09 (H-5, ddd, 10.3, 9.8, 5.4), 1.74 (H-6, dt, 15.7, 5.4), 2.41 (H-6, ddd, 15.7, 9.8, 2.7), 4.74 (H-7, dd, 5.4, 2.7), 2.66 (H-9, dd, 10.3, 1.5), 1.24 (H-10, s), 9.26 (H-11, s), 4.88 (H-1', d, 7.8), 4.97 (H-2', 9.0, 7.6), 5.23 (H-3', dd, 9.5, 9.0), 5.09 (H-4', t, 9.5), 3.74 (H-5', ddd, 9.5, 4.4, 2.4), 4.16 (H-6', dd, 14.5, 2.4), 4.31 (H-6', dd, 14.5, 4.4), 1.90, 2.00, 2.03, 2.11, 2.11 (OAc); (pentaacetate  $CDCl_3$ ) 94.1 (C-1), 158.3 (C-3), 125.6 (C-4), 24.3 (C-5), 34.5 (C-6), 80.5 (C-7), 78.2 (C-8), 47.4 (C-9), 21.5 (C-10), 189.5 (C-11), 95.6 (C-1'), 70.8 (C-2'), 72.4 (C-3')<sup>a</sup>, 68.3 (C-4'), 72.5 (C-5')<sup>a</sup>, 61.8 (C-6'). *Campsis chinensis* (Bignoniaceae) (127)

162. CAMPSISIDE



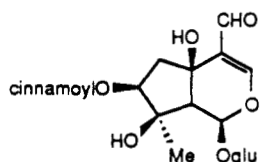
$C_{25}H_{30}O_{11}$  506.51  $[\alpha] -68.5^\circ$  (MeOH) (200 MHz  $CD_3OD$ ) 5.73 (H-1, d, 1.5), 7.41 (H-3, s), 3.15 (H-5, m), 1.81 (H-6 $\alpha$ , dt, 12, 6), 2.28 (H-6 $\beta$ , ddd, 12, 9, 2.5), 4.90 (H-7, m), 2.70 (H-9, dd, 10, 1.5), 1.29 (H-10, s), 9.18 (H-11, s), 4.67 (H-1', d, 8), 6.55/7.72 (H $\alpha$ , H $\beta$ , d, 16), 7.20–7.30 (H-2''–H-4'', m); ( $CD_3OD$ ) 96.1 (C-1), 162.4 (C-3), 126.3 (C-4), 25.8 (C-5), 36.1 (C-6), 81.1 (C-7), 79.4 (C-8), 48.8 (C-9), 22.1 (C-10), 192.8 (C-11), 100.2 (C-1'), 74.6 (C-2'), 78.0 (C-3')<sup>a</sup>, 71.6 (C-4'), 78.3 (C-5')<sup>a</sup>, 62.8 (C-6'), 167.9 (C=O), 119.1 (C $\alpha$ ), 146.4 (C $\beta$ ), 135.8 (C-1''), 129.9 (C-2'')<sup>b</sup>, 129.2 (C-3'')<sup>b</sup>, 131.4 (C-4''). *Campsis chinensis* (Bignoniaceae) (128)

## 163. CACHINESIDE IV



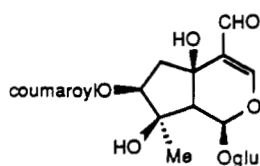
$C_{16}H_{24}O_{11}$  392.36 pentaacetate mp 118–120° [ $\alpha$ ]  $-138^\circ$  ( $CHCl_3$ ) (pentaacetate 200 MHz  $CDCl_3$ ) 5.77 (H-1, d, 1.2), 7.09 (H-3, s), 2.34 (H-6, dd, 16.6, 5.1), 2.46 (H-6, dd, 16.6, 2.7), 4.69 (H-7, dd, 5.1, 2.7), 2.87 (H-9, d, 1.2), 1.16 (H-10, s), 9.28 (H-11, s), 1.94, 2.01, 2.04, 2.12, 2.14 (OAc), 4.86 (H-1', d, 7.8), 4.98 (H-2', dd, 9.3, 7.8), 5.27 (H-3', t, 9.3), 5.10 (H-4', t, 9.3), 3.77 (H-5', ddd, 9.3, 4.4, 2.4), 4.16 (H-6', dd, 12.5, 2.4), 4.32 (H-6', dd, 12.5, 4.4); (pentaacetate  $CDCl_3$ ) 94.3 (C-1), 156.3 (C-3), 126.4 (C-4), 67.6 (C-5), 42.9 (C-6), 79.2 (C-7), 77.8 (C-8), 57.1 (C-9), 21.2 (C-10), 189.4 (C-11), 96.0 (C-1'), 71.0 (C-2'), 72.0 (C-3')<sup>a</sup>, 68.2 (C-4'), 72.4 (C-5')<sup>a</sup>, 61.6 (C-6'). *Campsis chinensis* (Bignoniaceae) (127)

## 164. PONDRANEOSIDE (5-Hydroxycampsiside)



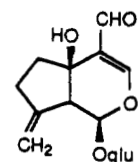
$C_{25}H_{30}O_{12}$  522.50 [ $\alpha$ ]  $-105.2^\circ$  (MeOH) (200 MHz  $CD_3OD$ ) 5.95 (H-1, d, 0.8), 7.39 (H-3, s), 2.48 (H-6 $\alpha$ , dd, 15.5, 4.4), 2.38 (H-6 $\beta$ , dd, 15.5, 2.4), 4.85 (H-7, m), 2.90 (H-9, d, 0.8), 1.17 (H-10, s), 9.28 (H-11, s), 4.65 (H-1', d, 8), 6.61/7.77 (H $\alpha$ , H $\beta$ , d's, 16.1), 7.7–7.4 (H-2''–H-4''); ( $CD_3OD$ ) 95.2 (C-1), 162.2 (C-3), 127.1 (C-4), 68.3 (C-5), 44.6 (C-6), 80.5 (C-7), 78.7 (C-8), 58.3 (C-9), 21.4 (C-10), 192.2 (C-11), 99.9 (C-1'), 74.5 (C-2'), 77.5 (C-3')<sup>a</sup>, 71.6 (C-4'), 78.4 (C-5'), 62.8 (C-6'), 168.0 (C=O), 119.2 (C $\alpha$ ), 146.4 (C $\beta$ ), 135.9 (C-1''), 130.0 (C-2'')<sup>b</sup>, 129.2 (C-3'')<sup>b</sup>, 131.4 (C-4''). *Campsis chinensis* (Bignoniaceae) (128–130)

## 165. CACHINESIDE III



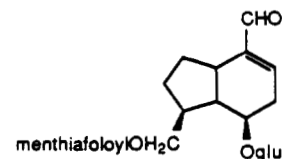
$C_{25}H_{30}O_{13}$  538.50 [ $\alpha$ ]  $-103.2^\circ$  (MeOH) (200 MHz  $CD_3OD$ ) 5.95 (H-1, d, 0.7), 7.38 (H-3, s), 2.46 (H-6, dd, 16, 6), 2.35 (H-6, dd, 16, 2), 4.83 (H-7, dd, 6, 2), 2.89 (H-9, d, 0.7), 1.16 (H-10, s), 9.28 (H-11), 4.66 (H-1', d, 7.7), 6.41/7.70 (H $\alpha$ , H $\beta$ , d's, 16), 6.81 (H-2'', d, 8.6), 7.48 (H-3'', d, 8.6); ( $CDCl_3$ ) 95.2 (C-1), 162.2 (C-3), 127.0 (C-4), 68.2 (C-5), 44.6 (C-6), 80.2 (C-7), 78.6 (C-8), 58.2 (C-9), 21.5 (C-10), 192.2 (C-11), 99.9 (C-1'), 74.4 (C-2'), 77.4 (C-3')<sup>a</sup>, 71.6 (C-4'), 78.3 (C-5')<sup>a</sup>, 62.7 (C-6'), 168.6 (C=O), 115.5 (C $\alpha$ ), 146.7 (C $\beta$ ), 127.3 (C-1''), 131.1 (C-2''), 116.8 (C-3''), 161.1 (C-4''). *Campsis chinensis* (Bignoniaceae) (127)

## 166. UGANDOSIDE



$C_{16}H_{22}O_9$  358.34 uv 240 (H $_2$ O) (250 MHz  $D_2O$ ) 6.00 (H-1, d, 2.0), 7.55 (H-3, s), 2.47 (H-6 $\alpha$ , m), 2.00 (H-6 $\beta$ , m,  $-13.0$ , 11.0), 2.47 (H-7 $\alpha$ , m), 2.19 (H-7 $\beta$ , m,  $-16.5$ , 7.5, 3), 3.07 (H-9, s), 5.19 (H-10, s), 9.23 (H-11, s), 4.82 (H-1', d). *Clerodendrum ugandense* (Verbenaceae) (29)

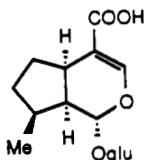
## 167. LAMOUROUXIDE I



$C_{26}H_{38}O_{11}$  526.58 (? MHz  $CDCl_3$ ) 7.25 (H-3, s), 2.9 (H-5), 9.25 (H-11, s), 4.6 (H-1', d, 8), 4.25–3 (H-2'–H-6'), 6.75 (H-3'', dt, 17, 1.3), 5.91 (H-7'', dd, 17, 1.3), 5.20 (H-8''), 1.8 (H-9'', H-10'', s's); (tetraacetate?) 96.4 (C-1), 160.1 (C-3), 124.0 (C-4), 32.2 (C-5), 29.8 (C-6), 27.3 (C-7), 39.2 (C-8), 43.9 (C-9), 67.0 (C-10), 190.1 (C-11), 96.8 (C-1'), 70.9 (C-2'), 72.4 (C-3'), 68.5 (C-4'), 72.4 (C-5'), 61.8 (C-6'), 168.0 (C-1''), 127.9 (C-2''), 142.8 (C-3''), 23.3 (C-4''), 38.4 (C-5''), 82.8 (C-

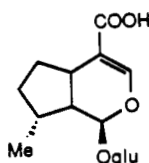
6<sup>n</sup>), 141.5 (C-7<sup>n</sup>), 113.6 (C-8<sup>n</sup>), 12.3 (C-9<sup>n</sup>), 23.8 (C-10<sup>n</sup>). *Lamourouxia multifida* (Scrophulariaceae) (131)

**168.** 1,5,9-*epi*-DEOXYLOGANIC ACID  
(revision of *Nepetolglucosylester*)



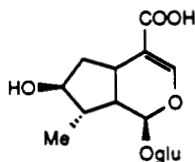
$C_{16}H_{24}O_9$  360.36 mp 106° (dec)  $[\alpha] +85.1^\circ$  (MeOH) uv 235 (EtOH) (100 MHz  $D_2O$ ) 5.45 (H-1, d, 4), 7.60 (H-3, s), 2.90 (H-9, m), 1.04 (H-10, d, 7), 3.35–3.65 (H-2'–H-5'), 3.95 (H-6', m); ( $D_2O$ ) 101.5 (C-1), 153.6 (C-3), 113.4 (C-4), 33.6 (C-5), 32.1 (C-6), 33.4 (C-7), 36.8 (C-8), 43.9 (C-9), 17.1 (C-10), 172.1 (C-11), 103.5 (C-1'), 74.4 (C-2'), 77.0 (C-3'), 70.6 (C-4'), 77.5 (C-5'), 61.9 (C-6'). *Nepeta cataria* (Labiatae) (132, 133)

**169.** 7-DEOXY-8-*epi*-LOGANIC ACID



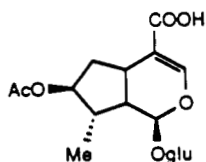
$C_{16}H_{24}O_9$  360.36 mp 210–213°  $[\alpha] -117^\circ$  (MeOH) uv 234 (MeOH) (400 MHz  $CD_3OD$ ) 5.44 (H-1, d, 5.2), 7.41 (H-3, bs), 2.91 (H-5, bq, 8.3), 2.08 (H-6e, dddd, 12.6, 8.3, 8.3, 8.3), 1.58 (H-6a, dddd, 12.6, 9.0, 8.3, 2.5), 1.80 (H-7e, dddd, 12.4, 8.3, 2.5), 1.39 (H-7a, dddd, 12.4, 9.0, 8.3, 8.3), 2.29 (H-8, ddq, 8.3, 8.0, 7.3), 2.23 (H-9, ddd, 8.3, 8.0, 5.2), 1.10 (H-10, d, 7.3), 4.70 (H-1', d, 8.0), 3.19 (H-2', dd, 9.2, 8.0), 3.39 (H-3', t, 9.2), 3.26 (H-4', t, 9.2), 3.31 (H-5', m), 3.91 (H-6', dd, 12.1, 2.2), 3.64 (H-6', dd, 12.1, 6.0); ( $CD_3OD$ ) 95.4 (C-1), 152.0 (C-3), 113.3 (C-4), 32.5 (C-5), 31.5 (C-6)<sup>a</sup>, 33.8 (C-7)<sup>a</sup>, 36.8 (C-8), 43.6 (C-9), 16.0 (C-10), 172.2 (C-11), 99.0 (C-1'), 74.0 (C-2'), 77.6 (C-3')<sup>b</sup>, 71.0 (C-4'), 77.2 (C-5')<sup>b</sup>, 62.2 (C-6'). *Argylia radiata* (Bignoniaceae) (134)

**170.** 8-*epi*-LOGANIC ACID



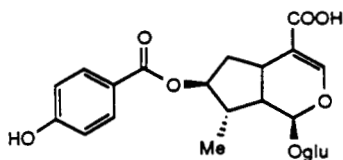
$C_{16}H_{24}O_{10}$  376.31 mp 138–139°  $[\alpha] -57.4^\circ$  (MeOH) uv 233 (MeOH) (360 MHz  $D_2O$ ) 5.51 (H-1, d, 2.5), 7.22 (H-3, s), 2.98 (H-5, m), 1.95, 1.85 (H-6, m's), 3.81 (H-7, m), 2.14 (H-8, m), 2.67 (H-9, dt, 9.2, 2.3), 0.96 (H-10, d, 7.3), 3.45–3.25 (H-2'–H-5'), 3.88 (H-6', dd, 12.6, 1.6), 3.68 (H-6', dd, 12.6, 5.9); (pyridine- $d_5$ ) 95.6 (C-1), 150.6 (C-3), 114.2 (C-4), 30.4 (C-5), 42.2 (C-6), 78.1 (C-7), 41.1 (C-8), 44.5 (C-9), 14.2 (C-10), 169.3 (C-11), 100.0 (C-1') 74.4 (C-2'), 78.3 (C-3'), 71.3 (C-4'), 78.1 (C-5'), 62.5 (C-6'). *Linaria cymbalaria* (Scrophulariaceae) (33, 88, 108)

**171.** 7-O-ACETYL-8-*epi*-LOGANIC ACID (MS-6)



$C_{18}H_{26}O_{11}$  418.40  $[\alpha] -88.3^\circ$  (?) uv 231 (?) (60 MHz ?) 5.51 (H-1, d, 4), 7.35 (H-3, s), 1.00 (H-10, d, 7), 2.00 (OAc), 4.73 (H-1', d, 7); ( $Me_2CO-d_6$ ) 95.2 (C-1), 151.8 (C-3), 113.1 (C-4), 30.6 (C-5), 38.4 (C-6), 81.8 (C-7), 42.3 (C-8), 42.3 (C-9), 14.2 (C-10), 171.5 (C-11), 169.1 (O=CMe), 21.2 (O=CMe), 99.2 (C-1'), 74.2 (C-2'), 77.3 (C-3'), 71.1 (C-4'), 77.6 (C-5'), 62.6 (C-6'). *Monochasma savatieri* (Scrophulariaceae) (135, 136)

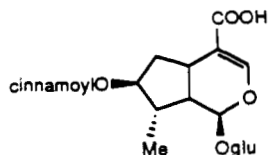
**172.** 7-O-*p*-HYDROXYBENZOYL-8-*epi*-LOGANIC ACID



$C_{23}H_{28}O_{12}$  496.47 no data available. *Veronica anagallis-aquatica* var. *anagaloides* (Scrophulariaceae) (137)

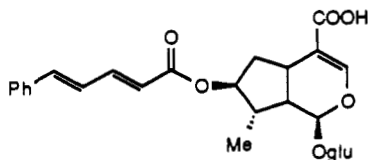


173. 7-O-CINNAMOYL-8-*epi*-LOGANIC ACID (isolated as the sodium salt)



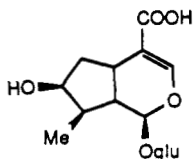
$C_{25}H_{30}O_{11}$  506.51  $[\alpha] -71.9^\circ (H_2O)$  uv 278, 236, 222, 217, 205 (MeOH) (250 MHz  $D_2O$ ) 5.52 (H-1, d, 2.3), 7.02 (H-3, d, <1.5), 3.08 (H-5, dddd, 9, 9, 5.3, <1.5), 2.24 (H-6 $\alpha$ , ddd, 15, 9, <3), 1.93 (H-6 $\beta$ , ddd, 15, 5.3, 5), 4.91 (H-7, m), 2.47 (H-8, m, 9, 7.5, 3.8), 2.76 (H-9, ddd, 9, 9, 2.3), 1.00 (H-10, d, 7.5), 4.72 (H-1', d, 8), 3.25 (H-2', dd, 9, 8), 3.46 (H-3', t, 9, 9), 3.36 (H-4', t, 9, 9), 3.44 (H-5', ddd, 9, 5.3, 1.5), 3.69 (H-6', dd, 13, 5.3), 3.90 (H-6'', dd, 13, 1.5), 6.54/7.71 (H $\alpha$ , H $\beta$ , d's, 16), 7.58 (H-2'', m), 7.43 (H-3'', H-4'', m); (DMSO- $d_6$ ) 93.3 (C-1), — (C-3, C-4), 31.3 (C-5), 38.0 (C-6), 81.1 (C-7), 41.3 (C-8)<sup>a</sup>, 40.9 (C-9)<sup>a</sup>, 13.8 (C-10), — (C-11), 98.1 (C-1'), 73.2 (C-2'), 76.8 (C-3'), 70.2 (C-4'), 77.1 (C-5'), 61.3 (C-6'), 165.9 (C=O), 118.3 (C $\alpha$ ), 144.2 (C $\beta$ ), 133.9 (C-1''), 128.8 (C-2''), 128.2 (C-3''), 130.3 (C-4''). *Avicennia officinalis* (Verbenaceae) (42)

174. 7-O-(5-PHENYL-2,4-PENTADIENOYL)-8-*epi*-LOGANIC ACID



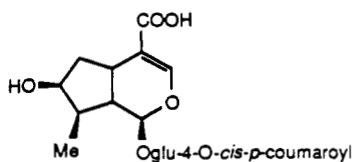
$C_{27}H_{32}O_{11}$  532.54 methyl ester uv 308, 232, 219, 205 (MeOH) (methyl ester 250 MHz  $CDCl_3$ /pyridine- $d_5$ ) 5.4 (H-1, d, 4), 7.3–6.9 (H-3, m), 3.09 (H-5, ddd, 9, 9, 7), 2.3 (H-6 $\alpha$ , ddd, 15, 9, 3), 1.96 (H-6 $\beta$ , ddd, 15, 7, 6), 4.99 (H-7, ddd, 6, 4, 3), 2.4 (H-8, m), 2.65 (H-9, ddd, 9, 7, 4), 1.05 (H-10, d, 7), 4.8 (H-1', d, 8), 3.8–3.4 (H-2'–H-5'), 4.05 (H-6', dd, 12, 4), 3.95 (H-6'', dd, 12, 5), 5.99 (H $\alpha$ , d, 15), 7.3–6.9 (H $\beta$ , H $\gamma$ , H $\delta$ , m), 7.3–6.9 (H-2''–H-4'', m), 3.8 (OMe); (methyl ester  $CDCl_3/CD_3OD$ ) 95.2 (C-1), 151.1 (C-3), 112.7 (C-4), 30.5 (C-5), 38.0 (C-6), 81.0 (C-7), 42.0 (C-8)<sup>a</sup>, 42.1 (C-9)<sup>a</sup>, 13.7 (C-10), 167.8 (C-11), 98.7 (C-1'), 73.4 (C-2'), 76.5 (C-3'), 70.3 (C-4'), 77.6 (C-5'), 62.0 (C-6'), 121.1 (C $\alpha$ ), 145.2 (C $\beta$ ), 126.2 (C $\gamma$ ), 141.0 (C $\delta$ ), 136.1 (C-1''), 128.9 (C-2''), 127.4 (C-3''), 129.2 (C-4''). *Avicennia marina* (Verbenaceae) (138)

175. LOGANIC ACID



$C_{16}H_{24}O_{10}$  376.36 (300 MHz  $CD_3OD$ ) 5.31 (H-1, d, 4.5), 7.42 (H-3, d, 1.5), 3.14 (H-5, m), 2.97 (H-6, ddd, 14, 8, 1.5), 1.69 (H-6, ddd, 14, 7.5, 5), 4.07 (H-7, m), 1.92 (H-8, m), 2.06 (H-9, m), 1.13 (H-10, d, 7.5), 4.69 (H-1', d, 8), 3.30 (H-4', m), 3.90 (H-6', dd, 12, 1.5), 3.65 (H-6'', dd, 12, 5); ( $CD_3OD$ ) 97.6 (C-1), 152.0 (C-3), 114.2 (C-4), 32.7 (C-5), 42.6 (C-6), 75.0 (C-7), 42.0 (C-8), 46.4 (C-9), 13.4 (C-10), 171.4 (C-11), 99.9 (C-1'), 74.6 (C-2'), 77.8 (C-3'), 71.4 (C-4'), 78.1 (C-5'), 62.7 (C-6'). (139–141)

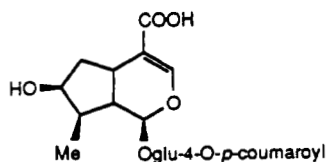
176. 4'-O-*cis-p*-COUMAROYL-LOGANIC ACID



$C_{25}H_{30}O_{12}$  522.50 uv 310, 295, 230 (MeOH) (300 MHz  $CD_3OD$ ) 5.27 (H-1, d, 4.5), 7.37 (H-3, d, 1.5), 3.12 (H-5, m), 2.24, 1.66 (H-6, m's), 4.04 (H-7, m), 1.88 (H-8, m), 2.04 (H-9, m), 1.09 (H-10, d, 7), 4.69 (H-1', d, 8), 4.80 (H-4', m), 3.65–3.48 (H-6', m), 5.80/6.93 (H $\alpha$ , H $\beta$ , d's, 13), 7.70 (H-2'', d, 8.5), 6.76 (H-3'', d, 8.5); ( $CD_3OD$ ) 97.7 (C-1), 151.8 (C-3), 114.6 (C-4), 32.2 (C-5), 42.7 (C-6), 75.1 (C-7), 42.1 (C-8), 46.6 (C-9), 13.4 (C-10), 171.1 (C-11), 100.1 (C-1'), 74.9 (C-2'), 75.8 (C-3'), 72.1 (C-4'), 76.4 (C-5'), 62.5 (C-6'), 167.4 (C=O), 116.1 (C $\alpha$ ), 146.1 (C $\beta$ ),

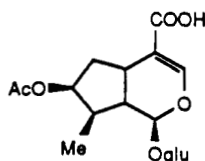
127.6 (C-1<sup>n</sup>), 133.9 (C-2<sup>n</sup>), 115.9 (C-3<sup>n</sup>), 160.2 (C-4<sup>n</sup>).  
*Gentiana pedicellata* (Gentianaceae) (140)

**177. 4'-O-trans-p-COUMAROYL-LOGANIC ACID**



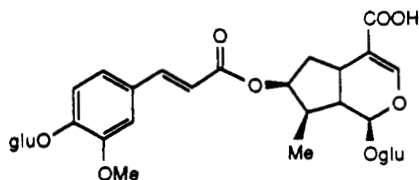
C<sub>25</sub>H<sub>30</sub>O<sub>12</sub> 522.50 uv 310, 295, 230 (MeOH) (300 MHz CD<sub>3</sub>OD) 5.28 (H-1, d, 4.5), 7.38 (H-3, d, 1.5), 3.12 (H-5, m), 2.24, 1.66 (H-6, m's), 4.04 (H-7, m), 1.88 (H-8, m), 2.04 (H-9, m), 1.10 (H-10, d, 7), 4.72 (H-1', d, 8), 4.80 (H-4', m), 3.65-3.48 (H-6', m), 6.36/7.68 (H $\alpha$ , H $\beta$ , d's, 16), 7.48 (H-2'', d, 8.5), 6.82 (H-3'', d, 8.5); (CD<sub>3</sub>OD) 97.7 (C-1), 151.8 (C-3), 114.6 (C-4), 32.2 (C-5), 42.7 (C-6), 75.1 (C-7), 42.1 (C-8), 46.6 (C-9), 13.4 (C-10), 171.1 (C-11), 100.1 (C-1'), 74.9 (C-2'), 75.8 (C-3'), 72.5 (C-4'), 76.5 (C-5'), 62.5 (C-6'), 168.6 (C=O), 114.8 (C $\alpha$ ), 147.3 (C $\beta$ ), 127.2 (C-1<sup>n</sup>), 131.3 (C-2<sup>n</sup>), 116.9 (C-3<sup>n</sup>), 161.4 (C-4<sup>n</sup>).  
*Gentiana pedicellata* (Gentianaceae) (140)

**178. 7-O-ACETYLOGANIC ACID**



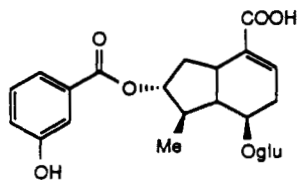
C<sub>18</sub>H<sub>26</sub>O<sub>11</sub> 418.40 [ $\alpha$ ] -60.2° (MeOH) uv 231 (EtOH) (100 MHz CD<sub>3</sub>OD) 5.26 (H-1, d, 4), 7.42 (H-3, d, 1), 1.06 (H-10, d, 5), 2.08 (OAc), 4.68 (H-1', d, 7); (CD<sub>3</sub>OD) 97.6 (C-1), 152.6 (C-3), 113.1 (C-4), 32.6 (C-5), 40.3 (C-6), 78.6 (C-7), 40.8 (C-8), 46.9 (C-9), 13.7 (C-10), 170.7 (C-11), 100.1 (C-1'), 74.6 (C-2'), 77.9 (C-3'), 71.5 (C-4'), 78.2 (C-5'), 62.7 (C-6'), 172.6 (O=CMe), 21.0 (O=CMe). *Alangium platani-folium* var. *trilobum* (Alangaceae) (135)

**179. PERICLYMENOSIDIC ACID**



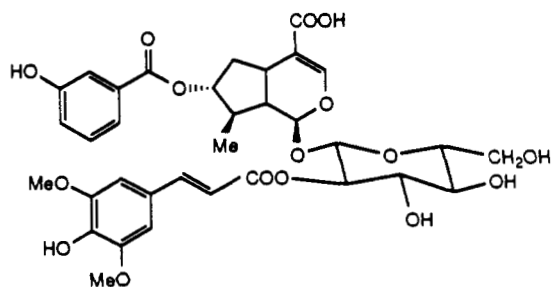
C<sub>32</sub>H<sub>42</sub>O<sub>18</sub> 714.67 [ $\alpha$ ] -54.7° (MeOH) uv 317, 293, 230, 217 (MeOH) (300 MHz CD<sub>3</sub>OD) 5.31-5.27 (H-1, m), 7.43 (H-3, s), 3.16 (H-5, m), 1.82 (H-6 $\alpha$ , m), 2.14 (H-6 $\beta$ , m), 5.31-5.27 (H-7, m), 2.17 (H-8, m), 2.36 (H-9, dd, 14.5, 7.8), 1.11 (H-10, d, 6.7), 4.69 (H-1', d, 7.8), 4.97 (H-1'', d, 7.2), 3.55-3.20 (H-2'-H-5', H-2'''-H-5'''), 3.93-3.87, 3.76-3.67 (H-6', H-6''', m), 6.45/7.63 (H $\alpha$ , H $\beta$ , d's, 15.9), 7.27 (H-2'', bs), 7.17 (H-5'', H-6'', bs), 3.90 (ArOMe); (CD<sub>3</sub>OD) 97.7 (C-1), 152.2 (C-3), 113.6 (C-4), 33.0 (C-5), 40.6 (C-6), 78.7 (C-7), 41.2 (C-8), 47.2 (C-9), 14.0 (C-10), 171.1 (C-11), 100.3 (C-1'), 74.8 (C-2'), 78.1 (C-3'), 71.7 (C-4'), 78.4 (C-5'), 62.9 (C-6'), 168.6 (O=C), 117.6 (C $\alpha$ ), 146.1 (C $\beta$ ), 130.6 (C-1<sup>n</sup>), 112.5 (C-2<sup>n</sup>), 151.0 (C-3<sup>n</sup>), 117.4 (C-5<sup>n</sup>), 123.7 (C-6<sup>n</sup>), 56.9 (ArOMe), 102.2 (C-1<sup>m</sup>), 74.8 (C-2<sup>m</sup>), 77.9 (C-3<sup>m</sup>), 71.3 (C-4<sup>m</sup>), 78.3 (C-5<sup>m</sup>), 62.5 (C-6<sup>m</sup>). *Lonicera coerulea* (Caprifoliaceae) (142)

**180. SWERTIASIDE [7-*epi*-(*m*-Hydroxybenzoyl)loganic acid]**

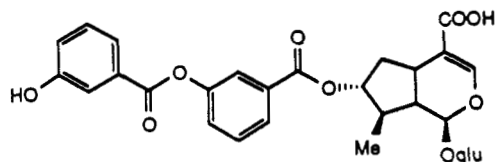


C<sub>23</sub>H<sub>28</sub>O<sub>12</sub> 496.47 [ $\alpha$ ] -109.1° (MeOH) uv 297, 235, 210 (MeOH) (200 MHz CD<sub>3</sub>OD) 5.46 (H-1, d, 4), 7.36 (H-3, bs), 3.04 (H-5, m), 1.98 (H-6, m), 3.9-3.1 (H-7), 2.10 (H-8, m), 2.60 (H-9, m), 1.22 (H-10, d, 7), 4.68 (H-1', d, 8), 7.36 (H-2'', bs), 6.98 (H-4'', dd, 8, 1), 7.24 (H-5'', t, 8), 7.42 (H-6'', d, 8); (CD<sub>3</sub>OD) 96.4 (C-1), 150.6 (C-3), 115.0 (C-4), 32.8 (C-5), 38.5 (C-6), 83.3 (C-7), 42.8 (C-8), 47.4 (C-9), 18.1 (C-10), 170.7 (C-11), 100.3 (C-1'), 74.7 (C-2'), 78.2 (C-3')<sup>a</sup>, 71.5 (C-4'), 77.9 (C-5')<sup>a</sup>, 62.7 (C-6'), 168.0 (C=O), 132.8 (C-1<sup>n</sup>), 117.0 (C-2<sup>n</sup>), 158.7 (C-3<sup>n</sup>), 121.3 (C-4<sup>n</sup>), 130.6 (C-5<sup>n</sup>), 121.7 (C-6<sup>n</sup>). *Swertia japonica* (Gentianaceae) (143)

## 181. SENBURISIDE I

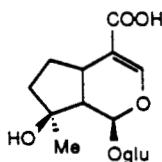


$C_{34}H_{38}O_{16}$  702.67  $[\alpha] -93.9^\circ$  (MeOH) uv 325, 235, 208 (MeOH) (200 MHz  $CD_3OD$ ) 5.45 (H-1, d, 4), 7.28 (H-3, bs), 2.88 (H-5, m), 3.96–3.18 (H-7), 1.98 (H-6, H-8, m), 2.46 (H-9, m), 1.20 (H-10, d, 7), 6.28/7.56 (H $\alpha$ , H $\beta$ , d's, 16), 6.86 (H-2'', s), 3.86 (ArOMe), 7.28 (H-2''', bs), 6.93 (H-4''', dd, 8, 2), 7.18 (H-5''', t, 8), 7.36 (H-6''', d, 8); ( $CD_3OD$ ) 95.9 (C-1), 151.0 (C-3), 113.7 (C-4), 32.3 (C-5), 37.8 (C-6), 83.4 (C-7), 42.6 (C-8), — (C-9), 17.9 (C-10), 170.4 (C-11), 98.3 (C-1'), 74.8 (C-2'), 76.0 (C-3'), 71.7 (C-4'), 78.5 (C-5'), 62.7 (C-6'), 167.9 (O=C), 115.9 (C $\alpha$ ), 147.2 (C $\beta$ ), 127.0 (C-1''), 107.2 (C-2''), 149.4 (C-3''), 139.6 (C-4''), 56.9 (ArOMe), 168.1 (O=C), 132.8 (C-1'''), 117.0 (C-2'''), 158.7 (C-3'''), 121.2 (C-4'''), 130.5 (C-5'''), 121.7 (C-6'''). *Swertia japonica* (Gentianaceae) (144)

182. SENBURISIDE II [7-*epi*-(Di-*m*-hydroxybenzoyl)loganic acid]

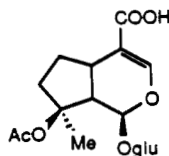
$C_{30}H_{32}O_{14}$  616.57  $[\alpha] -88.6^\circ$  (MeOH) uv 290, 230, 212 (MeOH) (200 MHz  $CD_3OD$ ) 5.44 (H-1, d, 4), 7.46 (H-3, bs), 3.06 (H-5, m), 2.14 (H-6, m), 1.96 (H-6, H-8, m), 2.60 (H-9, m), 1.22 (H-10, d, 7), 4.62 (H-1', d, 8), 3.90–3.12 (H-2'–H-6'), 7.78 (H-2'', bs), 7.32 (H-4'', dd, 8, 2)<sup>a</sup>, 7.52 (H-5'', t, 8), 7.90 (H-6'', d, 8), 7.56 (H-2''', bs), 7.08 (H-4''', dd, 8, 2)<sup>a</sup>, 7.34 (H-5''', t, 8), 7.64 (H-6''', d, 8); ( $CD_3OD$ ) 96.3 (C-1), 150.4 (C-3), 115.3 (C-4), 32.8 (C-5), 38.4 (C-6), 83.8 (C-7), 42.8 (C-8), 47.3 (C-9, in pyridine- $d_5$ ), 18.1 (C-10), 170.3 (C-11), 100.3 (C-1'), 74.8 (C-2'), 78.3 (C-3')<sup>b</sup>, 71.6 (C-4'), 78.0 (C-5')<sup>b</sup>, 62.7 (C-6'), 167.0 (O=C), 131.7 (C-1''), 123.8 (C-2''), 152.5 (C-3''), 127.7 (C-4''), 130.8 (C-5''), 128.1 (C-6''), 166.5 (O=C), 133.3 (C-1'''), 117.6 (C-2'''), 159.0 (C-3'''), 122.2 (C-4'''), 130.9 (C-5'''), 122.3 (C-6'''). *Swertia japonica* (Gentianaceae) (145)

## 183. MUSSAENOSIDIC ACID



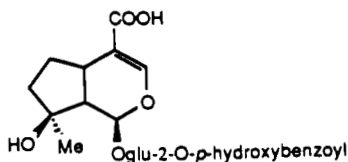
$C_{16}H_{24}O_{10}$  376.36  $[\alpha] -118^\circ$  (MeOH) (90 MHz  $D_2O$ ) 5.55 (H-1, d, 3), 7.44 (H-3, s), 2.32 (H-9, dd, 10, 3), 1.32 (H-10, s); ( $D_2O$ ) 95.2 (C-1), 152.2 (C-3), 113.0 (C-4), 30.4 (C-5), 29.6 (C-6), 40.3 (C-7), 80.4 (C-8), 51.4 (C-9), 23.8 (C-10), 171.6 (C-11), 99.1 (C-1'), 73.4 (C-2'), 76.4 (C-3'), 70.4 (C-4'), 77.0 (C-5'), 61.5 (C-6'). *Melampyrum cristatum* (Scrophulariaceae) (146)

## 184. 8-O-ACETYLMUSSAENOSIDIC ACID (MS-5)



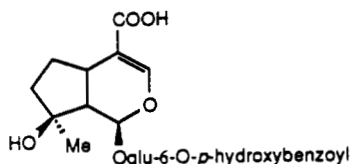
$C_{18}H_{26}O_{11}$  418.40  $[\alpha] -74.2^\circ$  (MeOH) uv 229 (MeOH) (60 MHz  $Me_2CO-d_6$ ) 5.72 (H-1, d, 3), 7.44 (H-3, s), 2.67 (H-9, dd, 9, 3), 1.53 (H-10, s), 1.97 (OAc), 4.71 (H-1' d, 7); ( $Me_2CO-d_6$ ) 95.1 (C-1), 152.6 (C-3), 111.5 (C-4), 32.5 (C-5), 29.1 (C-6), 39.3 (C-7), 90.1 (C-8), 50.6 (C-9), 22.3 (C-10), 171.9 (C-11), 169.0 (O=CMe), 21.3 (O=CMe), 100.0 (C-1'), 74.3 (C-2'), 77.6 (C-3'), 71.4 (C-4'), 77.6 (C-5'), 62.9 (C-6'). *Monochasma savatieri* (Scrophulariaceae) (136)

## 185. NEGUNDOSIDE (2'-O-p-Hydroxybenzoylmussaenosidic acid)



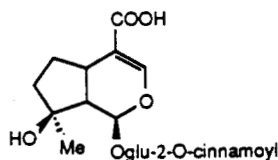
$C_{23}H_{28}O_{12}$  496.47 mp 160–162°  $[\alpha] -117.6^\circ$  (MeOH) uv 258 (MeOH) (? MHz  $DMSO-d_6$ ) 5.40 (H-1, d, 3, 3), 7.07 (H-3, d, 1), 2.20 (H-9, dd, 10, 3, 3), 1.20 (H-10, s), 7.76 (H-2", d, 8, 5), 6.87 (H-3", d, 8, 5); (?) 93.5 (C-1), 148.6 (C-3), 112.2 (C-4), 29.7 (C-5), 28.9 (C-6), 41.2 (C-7), 77.7 (C-8), 50.5 (C-9), 24.1 (C-10), 167.1 (C-11)<sup>a</sup>, 95.9 (C-1'), 77.3 (C-2'), 74.1 (C-3')<sup>b</sup>, 70.1 (C-4'), 73.1 (C-5')<sup>b</sup>, 60.8 (C-6'), 164.6 (C=O)<sup>a</sup>, 120.5 (C-1"), 131.2 (C-2"), 114.9 (C-3"), 161.5 (C-4"). *Vitex negundo* (Verbenaceae) (147)

## 186. 6'-O-p-HYDROXYBENZOYL-MUSSAENOSIDIC ACID

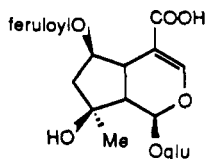


$C_{23}H_{28}O_{12}$  496.47  $[\alpha] -120^\circ$  (MeOH) uv 258 (MeOH) (90 MHz  $DMSO-d_6$ ) 5.16 (H-1, d, 3, 3), 7.40 (H-3, d, 1, 0), 2.13 (H-9, dd, 10, 3, 3), 1.20 (H-10, s), 7.90 (H-2", d, 8, 5), 6.93 (H-3", d, 8, 5); ( $DMSO-d_6$ ) 94.4 (C-1), 150.4 (C-3), 112.0 (C-4), 31.2 (C-5), 29.6 (C-6), 41.4 (C-7), 78.4 (C-8), 50.4 (C-9), 24.0 (C-10), 168.0 (C-11)<sup>a</sup>, 98.4 (C-1'), 74.0 (C-2'), 76.8 (C-3'), 70.4 (C-4'), 73.2 (C-5'), 63.2 (C-6'), 165.6 (C=O)<sup>a</sup>, 120.8 (C-1"), 131.2 (C-2"), 115.2 (C-3"), 162.4 (C-4"). *Vitex negundo* (Verbenaceae) (148)

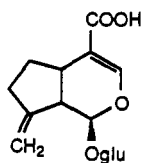
## 187. 2'-O-CINNAMOYLMUSSAENOSIDIC ACID



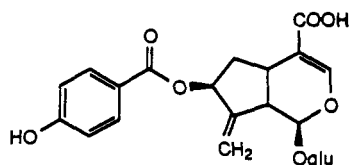
$C_{25}H_{30}O_{11}$  506.51 uv 282, 223, 218, 204 ( $H_2O$ ) (methyl ester 250 MHz pyridine- $d_5$ ) 6.01 (H-1, d, 3), 6.3 (H-3, s), 3.47 (H-5, ddd, 10, 9, 4), 2.4 (H-6 $\alpha$ , m), 1.8–1.5 (H-6 $\beta$ , m), 1.9 (H-7 $\alpha$ , ddd, 12, 8, 7), 1.8–1.5 (H-7 $\beta$ , m), 2.84 (H-9, dd, 10, 3), 1.55 (H-10, s), 3.24 (OMe), 5.52 (H-1', d, 8), 5.76 (H-2', t, 8), 4.56–4.00 (H-3'–H-6', m), 6.71/7.91 (H $\alpha$ , H $\beta$ , d's, 15), 7.45 (H-2" in  $CDCl_3/D_2O$ ), 7.3 (H-3" in  $CDCl_3/D_2O$ ); (methyl ester  $CD_3OD$ ) 94.8 (C-1), 151.2 (C-3), 114.2 (C-4), 31.0 (C-5), 30.1 (C-6), 41.7 (C-7), 79.5 (C-8), 51.3 (C-9), 24.2 (C-10), 168.7 (C-11), 52.6 (OMe), 97.5 (C-1'), 75.9 (C-2'), 74.9 (C-3'), 71.8 (C-4'), 78.6 (C-5'), 62.8 (C-6'), 118.7 (C $\alpha$ ), 146.3 (C $\beta$ ), 135.9 (C-1"), 130.0 (C-2"), 129.4 (C-3"), 131.5 (C-4"). *Avicennia marina* (Verbenaceae) (138)

**188. TARENININE (6-O-Feruloylshanzhi-side)**

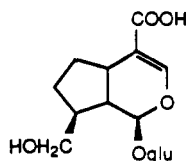
$C_{26}H_{32}O_{14}$  568.53 mp 158–160° [ $\alpha$ ]  $-117^\circ$  (MeOH) uv 323, 298, 233 (EtOH) (60 MHz  $CD_3OD$ ) 5.60 (H-1, d, 4), 7.53 (H-3, bs), 5.36 (H-6, m), 2.1–1.9 (H-7, m), 2.60 (H-9, dd, 10, 4), 1.38 (H-10, s), 3.92 (OMe), 7.20 (H-2, d, 2), 6.83 (H-5", d, 8), 7.00 (H-6", dd, 8, 2), 6.44/7.68 (H $\alpha$ , H $\beta$ , d's, 16); ( $CD_3OD$ ) 95.3 (C-1), 153.9 (C-3), 110.3 (C-4), 39.5 (C-5), 79.9 (C-6), 48.3 (C-7), 79.6 (C-8), 52.0 (C-9), 26.2 (C-10), 170.4 (C-11)<sup>a</sup>, 100.2 (C-1'), 75.2 (C-2')<sup>b</sup>, 78.4 (C-3'), 72.1 (C-4'), 75.1 (C-5')<sup>b</sup>, 63.4 (C-6'), 57.0 (OMe), 169.2 (O=C)<sup>a</sup>, 116.9 (C $\alpha$ )<sup>c</sup>, 147.0 (C $\beta$ ), 128.2 (C-1''), 112.1 (C-2''), 150.7 (C-3''), 149.6 (C-4''), 116.4 (C-5'')<sup>c</sup>, 124.4 (C-6''). *Tarenna graveolens* (Rubiaceae) (149)

**189. 7-DEOXYGARDOSIDE**

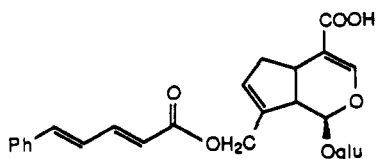
$C_{16}H_{22}O_9$  358.34 [ $\alpha$ ]  $-54.4$  (MeOH) uv 234 (MeOH) (400 MHz  $D_2O$ ) 5.44 (H-1, d, 4, 5), 7.36 (H-3, bs), 2.87 (H-5, m, 10.0), 1.96–2.25 (H-6, H-7, m), 2.94 (H-9, dd, 10.0, 4.5), 5.12 (H-10, bd, 4.0), 4.75 (H-1', d, 8.0), 3.23 (H-2', dd, 9.2, 8.0), 3.42 (H-3', t, 9.2, 9.2), 3.31 (H-4', t, 9.2, 9.2), 3.30 (H-5', m, 9.2, 4.2, 2.2), 3.84 (H-6', dd, 12.1, 2.2), 3.65 (H-6', dd, 12.1, 4.2); ( $D_2O$ ) 97.0 (C-1), 152.9 (C-3), 113.4 (C-4), 31.2 (C-5), 30.7 (C-6), 36.7 (C-7), 151.0 (C-8), 46.0 (C-9), 109.7 (C-10), 173.3 (C-11), 99.4 (C-1'), 73.6 (C-2'), 76.6 (C-3')<sup>a</sup>, 70.5 (C-4'), 77.3 (C-5')<sup>a</sup>, 61.5 (C-6'). *Argylia radiata* (Bignoniaceae) (150)

**190. 7-O-p-HYDROXYBENZOYL-GARDOSIDE**

$C_{23}H_{26}O_{12}$  494.45 no data available. *Veronica anagallis-aquatica* var. *anagalloides* (Scrophulariaceae) (137)

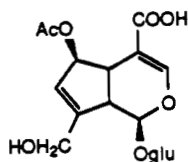
**191. ADOXOSIDIC ACID**

$C_{16}H_{24}O_{10}$  376.36 (360 MHz  $D_2O$ ) 5.24 (H-1, d, 5.0), 7.15 (H-3, d, 1.2), 2.85 (H-5, bq), 1.96, 1.44 (H-6, m's), 1.77, 1.32 (H-7, m's), 2.07 (H-8, m), 1.96 (H-9, m), 3.51 (H-10, dd, 10.0, 7.2), 3.57 (H-10, dd, 10.0, 6.5), 4.75 (H-1', d, 8.0), 3.26 (H-2', dd, 9.1, 8.0), 3.45–3.30 (H-3'–H-5'), 3.69 (H-6', dd, 12.4, 5.6), 3.87 (H-6', dd, 12.4, 2.1). *Castilleja integra* (Scrophulariaceae) (88)

**192. 10-O-(5-PHENYL-2,4-PENTADIENOYL)GENIPOSIDIC ACID**

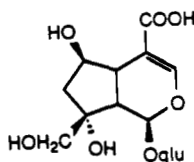
$C_{27}H_{30}O_{11}$  530.53 methyl ester uv 308, 232, 219, 203 (MeOH) (methyl ester 250 MHz  $CDCl_3$ ) 4.88 (H-1, d, 8), 7.55–6.8 (H-3, H $\beta$ , H $\gamma$ , H $\delta$ , m), 3.22 (H-5, ddd, 7, 7, 7), 2.87 (H-6, dd, 17, 7), 2.05 (H-6, dd, 17, 7), 5.73 (H-7, bs), 2.65 (H-9, t), 5.23, 4.64 (H-10, d's, 15), 4.71 (H-1', d, 7), 3.3–3.9 (H-2'–H-6'), 6.00 (H $\alpha$ , d, 15), 7.55–6.8 (H-2''–H-4''), 3.66 (OMe). *Avicennia marina* (Verbenaceae) (138)

## 193. 6-O-ACETYLSCANDOSIDE



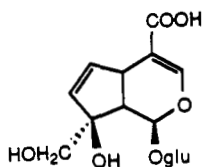
$C_{18}H_{24}O_{12}$  432.38 (methyl ester ? MHz) 5.27 (H-1, d, 4), 7.52 (H-3, bs), 5.69 (H-6, bdd), 5.82 (H-7, bs), 4.82 (H-10, bdd), 3.72 (OMe), 2.12 (OAc). *Galium verum* (Rubiaceae) (151)

## 194. UNEDIDE



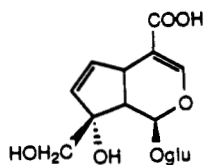
$C_{16}H_{24}O_{12}$  408.40  $[\alpha] -83^\circ$  (MeOH) uv 232 (?) (90 MHz  $D_2O$ ) 5.63 (H-1, d, 2.3), 7.54 (H-3, bs, 1.0), 2.90 (H-5, bdd, 9.7, 3.3), 4.37 (H-6, m), 1.93 (H-7, 13.3), 2.66 (H-9, dd, 9.7, 2.3), 3.63 (H-10, s); ( $D_2O$ ) 95.2 (C-1), 153.9 (C-3), 109.8 (C-4), 40.5 (C-5), 76.3 (C-6), 44.0 (C-7), 81.7 (C-8), 44.6 (C-9), 69.0 (C-10), 171.6 (C-11), 99.2 (C-1'), 73.4 (C-2'), 76.3 (C-3'), 70.3 (C-4'), 77.1 (C-5'), 61.4 (C-6'). *Arbutus unedo* (Ericaceae) (152)

## 195. GARDENOSIDIC ACID



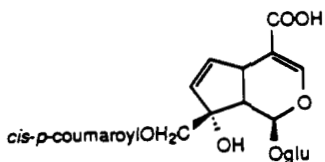
$C_{16}H_{22}O_{11}$  390.34 methyl ester hexaacetate mp 66–68°  $[\alpha] -70.7^\circ$  (MeOH) (methyl ester hexaacetate 200 MHz  $CDCl_3$ ) 6.13 (H-1, d, 2), 6.33 (H-6, dd, 6, 2.5), 5.90 (H-7, dd, 6, 1.5), 2.98 (H-9, dd, 9, 2), 3.73 (COOMe), 1.91–2.12 (OAc). *Galium mollugo* (Rubiaceae) (153, 154)

## 196. MONOTROPEIN



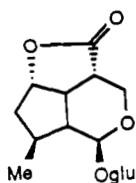
$C_{16}H_{22}O_{11}$  390.34 mp 161–163°  $[\alpha] -130.7^\circ$  ( $H_2O$ ) uv 235 (EtOH) (100 MHz  $D_2O$ ) 5.60 (H-1, d, 2.0), 7.40 (H-3, bs, 1.0), 3.6–3.3 (H-5, m), 6.21 (H-6, dd, 5.7, 2.8), 5.86 (H-7, dd, 5.7, 1.7), 2.66 (H-9, dd, 8.0, 2.0), 3.63 (H-10, bs); ( $D_2O$ ) 95.2 (C-1), 152.4 (C-3), 111.0 (C-4), 37.9 (C-5), 138.0 (C-6), 132.8 (C-7), 85.6 (C-8), 44.8 (C-9), 67.4 (C-10), 171.3 (C-11), 99.1 (C-1'), 73.5 (C-2'), 76.5 (C-3'), 70.4 (C-4'), 77.1 (C-5'), 61.5 (C-6'). *Arbutus unedo* (Ericaceae) (152, 155)

## 197. ANDROMEDOSIDE



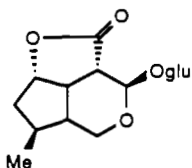
$C_{25}H_{28}O_{13}$  536.49 mp 126–128°  $[\alpha] -26.5^\circ$  (EtOH) uv 312, 300, 232, 210 (MeOH) (pentaacetate 90 MHz  $CDCl_3$ ) 6.21 (H-6, dd, 5.7, 2.4), 2.69 (H-9, dd, 8.7, 3.2), 5.95 (H $\alpha$ , d, 12.7), 7.61–7.05 (H-3, H-7, H-2'', H-3''), other signals 5.58–5.50 (2H, m), 5.17–4.88 (4H, m), 4.10 (4H, bs), 3.78–3.42 (2H, m), 2.28, 2.05, 2.03, 2.00, 1.96 (OAc); (pentaacetate  $CDCl_3$ ) 94.4 (C-1), 151.3 (C-3), 110.1 (C-4), 37.6 (C-5), 131.8 (C-6), 137.5 (C-7), 83.5 (C-8), 45.0 (C-9), 69.3 (C-10), 171.4–169.2 (C-11, O=CMe), 96.6 (C-1'), 70.8 (C-2'), 72.4 (C-3'), 68.3 (C-4'), 72.5 (C-5'), 61.9 (C-6'), 165.7 (C=O), 118.9 (C $\alpha$ ), 143.7 (C $\beta$ ), 132.4 (C-1''), 131.3 (C-2''), 121.3 (C-3''), 152.0 (C-4''), 21.1–20.6 (O=CMe). *Andromeda polifolia* (Ericaceae) (156)

## 198. DIHYDROBRASOSIDE



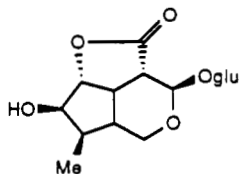
$C_{16}H_{24}O_9$  360.36 (500 MHz  $D_2O$ ) 5.25 (H-1, bs), 3.86 (H-3 $\alpha$ , bd, 12.5), 4.16 (H-3 $\beta$ , dd, 12.5, 4.4), 2.87 (H-4, dd, 10.4, 4.2), 3.26 (H-5, dt, 10.2, 6.0), 5.11 (H-6, dd, 6, 3.5), 2.14 (H-7 $\alpha$ , dd, 14.2, 5.2), 1.40 (H-7 $\beta$ , ddd, 14.2, 12.5, 4.0), 1.73 (H-8, nonet, 6.0), 1.54 (H-9, dd, 12, 10), 1.00 (H-10, d, 6.2), 4.64 (H-1', d, 8.0); ( $D_2O$ ) 94.6 (C-1), 55.2 (C-3), 37.5 (C-4), 35.9 (C-5), 86.7 (C-6), 40.9 (C-7), 34.5 (C-8), 45.6 (C-9), 16.8 (C-10), 182.3 (C-11), 98.0 (C-1'), 73.8 (C-2'), 76.6 (C-3'), 70.5 (C-4'), 77.1 (C-5'), 61.5 (C-6'). Catalytic hydrogenation of brasoside (157)

## 199. SEMPEROSIDE



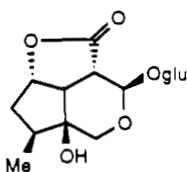
$C_{16}H_{24}O_9$  360.36 mp 179–181° [ $\alpha$ ] +52° (MeOH) (400 MHz  $D_2O$ ) 3.59 (H-1 $\alpha$ , bd, 12.7), 4.20 (H-1 $\beta$ , dd, 12.7, 4.1), 5.35 (H-3, s), 3.08 (H-4, d, 10.5), 3.23 (H-5, m), 5.08 (H-6, dd, 5.5, 4.5), 2.10 (H-7 $\alpha$ , dd, 14.2, 5.3), 1.36 (H-7 $\beta$ , ddd, 14.0, 13.0, 4.3), 1.74 (H-8, m), 1.44 (H-9, ddd, 12, 10, 4), 0.94 (H-10, d, 6.4), 4.61 (H-1', d, 8); ( $D_2O$ ) 57.8 (C-1), 98.1 (C-3), 42.3 (C-4), 36.2 (C-5), 87.2 (C-6), 41.4 (C-7), 33.4 (C-8), 41.4 (C-9), 16.5 (C-10), 179.5 (C-11), 103.1 (C-1'), 74.2 (C-2'), 76.5 (C-3'), 70.3 (C-4'), 77.2 (C-5'), 61.5 (C-6'). *Gelsemium sempervirens* (Loganiaceae) (157)

## 200. VEBRASIDE



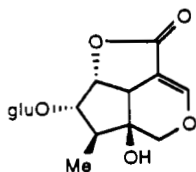
$C_{16}H_{24}O_{10}$  376.36 mp 131–133° [ $\alpha$ ] +80.7° ( $H_2O$ ) uv 187 ( $H_2O$ ) (250 MHz  $D_2O$ ) 3.68 (H-1 $\alpha$ , bd, 13.2), 4.39 (H-1 $\beta$ , dd, 13.2, 3.5), 5.47 (H-3, bs, <1), 3.22 (H-4, bd, 10.5, <1), 3.50 (H-5, m, 10.5, 7.0), 4.96 (H-6, bd, 7.0, <1), 4.20 (H-7, bd, 3.5, <1), 1.94 (H-8, m, 5.5, 3.5), 1.94 (H-9, m, 3.5), 1.07 (H-10, d, 5.5), 4.74 (H-1', d, 7.5), 3.37 (H-2', dd, 8.5, 7.5), 3.57 (H-3', dd, 8.5, 8.5), 3.45 (H-4', dd, 8.5, 8.5), 3.52 (H-5', m), 3.78 (H-6', dd, 12.0, 5.2), 3.90 (H-6', dd, 12.0, 2.8); ( $D_2O$ ) 57.6 (C-1), 98.0 (C-3), 41.8 (C-4), 34.7 (C-5), 88.4 (C-6), 77.4 (C-7), 37.6 (C-8), 37.4 (C-9), 10.9 (C-10), 179.0 (C-11), 103.2 (C-1'), 74.2 (C-2'), 77.2 (C-3'), 70.3 (C-4'), 76.5 (C-5'), 61.5 (C-6'). *Verbena brasiliensis* (Verbenaceae) (158)

## 201. 9-HYDROXYSEMPEROSIDE



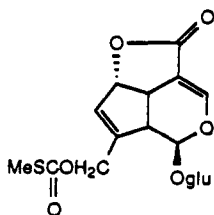
$C_{16}H_{24}O_{10}$  376.36 mp 132–135° [ $\alpha$ ] +58° (MeOH) (400 MHz  $D_2O$ ) 3.98/3.64 (H-1, 12.0), 5.45 (H-3, s), 3.41 (H-4, d, 11.4), 3.00 (H-5, m), 5.21 (H-6, dd, 6, 4.5), 2.13 (H-7 $\alpha$ , dd, 14, 6), 1.84 (H-7 $\beta$ , dt, 14, 4.5), 1.97 (H-8, m), 0.98 (H-10, d, 6.5), 4.72 (H-1', d, 8); ( $D_2O$ ) 60.7 (C-1), 97.9 (C-3), 44.6 (C-4), 46.9 (C-5), 85.7 (C-6), 38.5 (C-7), 37.0 (C-8), 74.9 (C-9), 10.5 (C-10), 178.5 (C-11), 103.3 (C-1'), 75.0 (C-2'), 75.7 (C-3'), 71.1 (C-4'), 77.4 (C-5'), 61.5 (C-6'). *Gelsemium sempervirens* (Loganiaceae) (157)

## 202. GELSEMIDE 7-GLUCOSIDE



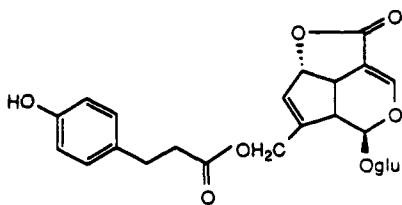
$C_{16}H_{22}O_{10}$  374.34 [ $\alpha$ ] -199° (MeOH) (90 MHz  $D_2O$ ) 4.24, 3.91 (H-1, 12), 7.51 (H-3, d, 2.5), 5.24 (H-6, t, 7.3), 4.36 (H-7, dd, 10, 7), 2.07 (H-8, m), 1.12 (H-10, d, 7), 4.57 (H-1', d, 7); ( $D_2O$ ) 67.2 (C-1), 154.1 (C-3), 102.0 (C-4), 47.7 (C-5), 78.5 (C-6), 84.1 (C-7), 41.1 (C-8), 72.1 (C-9), 9.8 (C-10), 174.3 (C-11), 102.0 (C-1'), 74.1 (C-2'), 76.5 (C-3'), 70.5 (C-4'), 76.9 (C-5'), 61.5 (C-6'). *Gelsemium sempervirens* (Loganiaceae) (157)

## 203. PAEDEROSIDE



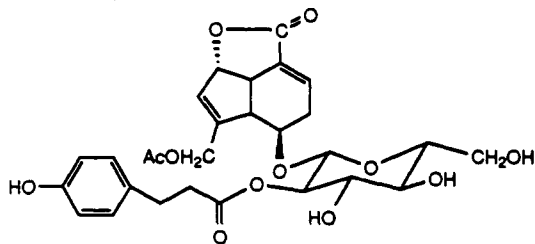
$C_{18}H_{22}O_{11}S$  446.43 mp 118°  $[\alpha] -44^\circ$  (MeOH) uv 233 (MeOH) (200 MHz  $CD_3OD$ ) 5.94 (H-1, d, 1.8), 7.30 (H-3, d, 2.2), 3.74 (H-5, m), 5.56 (H-6, bd, 7), 5.73 (H-7, m), 3.74 (H-9, m), 4.85 (H-10, m), 2.34 (SMe), 4.68 (H-1', d, 8.0), 3.19 (H-2', dd, 8.5, 8.0), 3.92 (H-6', dd, 12.0, 1.9). The aphid *Acyrthosiphon nipponicus* (159–161)

## 204. V1



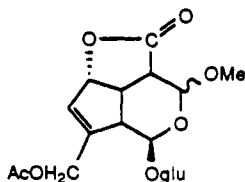
$C_{25}H_{28}O_{12}$  520.49 mp 118–120°  $[M]_{546} -920^\circ$  (MeOH) uv 280, 226 (EtOH) (100 MHz  $D_2O$ ) 5.86 (H-1, d, 1.5), 7.30 (H-3, d, 2), 5.57 (H-6, dd, 7, 2), 5.53 (H-7, d), 4.66 (H-10, bs), 4.79 (H-1', d, 7), 3.00–2.60 (H $\alpha$ , H $\beta$ ), 7.10 (H-2'', d, 8), 6.80 (H-3'', d, 8). *Galium verum* (Rubiaceae) (162)

## 205. V2



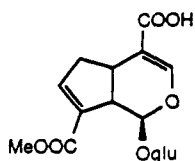
$C_{27}H_{28}O_{13}$  560.51 mp 145–150° (dec)  $[M]_{546} -871^\circ$  (MeOH) uv 279, 226 (EtOH) X-ray (100 MHz  $CD_3OD$ ) 6.1 (H-1, d, 1.5), 7.37 (H-3, d, 1.5), 5.61 (H-6, m), 5.81 (H-7, bs), 4.78 (H-10, bs), 2.16 (OAc), 4.79 (H-1', d, 7), 2.97–2.55 (H $\alpha$ , H $\beta$ ), 7.14 (H-2'', d, 2), 6.78 (H-3'', d, 2). *Galium verum* (Rubiaceae) (163)

## 206. V3



$C_{19}H_{26}O_{12}$  446.41  $[M]_{546} -197.5^\circ$  (MeOH) (100 MHz  $D_2O$ , 50°) 5.35 (H-1, d, 4.5), 5.08 (H-3, d, 4.5), 5.61 (H-6, dd, 6.0, 2.0), 6.12 (H-7, d, 2.0), 4.90 (H-10, bs), 4.83 (H-1', d, 7.5), 3.59 (OMe), 2.22 (OAc). Artifact, *Galium verum* (Rubiaceae) (162)

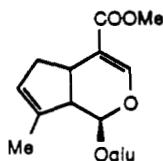
## 207. 10-METHYLIXOSIDE



$C_{17}H_{22}O_{11}$  402.35 mp 215–217° uv 220 (MeOH) (400 MHz pyridine- $d_5$ ) 6.74 (H-1, d, 3.5), 7.87 (H-3, bs), 3.55 (H-5, ddd, 8.0, 8.0, 2.5), 2.59 (H-6, dddd, 18.5, 2.5, 2.5, 2.5), 2.87 (H-6, dddd, 18.5, 8.0, 2.5, 2.5), 7.05 (H-7, ddd, 4.5, 2.5, 2.5), 3.74 (H-9, dddd, 8.0, 3.5, 2.5, 2.5, 2.5), 3.60 (COOMe), 5.33 (H-1', d, 8.0), 4.04 (H-2', dd, 9.2, 8.0), 4.23 (H-3', dd, 9.2, 9.2), 4.29 (H-4', dd, 9.2, 9.2), 3.90 (H-5', ddd, 9.2, 4.6, 2.5), 4.36 (H-6', dd, 12.0, 4.6), 4.45

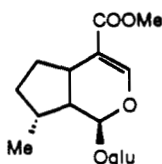


## 208. 10-DEOXYGENIPOSIDE

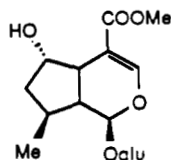


(H-6', dd, 12.0, 2.5); (pyridine-*d*<sub>5</sub>) 95.7 (C-1), 152.9 (C-3), 111.7 (C-4), 33.2 (C-5), 39.2 (C-6), 145.4 (C-7), 136.3 (C-8), 47.9 (C-9), 167.4 (C-10), 167.3 (C-11), 101.6 (C-1'), 76.0 (C-2'), 78.5 (C-3'), 71.2 (C-4'), 78.4 (C-5'), 62.4 (C-6'), 51.0 (OMe). *Randia dumetorum* (Rubiaceae) (164)

C<sub>17</sub>H<sub>24</sub>O<sub>9</sub> 372.37 mp 167–168° (500 MHz D<sub>2</sub>O) 5.49 (H-1, d, 4.7), 7.53 (H-3, bs), 3.21 (H-5, dt, 8, 4.6), 2.75 (H-6, bddd, 16, 7.5, 1.5), 2.13 (H-6, bd, 16), 5.57 (H-7, m), 2.90 (H-9, m), 1.81 (H-10, m), 3.76 (COOMe), 4.83 (H-1', d, 8.3). Prepared from asperuloside and gardenoside (165, 166)

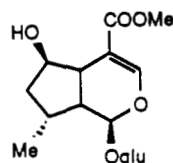
209. 7-DEOXY-8-*epi*-LOGANIN

C<sub>17</sub>H<sub>26</sub>O<sub>9</sub> 374.39 mp 150–152° [α] -128° (MeOH) (D<sub>2</sub>O) 96.3 (C-1), 152.6 (C-3), 113.8 (C-4), 32.6 (C-5), 31.6 (C-6), 33.1 (C-7), 36.1 (C-8), 43.4 (C-9), 16.3 (C-10), 171.2 (C-11), 52.6 (OMe), 99.3 (C-1'), 73.5 (C-2'), 76.6 (C-3'), 70.4 (C-4'), 77.1 (C-5'), 61.5 (C-6'). Prepared from geniposide pentaacetate (2)

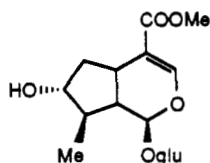
210. 6-*epi*-DIHYDROCORNIN

C<sub>17</sub>H<sub>26</sub>O<sub>10</sub> 390.39 (60 MHz D<sub>2</sub>O) 5.25 (H-1, d, 8.5), 7.72 (H-3, d, 1.5), 3.03 (H-5, m), 4.54 (H-6), 2.45–1.40 (H-7, H-8, H-9), 1.21 (H-10, d), 3.82 (OMe), 4.92 (H-1', d, 7.5); (D<sub>2</sub>O) 101.5 (C-1), 155.9 (C-3), 106.9 (C-4), 42.0 (C-5), 74.7 (C-6), 42.0 (C-7), 34.5 (C-8), 46.3 (C-9), 21.4 (C-10), 170.9 (C-11), 52.6 (OMe), 100.0 (C-1'), 73.6 (C-2'), 76.8 (C-3'), 70.5 (C-4'), 77.3 (C-5'), 61.6 (C-6'). Reduction of verbenalin (113, 167)

## 211. PENSTEMONOSIDE

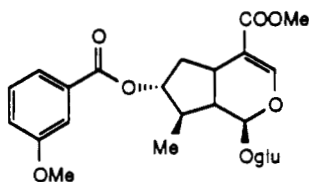


C<sub>17</sub>H<sub>26</sub>O<sub>10</sub> 390.39 mp 74–85° [α] -140.2 (MeOH) uv 232 (MeOH) (360 MHz D<sub>2</sub>O) 5.58 (H-1, d, 2.5), 7.48 (H-3, d, 0.9), 2.88 (H-5, bd), 4.23 (H-6, m), 1.80 (H-7, m), 1.50 (H-7, ddd, 14, 9.8, 4.2), 2.58 (H-8, m), 2.71 (H-9, td, 11.7, 9.3, 2.5), 1.02 (H-10, d, 7.2), 3.75 (OMe), 4.76 (H-1', d, 8.1), 3.25 (H-2', dd, 9.3, 8.1), 3.51–3.39 (H-3', H-4', H-5'), 3.92 (H-6', dd, 12.3, 2.0), 3.72 (H-6', dd, 12.3, 5.7); (CD<sub>3</sub>OD) 96.1 (C-1), 153.7 (C-3), 111.0 (C-4), 43.0 (C-5)<sup>a</sup>, 77.8 (C-6)<sup>b</sup>, 41.7 (C-7), 33.8 (C-8), 42.5 (C-9)<sup>a</sup>, 16.7 (C-10), 169.5 (C-11), 51.8 (OMe), 99.7 (C-1'), 74.5 (C-2'), 78.1 (C-3')<sup>b</sup>, 71.5 (C-4'), 77.8 (C-5')<sup>b</sup>, 62.7 (C-6'). *Penstemon barbatus* (Scrophulariaceae) (168, 169)

212. 7-*epi*-LOGANIN

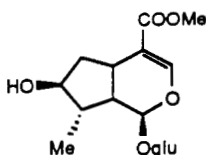
C<sub>17</sub>H<sub>26</sub>O<sub>10</sub> 390.39 [α] -95.5° (MeOH) (200 MHz CD<sub>3</sub>OD) 5.32 (H-1, d, 4), 7.40 (H-3, d, 1), 2.84 (H-5, m), 1.78, 1.34 (H-6, m's), 3.92–3.12 (H-7), 1.78 (H-8, m), 2.50 (H-9, m), 1.13 (H-10, d, 7), 4.64 (H-1', d, 8); (CD<sub>3</sub>OD) 97.8 (C-1), 152.5 (C-3), 113.3 (C-4), 31.5 (C-5), 42.0 (C-6), 79.7 (C-7), 44.0 (C-8), 47.1 (C-9), 17.7 (C-10), 169.5 (C-11), 51.7 (OMe), 100.4 (C-1'), 74.8 (C-2'), 78.3 (C-3')<sup>a</sup>, 71.7 (C-4'), 78.1 (C-5')<sup>a</sup>, 62.8 (C-6'). Prepared from swertiaside (5, 143)

213. 7-*epi*-O-(*m*-METHOXYBENZOYL)  
LOGANIN



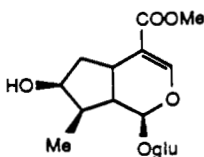
$C_{25}H_{32}O_{12}$  524.52 (200 MHz  $CD_3OD$ ) 5.52 (H-1, bd, 2), 7.44 (H-3, bs), 3.04 (H-5, m), 2.02 (H-6, m), 4.90 (H-7, m), 2.02 (H-8, m), 2.45 (H-9, m), 1.24 (H-10, d, 7), 3.66 (COOMe), 4.66 (H-1', d, 8), 3.92–3.10 (H-2'–H-6'), 7.44 (H-2'', bs), 7.12 (H-4'', dd, 8, 2), 7.34 (H-5'', t, 8), 7.50 (H-6'', d, 8), 3.84 (ArOMe); ( $CD_3OD$ ) 96.3 (C-1), 152.4 (C-3), 112.6 (C-4), 32.5 (C-5), 38.1 (C-6), 83.5 (C-7), 43.0 (C-8), — (C-9), 18.3 (C-10), 169.3 (C-11), 51.6 (COOMe), 100.3 (C-1'), 74.7 (C-2'), 78.4 (C-3')<sup>a</sup>, 71.6 (C-4'), 78.1 (C-5')<sup>a</sup>, 62.6 (C-6'), 167.7 (C=O), 132.9 (C-1''), 115.5 (C-2''), 161.3 (C-3''), 120.2 (C-4''), 130.6 (C-5''), 122.8 (C-6''), 56.0 (ArOMe). Synthesized from senburiside I (144)

214. 8-*epi*-LOGANIN



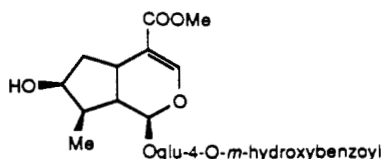
$C_{17}H_{26}O_{10}$  390.39 [ $\alpha$ ] –100.9° (MeOH) uv 236 (MeOH) (90 MHz  $D_2O$ ) 5.59 (H-1, d, 3.0), 7.45 (H-3, bs), 3.11 (H-5, m), 2.4–1.7 (H-6, m), 4.1–3.7 (H-7), 2.30 (H-8, m), 2.73 (H-9, dt, 8.5, 8.5, 3.0), 1.05 (H-10, d, 7.0), 3.76 (OMe), 4.81 (H-1', d, 7.5); ( $D_2O$ ) 96.5 (C-1), 152.2 (C-3), 114.0 (C-4), 29.4 (C-5), 39.6 (C-6), 79.0 (C-7), 43.5 (C-8), 41.8 (C-9), 14.0 (C-10), 170.7 (C-11), 52.6 (OMe), 99.1 (C-1'), 73.5 (C-2'), 76.6 (C-3'), 70.5 (C-4'), 77.1 (C-5'), 61.6 (C-6'). *Odontites verna* subsp. *serotina* (Scrophulariaceae) (170)

215. LOGANIN



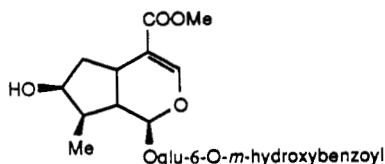
$C_{17}H_{26}O_{10}$  390.39 (300 MHz  $CD_3OD$ ) 5.37 (H-1, d, 4.5), 7.37 (H-3, d, 0.5), 3.10 (H-5, m), 2.25 (H-6, ddd, 14, 8, 1.5), 1.60 (H-6, ddd, 14, 7.5, 4.5), 4.04 (H-7, m), 1.86 (H-8, m), 2.03 (H-9, m), 1.08 (H-10, d, 7.5), 3.67 (OMe), 4.65 (H-1', d, 8), 3.20 (H-2', d, 8); ( $D_2O$ ) 97.5 (C-1), 151.7 (C-3), 113.8 (C-4), 30.6 (C-5), 41.2 (C-6), 74.8 (C-7), 40.9 (C-8), 45.7 (C-9), 12.8 (C-10), 170.5 (C-11), 52.5 (OMe), 99.4 (C-1'), 73.6 (C-2'), 76.5 (C-3'), 70.4 (C-4'), 77.1 (C-5'), 61.5 (C-6'). (2, 171, 172)

216. 4'-O-*m*-HYDROXYBENZOYL-  
LOGANIN



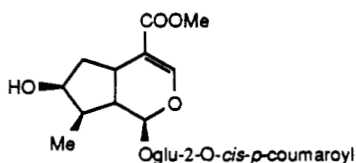
$C_{24}H_{30}O_{12}$  510.49 uv 297, 232 (MeOH) (300 MHz  $CD_3OD$ ) 5.30 (H-1, d, 4.5), 7.41 (H-3, d, 1.5), 3.12 (H-5, m), 2.24 (H-6, ddd, 14, 8, 1.5), 1.62 (H-6, ddd, 14, 8, 5), 4.04 (H-7, td, 5, 1.5), 1.88 (H-8, dqd, 9, 6.5, 5), 2.06 (H-9, td, 9, 4.5), 1.11 (H-10, d, 6.5), 3.68 (OMe), 4.76 (H-1', d, 8), 4.98 (H-4', t, 9), 7.44 (H-2'', dd, 1.5, 1), 7.02 (H-4'', ddd, 7.5, 1.5, 1), 7.29 (H-5'', t, 7.5), 7.52 (H-6'', dt, 7.5, 1); ( $CD_3OD$ ) 97.6 (C-1), 152.0 (C-3), 114.2 (C-4), 32.1 (C-5), 42.7 (C-6), 74.9 (C-7)<sup>a</sup>, 42.1 (C-8), 46.5 (C-9), 13.4 (C-10), 167.4 (C-11), 51.6 (OMe), 100.1 (C-1'), 75.0 (C-2')<sup>a</sup>, 75.8 (C-3'), 72.9 (C-4'), 76.4 (C-5'), 62.4 (C-6'), 169.5 (C=O), 132.4 (C-1''), 117.2 (C-2''), 158.6 (C-3''), 121.5 (C-4''), 130.6 (C-5''), 121.8 (C-6''). *Gentiana verna* (Gentianaceae) (173)

217. 6'-O-*m*-HYDROXYBENZOYL-  
LOGANIN



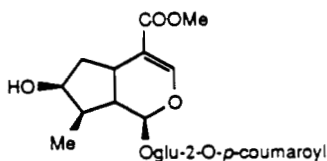
$C_{24}H_{30}O_{12}$  510.49 uv 302, 237 (EtOH) (100 MHz  $CD_3OD$ ) 7.37 (H-3, d, 1), 3.05 (H-5, dd, 13, 7), 2.16 (H-6, dd, 12, 7), 1.88 (H-6, m), 1.73 (H-8, m), 1.28 (H-9, m), 0.97 (H-10, d, 7), 3.68 (OMe), 7.42 (H-2'', bs), 6.99 (H-4'', dd, 8, 1), 7.26 (H-5'', t, 8), 7.48 (H-6'', d, 8); ( $CD_3OD$ ) 99.5 (C-1), 153.1 (C-3), 114.5 (C-4), 33.4 (C-5), 43.7 (C-6), 75.5 (C-7), 43.2 (C-8), 47.2 (C-9), 14.3 (C-10), 170.2 (C-11), 52.3 (OMe), 102.1 (C-1'), 75.6 (C-2'), 78.7 (C-3'), 72.5 (C-4'), 76.1 (C-5'), 65.7 (C-6'), 168.6 (C=O), 133.3 (C-1''), 117.9 (C-2''), 159.6 (C-3''), 122.1 (C-4''), 131.3 (C-5''), 122.1 (C-6''). *Erythraea centaurium* (Gentianaceae) (174)

218. 2'-O-*cis*-COUMAROYLLOGANIN



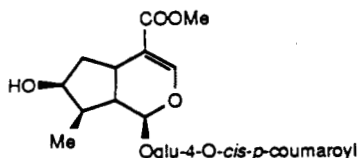
$C_{26}H_{32}O_{12}$  536.53 uv 305, 295, 230 (MeOH) (300 MHz  $CD_3OD$ ) 5.37 (H-1, d, 2.5), 7.26 (H-3, d, 1), 2.96-2.89 (H-5, m), 2.16-2.03 (H-6, H-9, m), 1.76-1.58 (H-6, H-8, m), 3.96 (H-7, m), 1.07 (H-10, d, 7), 3.41 (COOMe), 4.88 (H-1', d, 8), 4.76 (H-2', t, 8), 7.66 (H-2'', d, 8), 6.73 (H-3'', d, 8), 5.65/6.80 (H $\alpha$ , H $\beta$ , d's, 13); ( $CD_3OD$ ) 98.2 (C-1), 151.5 (C-3), 115.3 (C-4), 31.1 (C-5), 42.4 (C-6), 75.2 (C-7), 41.5 (C-8), 46.5 (C-9), 12.6 (C-10), 169.7 (C-11), 51.5 (OMe), 96.4 (C-1'), 74.5 (C-2'), 76.1 (C-3'), 71.9 (C-4'), 78.7 (C-5'), 62.7 (C-6'), 167.6 (C=O), 117.2 (C $\alpha$ ), 146.1 (C $\beta$ ), 127.9 (C-1''), 131.7 (C-2''), 116.7 (C-3''), 160.5 (C-4''). *Gentiana pedicellata* (Gentianaceae) (171)

219. 2'-O-*trans*-COUMAROYLLOGANIN

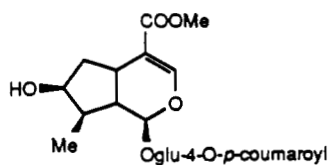


$C_{26}H_{32}O_{12}$  536.53 uv 305, 295, 230 (MeOH) (300 MHz  $CD_3OD$ ) 5.42 (H-1, d, 2.5), 7.20 (H-3, d, 1), 2.96-2.89 (H-5, m), 2.16-2.03 (H-6, H-9, m), 1.76-1.58 (H-6, H-8, m), 3.96 (H-7, m), 1.04 (H-10, d, 7), 3.09 (OMe), 4.84 (H-1', d, 8), 4.71 (H-2', t, 8), 7.46 (H-2'', d, 8), 6.81 (H-3'', d, 8), 6.23/7.55 (H $\alpha$ , H $\beta$ , d's, 16); ( $CD_3OD$ ) 97.9 (C-1), 151.0 (C-3), 115.3 (C-4), 30.8 (C-5), 42.1 (C-6), 75.2 (C-7), 41.2 (C-8), 46.5 (C-9), 12.4 (C-10), 169.5 (C-11), 51.4 (OMe), 97.1 (C-1'), 74.8 (C-2'), 76.1 (C-3'), 71.9 (C-4') 78.7 (C-5'), 62.7 (C-6'), 168.6 (O=C), 117.2 (C $\alpha$ ), 146.9 (C $\beta$ ), 127.7 (C-1''), 131.4 (C-2''), 116.1 (C-3''), 161.1 (C-4''). *Gentiana pedicellata* (Gentianaceae) (171)

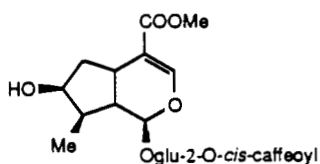
220. 4'-O-*cis*-*p*-COUMAROYLLOGANIN



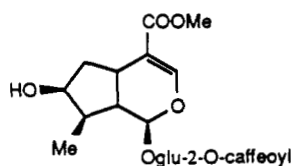
$C_{26}H_{32}O_{12}$  536.53 uv 310, 295, 230 (MeOH) (300 MHz  $CD_3OD$ ) 5.27 (H-1, d, 4.5), 7.37 (H-3, d, 1.5), 3.12 (H-5, m), 2.23, 1.62 (H-6, m's), 4.04 (H-7, m), 1.87 (H-8, m), 2.04 (H-9, m), 1.09 (H-10, d, 7), 3.69 (OMe), 4.69 (H-1', d, 8), 4.80 (H-4', m), 3.65-3.48 (H-6', m), 5.80/6.93 (H $\alpha$ , H $\beta$ , d's, 13), 7.70 (H-2'', d, 8.5), 6.76 (H-3'', d, 8.5); ( $CD_3OD$ ) 97.9 (C-1), 152.1 (C-3), 114.2 (C-4), 32.2 (C-5), 42.7 (C-6), 75.1 (C-7), 42.2 (C-8), 46.6 (C-9), 13.4 (C-10), 169.6 (C-11), 51.6 (OMe), 100.1 (C-1'), 74.9 (C-2'), 75.8 (C-3'), 72.1 (C-4'), 76.6 (C-5'), 62.5 (C-6'), 167.5 (O=C), 116.1 (C $\alpha$ ), 146.1 (C $\beta$ ), 127.2 (C-1''), 133.9 (C-2''), 115.9 (C-3''), 160.3 (C-4''). *Gentiana pedicellata* (Gentianaceae) (140)

221. 4'-O-*trans*-*p*-COUMAROYL-LOGANIN

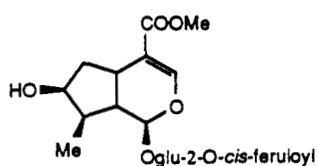
$C_{26}H_{32}O_{12}$  536.53 uv 310, 295, 230 (MeOH) (300 MHz  $CD_3OD$ ) 5.28 (H-1, d, 4.5), 7.38 (H-3, d, 1.5), 3.12 (H-5, m), 2.23, 1.62 (H-6, m's), 4.04 (H-7, m), 1.87 (H-8, m), 2.04 (H-9, m), 1.10 (H-10, d, 7), 3.69 (OMe), 4.72 (H-1', d, 8), 4.80 (H-4', m), 3.65–3.48 (H-6', m), 6.36/7.68 (H $\alpha$ , H $\beta$ , d's, 16), 7.48 (H-2'', d, 8.5), 6.82 (H-3'', d, 8.5); ( $CD_3OD$ ) 97.9 (C-1), 152.1 (C-3), 114.2 (C-4), 32.2 (C-5), 42.7 (C-6), 75.1 (C-7), 42.2 (C-8), 46.6 (C-9), 13.4 (C-10), 169.6 (C-11), 51.6 (OMe), 100.1 (C-1'), 74.9 (C-2'), 75.8 (C-3'), 72.5 (C-4'), 76.6 (C-5'), 62.5 (C-6'), 168.6 (O=C), 114.9 (C $\alpha$ ), 147.3 (C $\beta$ ), 127.6 (C-1''), 131.3 (C-2''), 116.9 (C-3''), 161.5 (C-4''). *Gentiana pedicellata* (Gentianaceae) (140)

222. 2'-O-*cis*-CAFFEYOYLLOGANIN

$C_{26}H_{32}O_{13}$  552.53 uv 323, 290, 230 (MeOH) (300 MHz  $CD_3OD$ ) 5.37 (H-1, d, 2.5), 7.26 (H-3, d, 1), 2.99–2.87 (H-5, m), 2.15–2.05, 1.76–1.60 (H-6, m's), 3.96 (H-7, m), 1.75–1.60 (H-8, m), 2.15–2.05 (H-9, m), 1.07 (H-10, d, 7), 3.58 (OMe), 4.80 (H-1', d, 8), 4.84 (H-2', t, 8), 5.63/6.75 (H $\alpha$ , H $\beta$ , d's, 13), 6.50 (H-2'', d, 2), 7.90 (H-5'', d, 8), 7.12 (H-6'', dd, 8, 2); ( $CD_3OD$ ) 98.5 (C-1), 150.8 (C-3), 115.0 (C-4), 31.3 (C-5), 42.3 (C-6), 75.2 (C-7), 41.5 (C-8), 46.6 (C-9), 12.5 (C-10), 169.6 (C-11), 51.4 (OMe), 95.9 (C-1'), 74.5 (C-2'), 76.0 (C-3'), 71.8 (C-4'), 78.6 (C-5'), 62.7 (C-6'), 168.0 (O=C), 115.1 (C $\alpha$ ), 146.8 (C $\beta$ ), 128.2 (C-1''), 115.4 (C-2''), 146.0 (C-3''), 149.1 (C-4''), 116.6 (C-5''), 123.1 (C-6''). *Gentiana pedicellata* (Gentianaceae) (171)

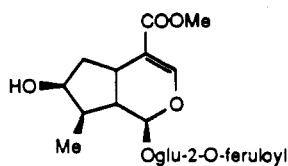
223. 2'-O-*trans*-CAFFEYOYLLOGANIN

$C_{26}H_{32}O_{13}$  552.53 uv 323, 290, 230 (MeOH) (300 MHz  $CD_3OD$ ) 5.42 (H-1, d, 2.5), 7.20 (H-3, d, 1), 2.99–2.87 (H-5, m), 2.15–2.05, 1.76–1.60 (H-6, m's), 3.96 (H-7, m), 1.75–1.60 (H-8, m), 2.15–2.05 (H-9, m), 1.06 (H-10, d, 7), 3.18 (OMe), 4.85 (H-1', d, 8), 4.79 (H-2', t, 8), 6.18/7.48 (H $\alpha$ , H $\beta$ , d's, 16), 7.04 (H-2'', d, 2), 6.79 (H-5'', d, 8), 6.95 (H-6'', dd, 8, 2); ( $CD_3OD$ ) 97.8 (C-1), 150.4 (C-3), 115.0 (C-4), 30.9 (C-5), 42.1 (C-6), 75.2 (C-7), 41.2 (C-8), 46.6 (C-9), 12.5 (C-10), 169.5 (C-11), 51.4 (OMe), 96.2 (C-1'), 74.7 (C-2'), 76.0 (C-3'), 71.8 (C-4'), 78.6 (C-5'), 62.7 (C-6'), 167.9 (O=C), 115.1 (C $\alpha$ ), 146.9 (C $\beta$ ), 128.0 (C-1''), 115.5 (C-2''), 146.0 (C-3''), 149.0 (C-4''), 116.6 (C-5''), 123.1 (C-6''). *Gentiana pedicellata* (Gentianaceae) (171)

224. 2'-O-*cis*-FERULOYLLOGANIN

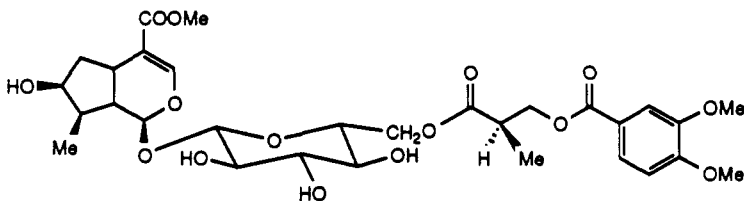
$C_{27}H_{34}O_{13}$  566.56 uv 320, 295, 230 (MeOH) (300 MHz  $CD_3OD$ ) 5.35 (H-1, d, 2.5), 7.26 (H-3, d, 1), 2.98–2.89 (H-5, m), 2.14–2.06 (H-6, H-9, m), 1.75–1.59 (H-6, H-8, m), 3.98 (H-7, m), 1.06 (H-10, d, 7), 3.46 (COOMe), 4.87 (H-1', d, 8), 4.84 (H-2', t, 8), 5.69/6.80 (H $\alpha$ , H $\beta$ , d's, 13), 7.18 (H-2'', d, 8), 6.76 (H-5'', d, 8), 7.10 (H-6'', dd, 8, 2), 3.87 (ArOMe); ( $CD_3OD$ ) 98.1 (C-1), 150.9 (C-3), 115.4 (C-4), 31.1 (C-5), 42.4 (C-6), 75.1 (C-7), 41.5 (C-8), 46.6 (C-9), 12.6 (C-10), 169.2 (C-11), 51.5 (COOMe), 96.8 (C-1'), 74.4 (C-2'), 76.0 (C-3'), 71.8 (C-4'), 78.6 (C-5'), 62.7 (C-6'), 168.3 (O=C), 115.5 (C $\alpha$ ), 146.2 (C $\beta$ ), 127.9 (C-1''), 112.3 (C-2''), 149.6 (C-3''), 147.6 (C-4''), 116.3 (C-5''), 124.2 (C-6''), 56.5 (ArOMe). *Gentiana pedicellata* (Gentianaceae) (171)

## 225. 2'-O-trans-FERULOYLLOGANIN



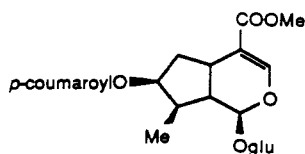
$C_{27}H_{34}O_{13}$  566.56 uv 320, 295, 230 (MeOH) (300 MHz  $CD_3OD$ ) 5.40 (H-1, d, 2.5), 7.21 (H-3, d, 1), 2.98–2.89 (H-5, m), 2.14–2.06 (H-6, H-9, m), 1.75–1.59 (H-6, H-8, m), 3.98 (H-7, m), 1.05 (H-10, d, 7), 3.18 (COOMe), 4.84 (H-1', d, 8), 4.80 (H-2', t, 8), 7.81 (H-2'', d, 2), 6.83 (H-5'', d, 8), 7.07 (H-6'', 8, 2), 3.92 (ArOMe), 6.25/7.55 (H $\alpha$ , H $\beta$ , d's, 16); ( $CD_3OD$ ) 97.7 (C-1), 150.5 (C-3), 115.1 (C-4), 30.9 (C-5), 42.1, (C-6), 75.1 (C-7), 41.3 (C-8), 46.6 (C-9), 12.5 (C-10), 169.0 (C-11), 51.3 (COOMe), 96.2 (C-1'), 74.7 (C-2'), 76.0 (C-3'), 71.8 (C-4'), 78.6 (C-5'), 62.7 (C-6'), 168.0 (O=C), 115.6 (C $\alpha$ ), 146.7 (C $\beta$ ), 127.1 (C-1''), 112.3 (C-2''), 149.5 (C-3''), 147.5 (C-4''), 116.5 (C-5''), 124.2 (C-6''), 56.6 (ArOMe). *Gentiana pedicellata* (Gentianaceae) (171)

## 226. 6'-O-[2(R)-METHYL-3-VERATROYLOXYPROPANOYL]LOGANIN



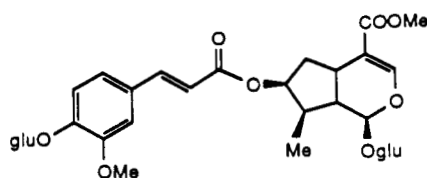
$C_{30}H_{40}O_{15}$  640.64 [ $\alpha$ ]  $-32^\circ$  (MeOH) uv 290, 255, 240, 225 (MeOH) (400 MHz  $CD_3OD$ ) 5.06 (H-1, d, 5), 7.34 (H-3, d, 1.5), 3.08 (H-5, m), 1.51 (H-6 $\alpha$ , ddd, 14, 8.5, 5), 2.22 (H-6 $\beta$ , ddd, 14, 7.5, 1.5), 3.99 (H-7, m), 1.81 (H-8, dqd, 9, 7, 5), 1.94 (H-9, td, 9, 5), 1.04 (H-10, d, 7), 3.67 (COOMe), 4.59 (H-1', d, 8), 3.18 (H-2', dd, 9, 8), 3.35–3.30 (H-3', H-4', m), 3.48 (H-5', ddd, 9, 6.5, 2), 4.59 (H-6', dd, 12, 2), 4.18 (H-6'', dd, 12, 6.5), 2.99 (H-2'', pd, 7, 5.5), 4.43 (H-3'', dd, 10.5, 7), 4.36 (H-3'', dd, 10.5, 5.5), 1.23 (H-4'', d, 7), 7.50 (H-2''', d, 2), 7.02 (H-5''', d, 8), 7.63 (H-6''', dd, 8, 2), 3.89, 3.87 (OMe); ( $CD_3OD$ ) 98.3 (C-1), 150.3 (C-3), 113.9 (C-4), 32.5 (C-5), 42.9 (C-6), 74.9 (C-7), 42.4 (C-8), 46.5 (C-9), 13.8 (C-10), 169.5 (C-11), 51.6 (COOMe), 100.3 (C-1'), 74.8 (C-2'), 77.7 (C-3'), 71.7 (C-4'), 75.8 (C-5'), 64.9 (C-6'), 175.2 (C-1''), 40.8 (C-2''), 67.0 (C-3''), 14.1 (C-4''), 167.5 (O=C), 123.5 (C-1'''), 113.6 (C-2'''), 150.3 (C-3'''), 155.1 (C-4'''), 112.2 (C-5'''), 125.0 (C-6'''), 56.6 (ArOMe). *Gentiana pyrenaica* (Gentianaceae) (175)

## 227. 7-O-p-COUMAROYLLOGANIN



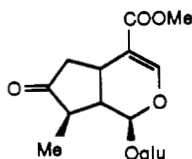
$C_{26}H_{32}O_{10}$  536.53 uv 281, 239 (MeOH) (360 MHz  $CD_3OD$ ) 5.20 (H-1, d, 4.5), 7.34 (H-3, d, 1), 3.06 (H-5, m), 1.69 (H-6 $\alpha$ , m), 2.24 (H-6 $\beta$ , ddd, 11, 8, 2), 5.16 (H-7, bt), 1.89 (H-8, m), 2.04 (H-9, m), 1.00 (H-10, d, 6.5), 4.57 (H-1', d, 8), 3.30–3.28 (H-2'–H-5'), 3.81 (H-6', dd, 12, 2), 3.70 (H-6'', dd, 12, 6), 3.60 (OMe), 6.14/7.45 (H $\alpha$ , H $\beta$ , d's, 16), 7.30 (H-2'', d, 9), 6.62 (H-3'', d, 9). *Desfontainia spinosa* (Loganiaceae) (176)

## 228. PERICLYMENOSIDE



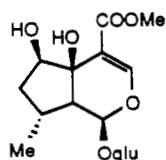
$C_{33}H_{44}O_{18}$  728.70  $[\alpha] -54.2^\circ$  (MeOH) uv 318, 293, 234, 220 (MeOH) (300 MHz  $CD_3OD$ ) 5.30–5.27 (H-1), 7.44 (H-3, s), 3.16 (H-5, m), 1.79 (H-6 $\alpha$ , m), 2.13 (H-6 $\beta$ , m), 5.30–5.27 (H-7), 2.17 (H-8, m), 2.34 (H-9, dd, 14.7, 8), 1.10 (H-10, d, 6.5), 3.70 (COOMe), 4.68 (H-1', d, 7.9), 3.56–3.20 (H-2'–H-5', H-2''–H-5''), 7.26 (H-2'', bs), 7.17 (H-5'', H-6'', bs), 6.45/7.62 (H $\alpha$ , H $\beta$ , d's, 15.9), 3.90 (ArOMe), 4.97 (H-1''', d, 7.1); ( $CD_3OD$ ) 97.8 (C-1), 152.8 (C-3), 113.2 (C-4), 32.8 (C-5), 40.5 (C-6), 78.7 (C-7), 41.1 (C-8), 47.2 (C-9), 14.0 (C-10), 169.5 (C-11), 52.0 (OMe), 100.3 (C-1'), 74.8 (C-2'), 78.0 (C-3'), 71.6 (C-4'), 78.4 (C-5'), 62.9 (C-6'), 168.6 (O=C), 117.6 (C $\alpha$ ), 146.2 (C $\beta$ ), 130.5 (C-1''), 112.5 (C-2''), 151.0 (C-3''), 150.1 (C-4''), 117.4 (C-5''), 123.7 (C-6''), 57.0 (ArOMe), 102.2 (C-1'''), 74.8 (C-2'''), 77.8 (C-3'''), 71.3 (C-4'''), 78.3 (C-5'''), 62.6 (C-6'''). *Lonicera periclymenum* (Caprifoliaceae) (139)

## 229. 7-KETOLOGANIN (7-Dehydrologanin)

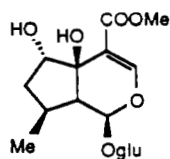


$C_{17}H_{24}O_{10}$  388.37 mp 194°  $[\alpha] -150.5^\circ$  (MeOH) uv 234 (MeOH) (300 MHz  $CD_3OD$ ) 5.61 (H-1, d, 3.2), 7.48 (H-3, d, 1.4), 3.5–3.1 (H-5, m), 2.51 (H-6 $\alpha$ , bddd, 19, 3.6, 1.3), 2.63 (H-6 $\beta$ , dd, 19.1, 8.0), 2.17–2.08 (H-8, m), 2.33 (H-9, ddd, 10.2, 7, 3.2), 1.15 (H-10, d, 7), 3.69 (COOMe), 4.67 (H-1', d, 7.8), 4.07–3.97 (H-2', m), 3.55–3.16 (H-3'–H-5', m), 3.9 (H-6', dd, 12, 2), 3.65 (H-6', dd, 12, 5.9); ( $CD_3OD$ ) 95.5 (C-1), 153.4 (C-3), 111.2 (C-4), 28.4 (C-5), 43.6 (C-6), 220.7 (C-7), 44.8 (C-8), 46.7 (C-9), 13.9 (C-10), 169.0 (C-11), 100.4 (C-1'), 74.8 (C-2'), 78.1 (C-3'), 71.7 (C-4'), 78.6 (C-5'), 62.9 (C-6'). Prepared from asperuloside, *Strychnos roborans* (Loganiaceae) (177–179)

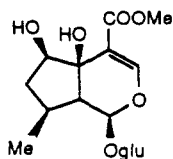
## 230. PENSTEMOSIDE



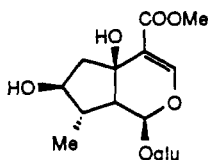
$C_{17}H_{26}O_{11}$  406.39  $[\alpha] -171^\circ$  (MeOH) uv 234 (MeOH) (400 MHz  $D_2O$ ) 5.77 (H-1, s), 7.57 (H-3, s), 4.25 (H-6, t, 4.3), 1.45 (H-7, ddd, 13.8, 7.5, 4.7), 1.76 (H-7, ddd, 13.8, 6.9, 3.8), 2.57 (H-8, H-9, m), 0.84 (H-10, d, 6.8), 3.69 (OMe), 4.69 (H-1', d, 8.2); ( $D_2O$ ) 96.3 (C-1), 155.5 (C-3), 112.3 (C-4), 73.2 (C-5), 76.3 (C-6), 39.6 (C-7), 30.5 (C-8), 49.2 (C-9), 16.2 (C-10), 169.1 (C-11), 52.6 (OMe), 99.4 (C-1'), 77.1 (C-2'), 76.2 (C-3'), 73.3 (C-4'), 70.4 (C-5'), 61.5 (C-6'). *Pedicularis palustris* (Scrophulariaceae) (180)

231.  $\alpha$ -DIHYDROHASTATOSIDE

$C_{17}H_{26}O_{11}$  406.39 (60 MHz  $D_2O$ ) 5.41 (H-1, d, 8.0), 7.72 (H-3, s), 4.44 (H-6, m), 2.24–1.73 (H-7, H-8, H-9), 1.12 (H-10, d, 6), 3.84 (OMe), 4.88 (H-1', d, 7); ( $D_2O$ ) 101.3 (C-1), 156.7 (C-3), 110.7 (C-4), 80.7 (C-5), 79.3 (C-6), 40.0 (C-7), 34.2 (C-8), 56.0 (C-9), 21.1 (C-10), 169.7 (C-11), 52.7 (OMe), 99.7 (C-1'), 73.5 (C-2'), 76.5 (C-3'), 70.4 (C-4'), 77.2 (C-5'), 61.5 (C-6'). Reduction of hastatoside (2, 5, 167)

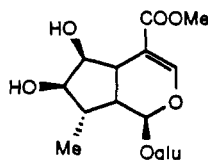
232.  $\beta$ -DIHYDROHASTATOSIDE

$C_{17}H_{26}O_{11}$  406.39 (60 MHz  $D_2O$ ) 5.82 (H-1, d, 1.5), 7.66 (H-3, s), 4.22 (H-6, m), 2.42–1.32 (H-7, H-8, H-9), 1.17 (H-10, d, 5.5), 3.84 (OMe), 4.85 (H-1', d, 7); ( $D_2O$ ) 96.0 (C-1), 154.8 (C-3), 112.2 (C-4), 73.3 (C-5), 76.2 (C-6), 39.8 (C-7), 30.8 (C-8), 54.8 (C-9), 19.6 (C-10), 169.4 (C-11), 52.8 (OMe), 99.7 (C-1'), 73.3 (C-2'), 76.2 (C-3'), 70.5 (C-4'), 77.3 (C-5'), 61.5 (C-6'). *Penstemon nitidus* (Scrophulariaceae), reduction of hastatoside (2, 5, 167, 181)

233. 5-HYDROXY-8-*epi*-LOGANIN

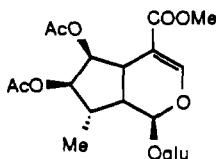
$C_{17}H_{26}O_{11}$  406.39 (400 MHz  $CD_3OD$ ) 5.74 (H-1, d, 1.6), 7.47 (H-3, s), 2.57 (H-6, dd, 13.6, 6.7), 2.03 (H-6, dd, 13.6, 5.6), 3.54 (H-7, m), 2.26 (H-8, m), 2.79 (H-9, dd, 10.3, 1.4), 0.95 (H-10, d, 7.4), 3.72 (OMe), 4.55 (H-1', d, 7.9); ( $CD_3OD$ ) 95.7 (C-1), 153.4 (C-3), 115.3 (C-4), 71.5 (C-5), 48.0 (C-6), 77.9 (C-7), 43.6 (C-8), 51.6 (C-9), 13.8 (C-10), 168.1 (C-11), 51.6 (OMe), 99.7 (C-1'), 74.4 (C-2'), 77.5 (C-3'), 71.7 (C-4'), 78.4 (C-5'), 62.8 (C-6'). Hydrogenation of strictoloside (182)

## 234. 5-DEOXPULCHELLOSIDE I

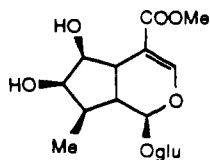


$C_{17}H_{26}O_{11}$  406.39 uv 238 (MeOH) (250 MHz  $D_2O$ ) 5.63 (H-1, d, 1.5), 7.50 (H-3, s), 2.96 (H-5, bd, 9, <1.5), 4.13 (H-6, bd, 4, <1.5), 3.65 (H-7, dd, 9, 4), 2.34 (H-8, m, 10, 9, 7), 2.89 (H-9, m), 1.11 (H-10, d, 7), 3.77 (OMe), 4.76 (H-1', d), 3.25 (H-2', t), 3.56–3.36 (H-3', H-4', H-5'), 3.95, 3.75 (H-6', dd's). *Citharexylum fruticosum* f. *subserratum* (Verbenaceae) (183)

## 235. BARBATOSIDE

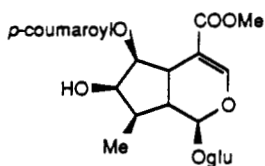


$C_{21}H_{30}O_{13}$  490.46 mp 91–94° uv 233 (MeOH) (400 MHz  $CD_3OD$ ) 5.60 (H-1, d, 3), 7.50 (H-3, d, 0.8), 3.05 (H-5, d, 9), 5.37 (H-6, dd, 4.3, 2.7), 4.76 (H-7, dd, 9.2, 4.3), 2.51 (H-8, m), 2.83 (H-9, ddd, 10.2, 9, 3), 1.09 (H-10, d, 7.3), 3.69 (OMe), 2.06, 1.97 (OAc), 4.61 (H-1', d, 7.9); ( $CD_3OD$ ) 95.7 (C-1), 154.0 (C-3), 109.8 (C-4), 37.8 (C-5)<sup>a</sup>, 78.4 (C-6), 79.7 (C-7), 37.4 (C-8)<sup>a</sup>, 40.2 (C-9), 13.5 (C-10), 172.3 (C-11)<sup>b</sup>, 51.8 (OMe), 100.0 (C-1'), 74.7 (C-2'), 78.1 (C-3')<sup>c</sup>, 71.8 (C-4'), 77.2 (C-5')<sup>c</sup>, 62.9 (C-6'), 171.7, 168.4 (O=CMe)<sup>b</sup>, 20.7, 20.6 (O=CMe). *Penstemon barbatus* (Scrophulariaceae) (184)

236. 6 $\beta$ -HYDROXYLOGANIN

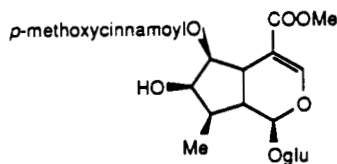
$C_{17}H_{26}O_{11}$  406.39 mp 220–222° [ $\alpha$ ] –107.2° (MeOH) (270 MHz  $D_2O$ ) 5.38 (H-1, d, 3.6), 7.48 (H-3, bs), 2.89 (H-5, bdd, 9, 5.4), 3.96 (H-6, t, 5), 3.89 (H-7, t, 5), 1.96 (H-8, m, 9.6, 6.5, 5.1), 2.26 (H-9, dt, 9.6, 9, 3.6), 1.09 (H-10, d, 6.5), 3.74 (OMe); ( $D_2O$ ) 97.4 (C-1), 153.1 (C-3), 111.3 (C-4), 38.4 (C-5), 79.5 (C-6), 75.1 (C-7), 37.9 (C-8), 44.7 (C-9), 13.4 (C-10), 170.8 (C-11), 52.8 (OMe), 99.4 (C-1'), 73.5 (C-2'), 76.5 (C-3'), 70.4 (C-4'), 77.2 (C-5'), 61.6 (C-6'). *Fouquieria diguetii* (Fouquieriaceae) (185)

237. 6-O-*trans*-*p*-COUMAROYL-6 $\beta$ -HYDROXYLOGANIN



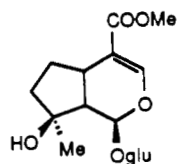
$C_{26}H_{32}O_{13}$  552.53 mp 200–202°  $[\alpha] -78.0^\circ$  (MeOH) uv 312, 301, 229 (MeOH) (400 MHz DMSO- $d_6$ ) 5.32 (H-1, d, 6), 7.40 (H-3, s), 3.09 (H-5, m), 4.98 (H-6, m), 4.06 (H-7, br, 4), 2.01 (H-8, m), 2.14 (H-9, m), 0.94 (H-10, d, 8), 3.61 (OMe), 4.94 (H-1', d, 7.5), 4.5–3.5 (H-2'–H-5', m), 4.42 (H-6', d, 9), 6.36/7.56 (H $\alpha$ , H $\beta$ , d's, 16), 7.51 (H-2'', d, 10), 6.75 (H-3'', d, 10), 9.98 (ArOH, bs); (CD<sub>3</sub>OD) 97.8 (C-1), 154.0 (C-3), 110.5 (C-4), 39.7 (C-5), 78.4 (C-6), 79.0 (C-7), 37.4 (C-8), 46.1 (C-9), 14.9 (C-10), 170.1 (C-11), 52.0 (OMe), 100.2 (C-1'), 74.7 (C-2'), 78.0 (C-3'), 71.6 (C-4'), 77.6 (C-5'), 62.8 (C-6'), 169.0 (O=C), 115.3 (C $\alpha$ ), 146.7 (C $\beta$ ), 127.3 (C-1''), 131.1 (C-2''), 116.8 (C-3''), 161.3 (C-4''). *Nyctantbes arbortristis* (Oleaceae) (186)

238. ARBORTRISTOSIDE A



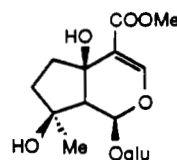
$C_{27}H_{34}O_{13}$  566.56 mp 226–228°  $[\alpha] -90^\circ$  (MeOH) uv 310, 300, 235 (EtOH) (? MHz DMSO- $d_6$ ) 5.35 (H-1, d, 8), 7.42 (H-3, s), 4.95 (H-6, m), 4.1 (H-7, t, 4.5), 2.15 (H-8, H-9, m), 1.00 (H-10, bs), 3.65 (COOMe), 4.95 (H-1', m), 4.48 (H-6', d, 9), 6.47/7.5 (H $\alpha$ , H $\beta$ , d's, 16), 7.65 (H-2'', d, 10), 6.95 (H-3'', d, 10), 3.79 (ArOMe); (DMSO- $d_6$ ) 95.1 (C-1), 152.1 (C-3), 108.5 (C-4), 42 (C-5), 76.7 (C-6), 70 (C-7), 35 (C-8), 44.6 (C-9), 14.9 (C-10), 167.2 (C-11), 51.1 (COOMe), 98.6 (C-1'), 73 (C-2'), 77.2 (C-3'), 70 (C-4'), 75.7 (C-5'), 61.2 (C-6'), 166.2 (O=C), 115.6 (C $\alpha$ ), 144.2 (C $\beta$ ), 126.7 (C-1''), 130 (C-2''), 114.4 (C-3''), 161.1 (C-4''), 55.3 (ArOMe). *Nyctantbes arbortristis* (Oleaceae) (187)

239. MUSSAENOSIDE



$C_{17}H_{26}O_{10}$  390.39  $[\alpha] -106^\circ$  (MeOH) uv 238 (MeOH) (360 MHz D<sub>2</sub>O) 5.51 (H-1, d, 2.8), 7.41 (H-3, s), 3.08 (H-5, m), 2.20, 1.69 (H-6, m's), 1.69, 1.44 (H-7, m's), 2.32 (H-9, dd, 9.7, 2.7), 1.26 (H-10, s), 3.69 (OMe), 4.75 (H-1', d, 8.1), 3.22 (H-2', dd, 9.3, 8.1), 3.45–3.30 (H-3', H-4', H-5'), 3.87 (H-6', dd, 12.4, 2.1), 3.69 (H-6', dd, 12.4, 5.8); (D<sub>2</sub>O) 95.2 (C-1), 151.9 (C-3), 113.3 (C-4), 30.3 (C-5), 29.6 (C-6), 40.4 (C-7), 80.4 (C-8), 51.4 (C-9), 23.7 (C-10), 170.6 (C-11), 52.6 (OMe), 99.1 (C-1'), 73.4 (C-2'), 76.5 (C-3'), 70.4 (C-4'), 77.1 (C-5'), 61.5 (C-6'). *Mussaenda* (Rubiaceae), *Besseyia plantaginea* (Scrophulariaceae) (2, 88, 188)

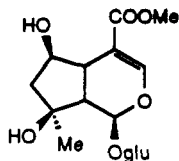
240. IPOLAMIIDE (revision of Tarphetalin)



$C_{17}H_{26}O_{11}$  406.39 mp 142–143°  $[\alpha] -139^\circ$  (MeOH) uv 231 (EtOH) (90 MHz D<sub>2</sub>O) 5.81 (H-1, d, 1.8), 7.52 (H-3, s), 2.49 (H-9, d, 0.8), 1.15 (H-10, s), 3.74 (OMe); (D<sub>2</sub>O) 94.4 (C-1), 153.0 (C-3), 113.8 (C-4), 71.3 (C-5), 37.9 (C-6), 39.4 (C-7), 79.0 (C-8), 60.6 (C-9), 22.7 (C-10), 169.0 (C-11), 52.6 (OMe), 99.2 (C-1'), 73.2 (C-2'), 76.1 (C-3'), 70.4 (C-4'), 77.1 (C-5'), 61.5 (C-6'). *Stachytarpheta jamaicensis* (Verbenaceae) (189–191)



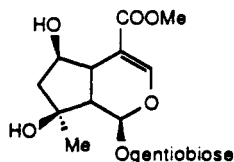
## 241. SHANZHISIDE METHYL ESTER



$C_{17}H_{26}O_{11}$  406.39 mp 116–124° [ $\alpha$ ] –115° (MeOH) uv 234 (EtOH) (250 MHz  $CD_3OD$ ) 5.57 (H-1, d, 3), 7.41 (H-3, d, 1), 2.99 (H-5, m, 10, 3.5, 1), 4.03 (H-6, m, 6.5, 6, 3.5), 2.01 (H-7, dd, 13, 6.5), 1.83 (H-7, dd, 13, 6), 2.61 (H-9, dd, 10, 3), 1.26 (H-10, s), 3.72 (OMe), 4.61 (H-1', d, 8), 3.91 (H-6', dd, 12, 2), 3.64 (H-6', dd, 12, 6); ( $CD_3OD$ ) 94.9 (C-1), 152.9 (C-3), 111.4 (C-4), 41.5 (C-5), 78.0 (C-6)<sup>a</sup>, 51.9 (C-7), 79.1 (C-8), 51.7 (C-9), 24.7 (C-10), 169.8 (C-11), 49.1 (OMe), 99.9 (C-1'), 74.6 (C-2'), 78.3 (C-3'), 71.6 (C-4'), 77.5 (C-5')<sup>a</sup>, 62.9 (C-6')

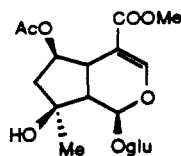
*Canthium subcordatum* (Rubiaceae) (192, 193)

## 242. SHANZHISIN METHYL ESTER GENTIOBIOSIDE



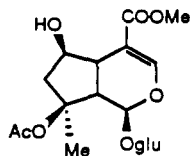
$C_{23}H_{36}O_{16}$  568.53 mp >150° (dec) [ $\alpha$ ] –56° (MeOH) uv 232 (MeOH) (250 MHz  $CD_3OD$ ) 5.54 (H-1, d, 3), 7.41 (H-3, d, 1), 3.02 (H-5, dd, 9.5, 4), 4.05 (H-6, ddd, 6, 6, 4), 2.04 (H-7, dd, 13.5, 6), 1.82 (H-7, dd, 13.5, 6), 1.28 (H-10, s), 4.64 (H-1', d, 8), 4.18 (H-6', dd, 12, 2), 4.38 (H-1'', d, 8), 3.88 (H-6'', bd, 12), 3.73 (COOMe), other signals 3.66 (m, 1-2Hs), 3.50 (dd, 8, 8), 2.58 (dd, 9.5, 3), 3.44–3.12; ( $CD_3OD$ ) 95.5 (C-1), 153.1 (C-3), 111.8 (C-4), 42.0 (C-5), 77.6 (C-6)<sup>a</sup>, 52.1 (C-7)<sup>b</sup>, 79.4 (C-8), 51.6 (C-9)<sup>b</sup>, 25.0 (C-10), 170.0 (C-11), 100.2 (C-1''), 105.3 (C-1''), 63.0 (C-6''), 78.1, 77.8<sup>a</sup>, 76.2, 75.4, 74.8, 71.9, 70.3 (C-2'–C-6', C-2''–C-5''). *Canthium subcordatum* (Rubiaceae) (192)

## 243. 6-O-ACETYLSHANZHISIDE METHYL ESTER



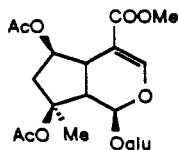
$C_{19}H_{28}O_{12}$  448.42 mp 227–228° [ $\alpha$ ] –118.7° (MeOH) uv 233 (MeOH) X-ray (80 MHz  $D_2O$ ) 5.56 (H-1, d, 4), 7.58 (H-3, s), 3.40 (H-5, m), 5.14 (H-6, m), 2.31 (H-7, dd, 14, 7), 1.91 (H-7, dd, 14, 4.5), 2.64 (H-9, dd, 9.5, 4), 1.38 (H-10, s), 3.75 (OMe), 2.17 (OAc), 4.87 (H-1', d, 7.5), 4.20–3.45 (H-2'–H-6'); ( $D_2O$ ) 94.2 (C-1), 152.8 (C-3), 108.5 (C-4), 37.3 (C-5), 78.3 (C-6), 45.6 (C-7), 78.3 (C-8), 49.8 (C-9), 24.1 (C-10), 169.1 (C-11), 51.9 (OMe), 173.6 (O=CMe), 20.7 (O=CMe), 98.4 (C-1'), 72.8 (C-2'), 75.8 (C-3')<sup>a</sup>, 69.7 (C-4'), 76.4 (C-5')<sup>a</sup>, 60.9 (C-6'). *Barleria lupulina* (Acanthaceae) (194)

## 244. 8-O-ACETYLSHANZHISIDE METHYL ESTER (revision of Barlerin)



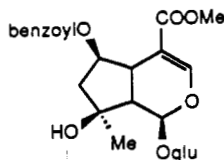
$C_{19}H_{28}O_{12}$  448.42 mp 180° [ $\alpha$ ] –85° (MeOH) uv 235 (EtOH) (?MHz  $D_2O$ ) 5.98 (H-1, d, 1.5), 7.61 (H-3, s), 3.02 (H-5, H-9, m), 2.16 (H-7, m), 1.50 (H-10, s), 3.72 (OMe), 2.00 (OAc), 4.70 (H-1', d, 7), 3.40 (H-6', m); ( $D_2O$ ) 95.4 (C-1), 153.5 (C-3), 109.2 (C-4), 41.0 (C-5), 75.3 (C-6), 46.7 (C-7), 89.8 (C-8), 48.8 (C-9), 22.5 (C-10), 61.5 (C-6'). *Barleria prionitis* (Acanthaceae) (149, 195, 196)

## 245. 6,8-DI-O-ACETYLSHANZHISIDE METHYL ESTER (revision of Acetylbarlerin)



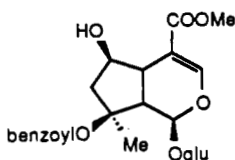
$C_{21}H_{30}O_{13}$  490.46 [ $\alpha$ ] –99° (MeOH) uv 235 (EtOH) (? MHz  $D_2O$ ) 5.90 (H-1, d, 2), 7.61 (H-3, s), 5.20 (H-6, m), 1.50 (H-10, s), 3.72 (OMe), 2.10, 2.05 (OAc), 4.70 (H-1', d, 7); ( $D_2O$ ) 95.1 (C-1), 154.3 (C-3), 108.0 (C-4), 38.7 (C-5), 78.8 (C-6), 44.3 (C-7), 89.5 (C-8), 48.9 (C-9), 22.4 (C-10), 61.5 (C-6'). *Barleria prionitis* (Acanthaceae) (195, 196)

**246. 6-O-BENZOYLSHANZHISIDE METHYL ESTER**



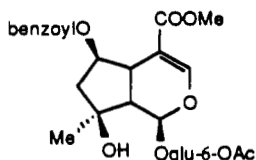
$C_{24}H_{30}O_{12}$  510.49  $[\alpha] -96^\circ$  ( $CHCl_3$ ) uv 281, 275, 241 (MeOH) (270 MHz  $CDCl_3$ ) 5.49 (H-1, d, 1.5), 7.38 (H-3, s), 5.49 (H-6, m), 1.35 (H-10, s), 4.00 (OMe), 4.74 (H-1', d, 9), 4.40–3.30 (H-6'), 8.02 (H-2', d, 8), 7.38 (H-3', t, 8), 7.52 (H-4', t, 8); ( $CDCl_3$ ) 93.6 (C-1), 151.8 (C-3), 108.6 (C-4), 36.9 (C-5), 78.2 (C-6), 46.7 (C-7), 77.6 (C-8), 50.0 (C-9), 24.3 (C-10), 167.2 (C-11), 51.0 (OMe), 98.4 (C-1'), 73.0 (C-2'), 76.3 (C-3'), 70.0 (C-4'), 76.3 (C-5'), 61.5 (C-6'), 166.1 (C=O), 130.1 (C-1''), 129.3 (C-2''), 128.1 (C-3''), 132.7 (C-4''). *Plectronia odorata* (Rubiaceae) (197)

**247. 8-O-BENZOYLSHANZHISIDE METHYL ESTER**



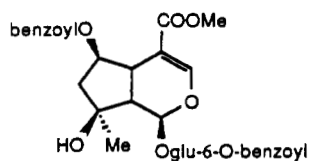
$C_{24}H_{30}O_{12}$  510.49  $[\alpha] -34^\circ$  ( $CHCl_3$ ) uv 280, 275, 243 (MeOH) (270 MHz  $CDCl_3$ ) 5.93 (H-1, d, 1.5), 7.43 (H-3, s), 1.60 (H-10, s), 3.52 (OMe), 4.72 (H-1', d, 9), 3.90–3.20 (H-6'), 7.99 (H-2'', d, 8), 7.39 (H-3'', t, 8), 7.52 (H-4'', t, 8); ( $CDCl_3$ ) 94.5 (C-1), 152.2 (C-3), 108.8 (C-4), 40.8 (C-5), 76.3 (C-6), 46.8 (C-7), 88.5 (C-8), 48.4 (C-9), 21.7 (C-10), 168.1 (C-11), 51.6 (OMe), 99.0 (C-1'), 73.0 (C-2'), 76.1 (C-3'), 69.8 (C-4'), 75.4 (C-5'), 61.7 (C-6'), 166.3 (C=O), 130.9 (C-1''), 129.6 (C-2''), 128.4 (C-3''), 133.0 (C-4''). *Plectronia odorata* (Rubiaceae) (197)

**248. 6-O-BENZOYL-6'-O-ACETYL-SHANZHISIDE METHYL ESTER**



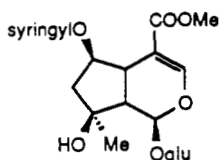
$C_{26}H_{32}O_{13}$  552.53  $[\alpha] -78^\circ$  ( $CHCl_3$ ) uv 281, 275, 242 (MeOH) (270 MHz  $CDCl_3$ ) 5.34 (H-1, d, 1.5), 7.45 (H-3, s), 3.53 (H-5, dd, 9, 4.5), 5.36 (H-6, ddd, 7, 4.5, 1), 2.23 (H-7 $\alpha$ ; dd, 16, 7), 1.99 (H-7 $\beta$ , dd, 16, 1), 2.63 (H-9, dd, 9, 1.5), 1.38 (H-10, s), 3.57 (COOMe), 4.74 (H-1', d, 9), 4.00–3.30 (H-5'), 4.41 (H-6', dd, 12, 6.5), 4.27 (H-6'', dd, 12, 2), 2.10 (OAc), 8.03 (H-2'', d, 8), 7.40 (H-3'', t, 8), 7.52 (H-4'', t, 8); ( $CDCl_3$ ) 94.1 (C-1), 152.0 (C-3), 108.6 (C-4), 38.5 (C-5), 78.7 (C-6)<sup>a</sup>, 46.4 (C-7), 78.8 (C-8)<sup>a</sup>, 50.7 (C-9), 24.9 (C-10), 171.6 (C-11), 51.5 (OMe), 98.3 (C-1'), 73.2 (C-2'), 76.0 (C-3'), 69.9 (C-4'), 74.2 (C-5'), 63.1 (C-6'), 165.9 (O=C), 130.2 (C-1''), 129.6 (C-2''), 128.4 (C-3''), 133.0 (C-4''). *Plectronia odorata* (Rubiaceae) (197)

**249. 6,6'-DI-O-BENZOYL-SHANZHISIDE METHYL ESTER**



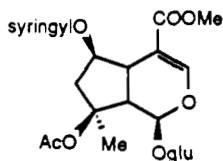
$C_{31}H_{34}O_{13}$  614.60  $[\alpha] -68^\circ$  ( $CHCl_3$ ) uv 281, 275, 243 (MeOH) (270 MHz  $CDCl_3$ ) 5.36 (H-1, d, 1.5), 7.48 (H-3, s), 3.54 (H-5, dd, 9, 2), 5.36 (H-6, m), 2.26 (H-7 $\alpha$ , dd, 16, 7), 2.00 (H-7 $\beta$ , dd, 16, 1), 2.66 (H-9, dd, 9, 1.5), 1.35 (H-10, s), 3.61 (COOMe), 4.74 (H-1', d, 9), 4.40–3.50 (H-5'), 4.74 (H-6', dd, 13, 7), 4.61 (H-6'', dd, 13, 2), 8.08 (H-2'', H-2''', d, 8), 7.48 (H-3'', H-3''', t, 8), 7.58 (H-4'', H-4''', t, 8). *Plectronia odorata* (Rubiaceae) (197)

**250. 6-O-SYRINGYLSHANZHISIDE METHYL ESTER**



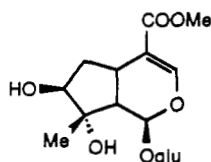
$C_{26}H_{34}O_{15}$  586.55  $[\alpha] -117.3^\circ$  (MeOH) uv 275, 221 (MeOH) (100 MHz pyridine- $d_5$ ) 6.07 (H-1, d, 4.5), 7.74 (H-3, s), 1.43 (H-10, s), 3.55 (COOMe), 5.37 (H-1', d, 7.2), 7.78 (H-2'', s), 3.80 (ArOMe); (pyridine- $d_5$ ) 94.9 (C-1), 152.6 (C-3), 109.3 (C-4), 38.2 (C-5), 78.3 (C-6), 48.1 (C-7), 77.7 (C-8), 51.3 (C-9), 25.7 (C-10), 167.1 (C-11)<sup>a</sup>, 51.3 (COOMe), 120.9 (C-1''), 108.4 (C-2''), 148.6 (C-3''), 142.7 (C-4''), 166.4 (O=C), 56.4 (ArOMe). Hydrolysis of 6-O-syringyl-8-O-acetylshanzhiside methyl ester (198)

**251. 6-O-SYRINGYL-8-O-ACETYL-SHANZHISIDE METHYL ESTER**



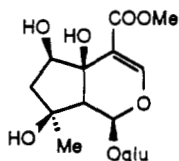
$C_{28}H_{36}O_{16}$  628.58  $[\alpha] -71.0^\circ$  (MeOH) uv 276, 221 (MeOH) (100 MHz pyridine- $d_5$ ) 6.31 (H-1, d, 3.6), 7.74 (H-3, d, 1.2), 1.71 (H-10, s), 3.60 (COOMe), 1.93 (OAc), 5.36 (H-1', d, 7.2), 7.69 (H-2'', s), 3.83 (ArOMe); (pyridine- $d_5$ ) 95.1 (C-1), 153.6 (C-3), 107.7 (C-4), 39.2 (C-5), 78.1 (C-6), 44.7 (C-7), 88.3 (C-8), 49.7 (C-9), 21.5 (C-10)<sup>a</sup>, 166.6 (C-11)<sup>b</sup>, 51.1 (COOMe), 170.5 (O=CMe), 21.9 (O=CMe)<sup>a</sup>, 165.9 (O=C)<sup>b</sup>, 120.4 (C-1''), 108.4 (C-2''), 148.5 (C-3''), 143.0 (C-4''), 56.4 (ArOMe). *Salvia digitaloides* (Labiatae) (198)

**252. 8-*epi*-CARYPTOSIDE**



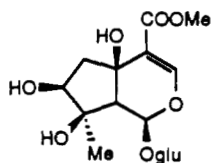
$C_{17}H_{26}O_{11}$  406.39 pentaacetate mp  $167^\circ$  (pentaacetate, ? MHz  $CDCl_3$ ) 5.35 (H-1, d, 9), 7.32 (H-3, s), 3.15 (H-5, m), 5.15-4.2 (H-7), 2.19 (H-9, m), 1.35 (H-10, s), 3.65 (OMe), 5.15-4.2 (H-1'-H-6'), 2.08, 2.0, 1.98, 1.85 (OAc); (pentaacetate  $CDCl_3$ ) 93.4 (C-1), 151.2 (C-3), 109.4 (C-4), 33.8 (C-5), 46.8 (C-6), 72.3 (C-7), 79.9 (C-8), 46.8 (C-9), — (C-10), 166.5 (C-11), 50.8 (OMe), 95.8 (C-1'), 70.7 (C-2'), 72.5 (C-3'), 68.2 (C-4'), 75.8 (C-5'), 61.7 (C-6'), 170.6, 170.1, 169.9, 169.4, 169.0 (O=CMe), 24.5, 21.2, 20.7, 20.6, 20.2 (O=CMe). *Barleria prionitis* (Acanthaceae) (19, 199)

**253. 6 $\beta$ -HYDROXYIPOLAMIIDE**



$C_{17}H_{26}O_{12}$  422.39 mp  $192-193^\circ$   $[\alpha] -161^\circ$  (MeOH) uv 231 (MeOH) (90 MHz  $D_2O$ ) 5.86 (H-1, s), 7.60 (H-3, s), 4.15 (H-6, t), 2.16, 1.90 (H-7, 13.5, 8, 6.4), 2.63 (H-9, s), 1.18 (H-10, s), 3.77 (OMe); ( $D_2O$ ) 94.2 (C-1), 154.5 (C-3), 112.8 (C-4), 70.4 (C-5), 74.5 (C-6), 47.0 (C-7), 74.7 (C-8), 59.1 (C-9), 23.6 (C-10), 169.0 (C-11), 52.7 (OMe), 99.3 (C-1'), 73.3 (C-2'), 76.1 (C-3')<sup>a</sup>, 70.4 (C-4'), 77.2 (C-5')<sup>a</sup>, 61.5 (C-6'). *Stachytarpheta mutabilis* (Verbenaceae) (200)

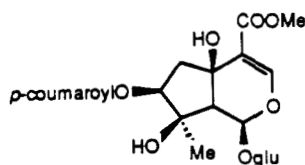
**254. LAMIIDE**



$C_{17}H_{26}O_{12}$  422.39 mp  $186-188^\circ$   $[\alpha] -127^\circ$  (MeOH) uv 229 (EtOH) (400 MHz  $CD_3OD$ ) 5.81 (H-1, d, 0.8), 7.42 (H-3, s), 2.35 (H-6, dd, 15, 5.1), 2.24 (H-6, dd, 15, 3.3), 3.51 (H-7, dd, 5, 3.4), 2.78 (H-9, bs), 1.08 (H-10, s), 3.72 (OMe), 4.59 (H-1', d, 7.9); ( $CD_3OD$ ) 95.3 (C-1), 152.4 (C-3), 115.4 (C-4), 69.2 (C-5), 46.7 (C-6), 77.6 (C-7), 79.1 (C-8), 58.0 (C-9), 21.2 (C-10), 168.0 (C-11), 99.6 (C-1'), 74.3 (C-2'), 77.4 (C-3'), 71.6 (C-4'), 78.3 (C-5'), 62.7 (C-6'), 51.7 (OMe). *Penstemon strictus* (Scrophulariaceae) (182, 201)

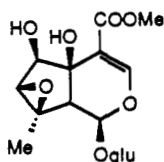
## 255. DURANTOSIDE 4

$C_{26}H_{32}O_{14}$  568.53 no data available. *Duranta plum-eri* (Verbenaceae) (202)



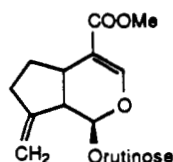
## 256. SESAMOSIDE

$C_{17}H_{24}O_{12}$  420.37 uv 234 (MeOH) (200 MHz  $CD_3OD$ ) 5.50 (H-1, d, 8.7), 7.58 (H-3, s), 4.32 (H-6, d, 1.4), 3.46 (H-7, d, 1.4), 2.52 (H-9, d, 8.7), 1.51 (H-10, s), 3.75 (COOMe), 4.72 (H-1', d, 7.8); ( $CD_3OD$ ) 96.7 (C-1), 155.4 (C-3), 112.9 (C-4), 74.9 (C-5), 77.5 (C-6), 65.9 (C-7), 63.7 (C-8), 54.3 (C-9), 17.8 (C-10), 169.0 (C-11), 52.3 (OMe), 99.9 (C-1'), 74.6 (C-2'), 77.7 (C-3')<sup>a</sup>, 71.7 (C-4'), 78.7 (C-5')<sup>a</sup>, 63.0 (C-6'). *Sesamum angolense* (Pedaliaceae) (203)



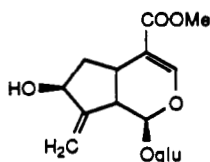
## 257. JIOGLUTOSIDE B

$C_{23}H_{34}O_{13}$  518.51  $[\alpha] -50.1^\circ$  (MeOH) uv 237 (EtOH) (500 MHz  $CD_3OD$ ) 5.29 (H-1, d, 5.3), 7.46 (H-3, d, 1.2), 3.01 (H-5, bq, 7), 2.06, 1.69 (H-6, m's), 2.34 (H-7, m), 2.77 (H-9, t), 5.11 (H-10, bdq, 7.3, 2.1), 3.67 (OMe), 4.65 (H-1', d, 7.9), 3.20 (H-2', dd, 9.1, 7.9), 3.36 (H-3', t, 9), 3.29 (H-4', dd, 9.7, 9), 3.43 (H-5', ddd, 9.7, 6.2, 1.9), 3.97 (H-6', dd, 11.3, 1.9), 3.63 (H-6'', dd, 11.3, 6.2), 4.73 (H-1'', d, 1.7), 3.81 (H-2'', dd, 3.4, 1.7), 3.65 (H-3'', dd, 9.5, 3.4), 3.36 (H-4'', t, 9.5), 3.64 (H-5'', dq, 9.5, 6.3), 1.25 (H-6'', d, 6.3); ( $CD_3OD$ ) 96.8 (C-1), 153.7 (C-3), 111.2 (C-4), 35.7 (C-5), 31.9 (C-6, C-7), 149.9 (C-8), 46.1 (C-9), 110.3 (C-10), 169.2 (C-11), 51.7 (OMe), 100.1 (C-1'), 74.6 (C-2'), 77.8 (C-3'), 71.5 (C-4'), 76.9 (C-5'), 68.0 (C-6'), 102.1 (C-1''), 72.1 (C-2''), 72.3 (C-3''), 73.8 (C-4''), 69.7 (C-5''), 18.0 (C-6''). *Rebmannia glutinosa* var. *bueichingensis* (Scrophulariaceae) (75)



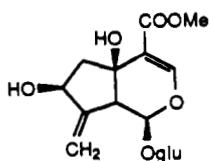
## 258. GARDOSIDE METHYL ESTER

$C_{17}H_{24}O_{10}$  388.37  $[\alpha] -35.1^\circ$  (MeOH) uv 240 (MeOH) (400 MHz  $D_2O$ ) 5.40 (H-1, d, 4.0), 7.40 (H-3, d, 0.5), 3.1–3.0 (H-5), 2.0–1.8 (H-6), 4.37 (H-7, bt, 6.0), 3.1–3.0 (H-9), 5.30 (H-10, bs), 3.65 (COOMe), 4.85 (H-1', d, 8.0), 3.22 (H-2', dd, 9.2, 8.0), 3.48–3.35 (H-3'), 3.30 (H-4', bt, 11), 3.48–3.35 (H-5'), 3.95 (H-6', dd, 13.3, 2.2), 3.62 (H-6'', dd, 13.3, 6.6); ( $D_2O$ ) 96.5 (C-1), 153.1 (C-3), 113.5 (C-4), 30.6 (C-5), 39.0 (C-6), 72.8 (C-7), 150.9 (C-8), 43.8 (C-9), 111.1 (C-10), 169.9 (C-11), 52.4 (OMe), 99.0 (C-1'), 73.2 (C-2'), 76.8 (C-3')<sup>a</sup>, 70.1 (C-4'), 76.1 (C-5')<sup>a</sup>, 61.2 (C-6'). *Parentucellia viscosa*, *Melampyrum arvense* (Scrophulariaceae) (146, 204)

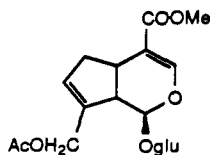


## 259. STRICTOLOSIDE

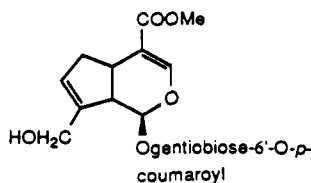
$C_{17}H_{24}O_{11}$  404.37 mp 88–91° (400 MHz  $CD_3OD$ ) 5.87 (H-1, d, 1.8), 7.50 (H-3, s), 2.92 (H-6, dd, 12, 7), 1.88 (H-6, dd, 12, 10.5), 4.12 (H-7, m), 3.14 (H-9, m), 5.33, 5.27 (H-10, r's, 2.4), 3.72 (COOMe), 4.57 (H-1', d, 7.9); ( $CD_3OD$ ) 96.7 (C-1), 154.8 (C-3), 112.5 (C-4), 69.9 (C-5), 46.1 (C-6), 71.9 (C-7), 151.4 (C-8), 53.6 (C-9), 111.5 (C-10), 167.8 (C-11), 51.7 (OMe), 100.0 (C-1'), 74.3 (C-2'), 77.5 (C-3'), 71.6 (C-4'), 78.4 (C-5'), 62.7 (C-6'). *Penstemon strictus* (Scrophulariaceae) (182)



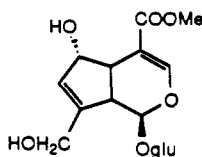
## 260. 10-O-ACETYLGENIPOSIDE



$C_{19}H_{26}O_{11}$  430.41 mp 173–175°  $[\alpha] +22.1$  (MeOH) uv 239 (MeOH) (60 MHz  $CD_3OD$ ) 5.13 (H-1, d, 8.0), 7.51 (H-3, d, 1.0), 5.83 (H-7, m), 3.68 (OMe), 2.04 (OAc). *Gardenia jasminoides* forma *grandiflora* (Rubiaceae) (205)

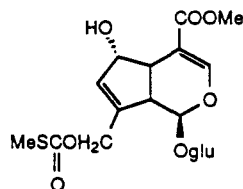
261. 6''-O-*p*-COUMAROYLGENIPIIN GENTIOBIOSIDE

$C_{32}H_{40}O_{17}$  696.66  $[\alpha] +3.9^\circ$  (MeOH) uv 313, 300, 230 (MeOH) (? MHz  $D_2O/Me_2CO-d_6$ ) 5.21 (H-1, d, 7.3), 7.46 (H-3, d, 1.0), 3.14 (H-5, dd, 14.5, 7.7), 2.76, 2.21 (H-6, m's), 5.81 (H-7, bs), 2.76 (H-9, t, 7.7), 4.31, 4.19 (H-10, d's, 14.0), 3.69 (COOMe), 4.77 (H-1', d, 8.1), 3.55–3.27 (H-2'–H-5', H-2''–H-5''), 4.14 (H-6', dd, 11.7, 1.8), 3.88 (H-6', m), 4.48 (H-1'', d, 7.7), 4.53 (H-6'', dd, 12.1, 1.8), 4.31 (H-6'', dd, 12.1, 5.9), 6.40/7.66 (H $\alpha$ , H $\beta$ , d's, 16.1), 7.56 (H-2''', d, 8.8), 6.90 (H-3''', d, 8.8); ( $D_2O/Me_2CO-d_6$ ) 98.0 (C-1), 143.6 (C-3), 112.2 (C-4), 35.6 (C-5), 39.2 (C-6), 128.9 (C-7), 148.9 (C-8), 46.5 (C-9), 60.7 (C-10), 169.5 (C-11), 52.1 (OMe), 100.0 (C-1'), 74.6 (C-2')<sup>a</sup>, 76.9 (C-3')<sup>b</sup>, 70.9 (C-4')<sup>c</sup>, 76.9 (C-5'), 69.5 (C-6'), 104.1 (C-1''), 73.9 (C-2'')<sup>a</sup>, 76.3 (C-3'')<sup>b</sup>, 70.4 (C-4'')<sup>c</sup>, 74.2 (C-5''), 64.5 (C-6''), 168.9 (O=C), 114.8 (C $\alpha$ ), 146.6 (C $\beta$ ), 126.7 (C-1'''), 131.2 (C-2'''), 116.8 (C-3'''), 153.1 (C-4'''). *Gardenia jasminoides* (Rubiaceae) (206)

262. 6 $\alpha$ -HYDROXYGENIPOSIDE (Deacetyldaphylloside, Deacetylasperulosidic acid methyl ester)

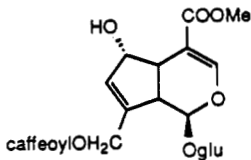
$C_{17}H_{24}O_{11}$  404.37 mp 129–133° uv 238 ( $H_2O$ ) (200 MHz  $D_2O$ ) 5.05 (H-1, d, 9.0), 7.65 (H-3, d, 1.2), 3.26 (H-5, m), 6.01 (H-7, m), 2.56 (H-9, br, 9.0), 4.45 (H-10, 2d's, 15), 3.47 (COOMe); ( $CD_3OD$ ) 101.6 (C-1), 155.4 (C-3), 108.3 (C-4), 42.7 (C-5), 75.4 (C-6), 130.0 (C-7), 151.5 (C-8), 45.9 (C-9), 61.7 (C-10), 169.5 (C-11), 51.6 (OMe), 100.5 (C-1'), 75.0 (C-2'), 77.8 (C-3'), 71.6 (C-4'), 78.5 (C-5'), 62.8 (C-6'). Hydrolysis of asperuloside and gardenoside (207–209)

## 263. METHYL PAEDEROSIDATE



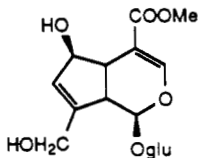
$C_{19}H_{26}O_{12}S$  478.47  $[\alpha] +13^\circ$  (MeOH) (200 MHz  $CD_3OD$ ) 5.06 (H-1, d, 8.4), 7.66 (H-3, d, 1.2), 3.04 (H-5, m, 7.8, 6.0, 1.2), 3.62 (H-6, dd, 12.0, 6.0), 6.02 (H-7, m), 2.63 (H-9, dd, 8.4, 7.8), 5.10, 4.94 (H-10, bd's, 15), 3.74 (OMe), 2.34 (SMe), 4.72 (H-1', d, 7.6), 3.86 (H-6', dd, 12.0, 1.2); ( $D_2O$ ) 101.7 (C-1), 157.7 (C-3), 109.3 (C-4), 42.8 (C-5), 72.6 (C-6), 134.4 (C-7), 146.3 (C-8), 47.2 (C-9), 68.1 (C-10), 172.4 (C-11), 54.6 (OMe), 176.5 (O=CSMe), 15.6 (O=CSMe), 103.0 (C-1'), 76.7 (C-2'), 78.4 (C-3'), 72.3 (C-4'), 78.9 (C-5'), 63.6 (C-6'). Artifact of the extraction of the aphid *Acyrtosiphon nipponicus* (159)

264. 10-O-CAFFEYOYLDEACETYL-DAPHYLLOSIDE



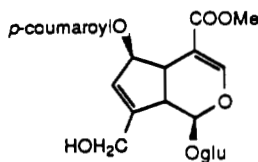
$C_{26}H_{30}O_{14}$  556.52  $[\alpha] -3.6^{\circ}$  (MeOH) uv 330, 303, 235, 223 (MeOH) (heptaacetate 250 MHz  $CDCl_3$ ) 4.80 (H-1, d, 8), 7.54 (H-3, d, 1.5), 3.25 (H-5, td, 8, 1.5), 5.74 (H-6, dd, 8, 2), 6.07 (H-7, d, 2), 2.65 (H-9, t, 8), 4.92 (H-10), 3.71 (COOMe), 4.94 (H-1', d), 5.23–5.05 (H-2'–H-4'), 3.73 (H-5', m), 4.17 (H-6'), 2.3–1.93 (OAc), 6.40/7.63 (H $\alpha$ , H $\beta$ , d's, 16), 7.36 (H-2'', d, 2), 7.20 (H-5'', d, 8.5), 7.41 (H-6'', dd, 8.5, 2); ( $CD_3OD$ ) 100.7 (C-1), 155.4 (C-3), 108.0 (C-4), 42.3 (C-5), 75.3 (C-6), 131.7 (C-7), 146.1 (C-8), 46.3 (C-9), 63.3 (C-10), 169.3 (C-11), 51.9 (OMe), 101.4 (C-1'), 74.8 (C-2'), 77.8 (C-3'), 71.5 (C-4'), 78.3 (C-5'), 62.9 (C-6'), 168.8 (O=C), 114.8 (C $\alpha$ )<sup>a</sup>, 147.4 (C $\beta$ ), 127.6 (C-1''), 116.5 (C-2''), 146.7 (C-3''), 149.6 (C-4''), 115.3 (C-5'')<sup>a</sup>, 123.1 (C-6''). *Randia formosa* (Rubiaceae) (210)

265. 6 $\beta$ -HYDROXYGENIPOSIDE (Scandoside methyl ester)



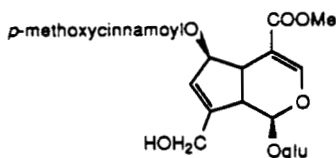
$C_{17}H_{24}O_{11}$  404.37 ( $CD_3OD$ ) 98.4 (C-1), 153.9 (C-3), 110.0 (C-4), 47.1 (C-5), 82.9 (C-6), 130.0 (C-7), 147.9 (C-8), 47.6 (C-9), 61.4 (C-10), 171.0 (C-11), 52.1 (OMe), 100.3 (C-1'), 74.8 (C-2'), 77.9 (C-3'), 71.5 (C-4'), 78.4 (C-5'), 61.0 (C-6'). (208, 211)

266. 6-O-*p*-COUMAROYLSCANDOSIDE METHYL ESTER (Oldenlandoside I)



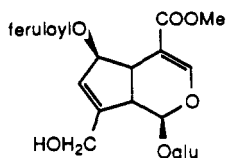
$C_{26}H_{30}O_{13}$  550.52 mp 141–142°  $[\alpha] -180^{\circ}$  (MeOH) uv 314, 302, 231 (EtOH) (60 MHz  $CD_3OD$ ) 5.15 (H-1, d, 5), 7.32 (H-3, d), 5.53 (H-6, bs), 5.70 (H-7, bs), 4.30 (H-10, bs), 3.53 (COOMe), 6.15/7.43 (H $\alpha$ , H $\beta$ , d's, 16), 7.27 (H-2'', d, 8), 6.63 (H-3'', d, 8); (DMSO- $d_6$ ) 95.2 (C-1), 152.2 (C-3), 108.1 (C-4), 41.1 (C-5), 81.4 (C-6), 124.7 (C-7), 149.9 (C-8), 45.5 (C-9), 58.9 (C-10), 166.4 (C-11)<sup>a</sup>, 51.0 (OMe), 98.4 (C-1'), 73.1 (C-2'), 77.2 (C-3'), 69.9 (C-4'), 76.5 (C-5'), 61.0 (C-6'), 166.0 (O=C)<sup>a</sup>, 114.3 (C $\alpha$ ), 144.6 (C $\beta$ ), 125.0 (C-1''), 130.2 (C-2''), 115.7 (C-3''), 159.7 (C-4''). *Oldenlandia diffusa* = *Hedyotis diffusa* (Rubiaceae) (212, 213)

267. 6-O-*p*-METHOXYCINNAMOYL-SCANDOSIDE METHYL ESTER



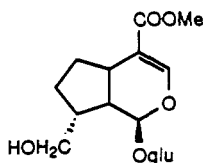
$C_{27}H_{32}O_{13}$  564.54 mp 114–116°  $[\alpha] -165^{\circ}$  (MeOH) uv 312, 299, 230 (EtOH) (60 MHz DMSO- $d_6$ ) 5.34 (H-1, d, 5), 7.50 (H-3, s), 5.78 (H-7, m), 3.60 (COOMe), 6.47/7.67 (H $\alpha$ , H $\beta$ , d's, 16), 7.58 (H-2'', d, 8), 7.00 (H-3'', d, 8), 3.81 (ArOMe); (DMSO- $d_6$ ) 95.3 (C-1), 152.2 (C-3), 108.1 (C-4), 40.1 (C-5), 81.6 (C-6), 124.7 (C-7), 149.9 (C-8), 45.6 (C-9), 58.9 (C-10), 166.4 (C-11)<sup>a</sup>, 51.0 (COOMe), 98.5 (C-1'), 73.1 (C-2'), 77.2 (C-3'), 69.9 (C-4'), 76.5 (C-5'), 61.0 (C-6'), 165.8 (O=C), 144.1 (C $\alpha$ ), 114.3 (C $\beta$ ), 126.6 (C-1''), 130.0 (C-2''), 115.5 (C-3''), 150.1 (C-4''), 55.2 (ArOMe). *Hedyotis diffusa* (Rubiaceae) (213)

268. 6-O-FERULOYLSCANDOSIDE  
METHYL ESTER (Oldenlandoside II)



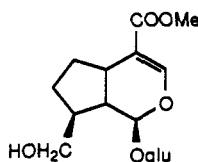
$C_{27}H_{32}O_{14}$  580.54 mp 124–126°  $[\alpha] -164^{\circ}$  (MeOH) uv 327.5, 299, 236, 221 (EtOH) (60 MHz DMSO- $d_6$ ) 5.35 (H-1, d, 4.5), 7.50 (H-3, s), 5.78 (H-7, m), 3.60 (COOMe), 6.45/7.62 (H $\alpha$ , H $\beta$ , d's, 16), 7.35 (H-2'', m), 6.83 (H-5'', d, 8.5), 7.20 (H-6'', d, 8.5), 3.83 (ArOMe); (DMSO- $d_6$ ) 95.3 (C-1), 151.7 (C-3), 108.1 (C-4), 39.9 (C-5), 81.3 (C-6), 124.7 (C-7), 149.5 (C-8), 45.5 (C-9), 58.6 (C-10), 166.1 (C-11)<sup>a</sup>, 50.6 (COOMe), 98.5 (C-1'), 73.0 (C-2'), 76.9 (C-3'), 69.9 (C-4'), 76.4 (C-5'), 60.9 (C-6'), 165.6 (O=C)<sup>a</sup>, 144.3 (C $\alpha$ ), 114.6 (C $\beta$ ), 125.5 (C-1''), 111.7 (C-2''), 149.1 (C-3''), 147.7 (C-4''), 115.4 (C-5''), 122.4 (C-6''), 55.7 (ArOMe). *Oldenlandia diffusa* = *Hedyotis diffusa* (Rubiaceae) (212, 213)

269. 8 $\alpha$ -DIHYDROGENIPOSIDE



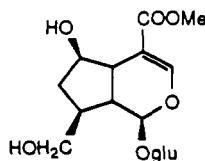
$C_{17}H_{26}O_{10}$  390.39 mp 148.5–150°  $[\alpha] -82.2^{\circ}$  (MeOH) uv 238.5 (MeOH) (60 MHz D<sub>2</sub>O) 5.52 (H-1, d, 5.5), 7.51 (H-3, s), 3.75 (OMe), 4.85 (H-1', d, 7); (D<sub>2</sub>O) 96.1 (C-1), 152.7 (C-3), 112.4 (C-4), 34.8 (C-5), 27.0 (C-6)<sup>a</sup>, 31.3 (C-7)<sup>a</sup>, 42.2 (C-8)<sup>b</sup>, 44.7 (C-9)<sup>b</sup>, 63.3 (C-10), 170.3 (C-11), 52.5 (OMe), 99.4 (C-1'), 73.6 (C-2'), 77.1 (C-3'), 70.4 (C-4'), 76.5 (C-5'), 61.6 (C-6'). Catalytic hydrogenation (Pt) of geniposide (44, 214)

270. ADOXOSIDE (8 $\beta$ -Dihydrogeniposide, 6,7-Dihydroapodantheroside)



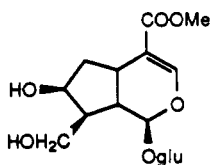
$C_{17}H_{26}O_{10}$  390.39  $[\alpha] -81.0^{\circ}$  (MeOH) uv 234 (MeOH) (360 MHz D<sub>2</sub>O) 5.23 (H-1, d, 6), 7.48 (H-3, d, 1.0), 2.83 (H-5, bq, 14.3, 7.0), 2.08, 1.42 (H-6, m's), 1.80, 1.32 (H-7, m's), 2.08 (H-8, m), 1.96 (H-9, bdd, 13.7, 6.0), 3.58 (H-10, dd, 11.0, 7.0), 3.53 (H-10, dd, 11.0, 7.5), 3.70 (OMe), 4.78 (H-1', d, 8.1), 3.28 (H-2', dd, 9.2, 8.1), 3.45–3.35 (H-3'–H-5'), 3.88 (H-6', dd, 12.4, 2.1), 3.70 (H-6', dd, 12.4, 5.5); (D<sub>2</sub>O) 98.6 (C-1), 153.2 (C-3), 111.8 (C-4), 35.0 (C-5), 32.4 (C-6), 27.8 (C-7), 43.1 (C-8), 43.7 (C-9), 65.9 (C-10), 170.7 (C-11), 52.6 (OMe), 99.9 (C-1'), 73.6 (C-2'), 76.6 (C-3'), 70.4 (C-4'), 77.1 (C-5'), 61.5 (C-6'). *Castilleja integra*, *Euphrasia rostkoviana* (Scrophulariaceae) (2, 66, 88, 215)

271. 6 $\beta$ -HYDROXYADOXOSIDE

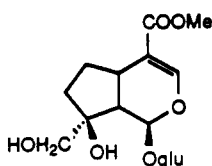


$C_{17}H_{26}O_{11}$  406.39  $[\alpha] -83.4^{\circ}$  (MeOH) (360 MHz D<sub>2</sub>O) 5.48 (H-1, d, 3.9), 7.49 (H-3, d, 1.3), 2.90 (H-5, bdd, 7.8, 3.4), 4.21 (H-6, bdd, 7.8, 3.7), 2.12, 1.37 (H-7, m's), 2.12 (H-8, m), 2.33 (H-9, m), 3.64 (H-10, dd, 11.0, 6.3), 3.60 (H-10, 11.0, 6.1), 3.73 (OMe), 4.77 (H-1', d, 8.1), 3.25 (H-2', dd, 9.3, 8.1), 3.50–3.35 (H-3'–H-5'), 3.90 (H-6', dd, 12.3, 2.1), 3.70 (H-6', dd, 12.3, 5.7); (D<sub>2</sub>O) 97.3 (C-1), 153.5 (C-3), 109.4 (C-4), 41.0 (C-5)<sup>a</sup>, 76.9 (C-6)<sup>b</sup>, 35.7 (C-7), 41.6 (C-8)<sup>a</sup>, 42.6 (C-9)<sup>a</sup>, 65.9 (C-10), 170.5 (C-11), 52.6 (OMe), 99.5 (C-1'), 73.4 (C-2'), 76.4 (C-3')<sup>b</sup>, 70.4 (C-4'), 77.2 (C-5'), 61.5 (C-6'). *Castilleja integra* (Scrophulariaceae) (88)

## 272. 10-HYDROXYLOGANIN

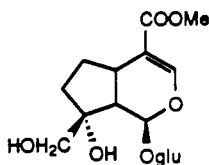


$C_{17}H_{26}O_{11}$  406.39 hexaacetate  $[\alpha] -58.9^\circ$  (MeOH) uv 236 (MeOH) (200 MHz  $CD_3OD$ ) 5.16 (H-1, d, 6), 7.46 (H-3, d, 1.2), 1.54 (H-6ax, ddd, 14, 10, 4.5), 2.26 (H-6eq, ddd, 14, 7, 1.5), 4.30 (H-7, t), 2.08 (H-8, H-9, m), 4.81 (H-1', d, 8 in  $D_2O$ ), 3.76 (COOMe in  $D_2O$ ). *Galium mollugo* (Rubiaceae) (153, 216)

273. 8-*epi*-SPLENDOSIDE

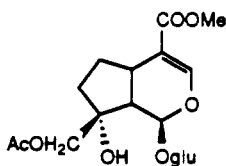
$C_{17}H_{26}O_{11}$  406.39 mp 100–102°  $[\alpha] -66.7^\circ$  (MeOH) ( $D_2O$ ) 95.2 (C-1), 152.5 (C-3), 112.4 (C-4), 32.5 (C-5), 29.4 (C-6), 34.3 (C-7), 84.7 (C-8), 50.4 (C-9), 66.0 (C-10), 171.2 (C-11), 52.7 (OMe), 99.4 (C-1'), 73.5 (C-2'), 76.4 (C-3'), 70.3 (C-4'), 77.1 (C-5'), 61.5 (C-6'). Catalytic hydrogenation of gardenoside (2, 217)

## 274. SPLENDOSIDE



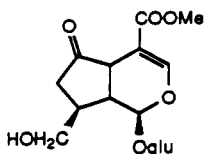
$C_{17}H_{26}O_{11}$  406.39 pentaacetate mp 124–125°  $[\alpha] -68.5^\circ$  (EtOH) (90 MHz  $D_2O$ ) 5.54 (H-1, d, 4), 7.52 (H-3, d, 1.5), 3.0 (H-5, m), 2.34 (H-9, dd, 9, 4), 3.60 (H-10, s), 3.76 (OMe); ( $D_2O$ ) 96.0 (C-1), 153.0 (C-3), 112.2 (C-4), 33.6 (C-5), 30.6 (C-6), 36.0 (C-7), 82.9 (C-8), 45.7 (C-9), 68.6 (C-10), 170.4 (C-11), 52.6 (OMe), 99.8 (C-1'), 73.5 (C-2'), 76.5 (C-3'), 70.3 (C-4'), 77.1 (C-5'), 61.5 (C-6'). *Fouquieria diguetii* (Fouquieriaceae) (185)

## 275. SPLENDOSIDE 10-ACETATE (10-O-Acetylsplendoside)



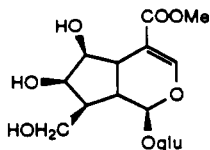
$C_{19}H_{28}O_{12}$  448.42 (90 MHz  $D_2O$ ) 4.11 (H-10, s), 2.12 (OAc); ( $D_2O$ ) 95.5 (C-1), 152.6 (C-3), 112.6 (C-4), 32.4 (C-5), 30.1 (C-6), 36.3 (C-7), 80.9 (C-8), 46.6 (C-9), 71.0 (C-10), 170.6 (C-11), 52.5 (OMe), 99.4 (C-1'), 73.4 (C-2'), 76.3 (C-3'), 70.2 (C-4'), 77.0 (C-5'), 61.4 (C-6'). *Fouquieria diguetii* (Fouquieriaceae) (185)

## 276. 10-HYDROXYCORNIN



$C_{17}H_{24}O_{11}$  404.37 no data available. *Penstemon nitidus* (Scrophulariaceae) (181)

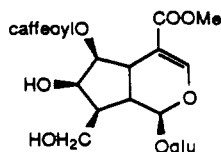
## 277. NYCTANTHOSIDE (revision of stereochemistry at C-8)



$C_{17}H_{26}O_{12}$  422.39 no data given. (185)

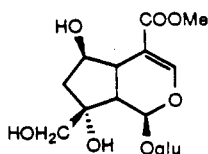


**278. ARBORTRISTOSIDE B (6-O-Caffeoyl-nyctanthoside)**



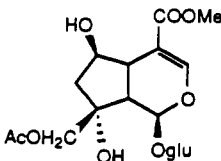
$C_{26}H_{32}O_{15}$  584.53  $[\alpha] -69^\circ$  (MeOH) mp 156–158 $^\circ$  (octaacetate) (octaacetate, ? MHz  $CDCl_3$ ) 5.4 (H-1, d, 8), 7.39 (H-3, s), 3.05 (H-5, dd, 7.5, 1.5), 5.4 (H-6), 2.38 (H-9, m), 4.25 (H-10, m), 3.7 (COOMe), 5.4 (H-1', d, 8), 5.3–4.7 (H-2'–H-4', m), 4.25 (H-6', m), 6.36/7.65 (H $\alpha$ , H $\beta$ , d's, 16), 7.39 (H-2'', d, 2), 7.21 (H-5'', d, 10), 7.45 (H-6'', dd, 10, 2); (octaacetate  $CDCl_3$ ) 94.5 (C-1), 151.7 (C-3), 108.8 (C-4), 39.4 (C-5), 76.4 (C-6), 72 (C-7), 35.3 (C-8), 41.6 (C-9), 63.4 (C-10), 168 (C-11), 51.6 (OMe), 96.0 (C-1'), 70.6 (C-2'), 72.4 (C-3'), 68.1 (C-4'), 72.4 (C-5'), 61.5 (C-6'), 166.2 (O=C), 118.5 (C $\alpha$ ), 143.8 (C $\beta$ ), 133.0 (C-1''), 124.1 (C-2''), 142.6 (C-3''), 143.8 (C-4''), 123.0 (C-5''), 126.5 (C-6''), 170.6, 170.2, 169.9, 169.6, 169.4, 169.1 (O=CMe), 20.6, 20.1 (O=CMe). *Nyctanthes arbortristis* (Oleaceae) (187)

**279. 6 $\beta$ -HYDROXYSPLENDOSIDE**



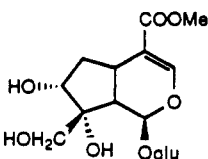
$C_{17}H_{26}O_{12}$  422.39 pentaacetate mp 140–141 $^\circ$   $[\alpha] -80.5^\circ$  ( $CHCl_3$ ) (270 MHz  $D_2O$ ) 5.63 (H-1, d, 2.5), 7.54 (H-3, d, 1.5), 2.94 (H-5, bdd, 9, 3), 4.34 (H-6, m, 9, 2.5), 2.65 (H-9, dd), 3.67 (H-10, s), 3.76 (OMe); ( $D_2O$ ) 95.1 (C-1), 153.6 (C-3), 109.8 (C-4), 40.4 (C-5), 76.3 (C-6), 44.0 (C-7), 81.7 (C-8), 44.5 (C-9), 69.0 (C-10), 170.4 (C-11), 52.7 (OMe), 99.2 (C-1'), 73.4 (C-2'), 76.3 (C-3'), 70.3 (C-4'), 77.0 (C-5'), 61.4 (C-6'). *Fouquieria diguetii* (Fouquieriaceae) (185)

**280. 6 $\beta$ -HYDROXYSPLENDOSIDE 10-ACETATE**



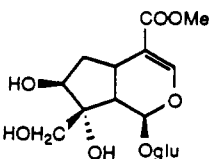
$C_{19}H_{28}O_{13}$  464.42 (90 MHz  $D_2O$ ) 4.25 (H-10, bs), 2.19 (OAc); ( $D_2O$ ) 94.8 (C-1), 153.5 (C-3), 109.3 (C-4), 40.2 (C-5), 75.9 (C-6), 44.2 (C-9), 80.0 (C-8), 45.2 (C-9), 72.0 (C-10), — (C-11), 52.6 (OMe), 99.0 (C-1'), 73.3 (C-2'), 76.3 (C-3'), 70.2 (C-4'), 77.0 (C-5'), 61.4 (C-6'). *Fouquieria diguetii* (Fouquieriaceae) (185)

**281. 7 $\alpha$ -HYDROXYSPLENDOSIDE**



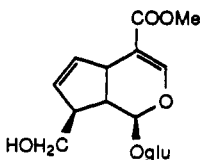
$C_{17}H_{26}O_{12}$  422.39 hexaacetate mp 175–176 $^\circ$   $[\alpha] -99.2^\circ$  ( $CHCl_3$ ) (hexaacetate 270 MHz  $CDCl_3$ ) 5.51 (H-1, d, 3.5), 7.37 (H-3, bs), 2.90 (H-5, q), 2.64 (H-6 $\alpha$ , dt, 13.0, 8.0, 7.0), 1.73 (H-6 $\beta$ , dt, 13.0, 9.0, 7.5), 4.96 (H-7, dd, 9.0, 7.0), 2.38 (H-9, dd, 10.0, 3.5), 4.08 (H-10), 3.71 (OMe); (hexaacetate  $CDCl_3$ ) 93.1 (C-1), 149.6 (C-3), 112.2 (C-4), 27.5 (C-5), 34.9 (C-6), 74.8 (C-7), 78.1 (C-8), 43.2 (C-9), 66.5 (C-10), — (C-11), 51.1 (OMe), 96.1 (C-1'), 70.3 (C-2'), 72.0 (C-3'), 67.9 (C-4'), 72.0 (C-5'), 61.4 (C-6'). Oxidation of geniposide pentaacetate (185)

**282. 7 $\beta$ -HYDROXYSPLENDOSIDE**



$C_{17}H_{26}O_{12}$  422.39 hexaacetate mp 131–133 $^\circ$   $[\alpha] -57.0^\circ$  ( $CHCl_3$ ) (hexaacetate 270 MHz  $CDCl_3$ ) 5.38 (H-1, d, 4.5), 7.40 (H-3, d, 1.5), 3.05 (H-5, m), 2.25 (H-6 $\alpha$ , ddd, 14.0, 7.5, 4.5), 2.10 (H-6 $\beta$ , ddd, 14.0, 7.5, 4.5), 5.00 (H-7, t, 4.5, 4.5), 2.45 (H-9, dd, 9.5, 4.5), 4.18 (H-10), 3.71 (OMe), 2.09–1.96 (OAc); (hexaacetate  $CDCl_3$ ) 94.1 (C-1), 150 (C-3), 111.4 (C-4), 29.7 (C-5), 35.9 (C-6), 80.2 (C-7), 80.6 (C-8), 44.4 (C-9), 66.3 (C-10), 166.5 (C-11), — (OMe), 96.6 (C-1'), 70.2 (C-2'), 72.0 (C-3'), 67.9 (C-4'), 72.0 (C-5'), 61.4 (C-6'). *Fouquieria diguetii* (Fouquieriaceae) (185)

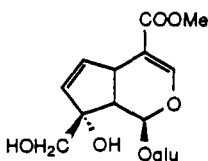
## 283. APODANTHEROSIDE



$C_{17}H_{24}O_{10}$  388.27 pentaacetate mp 126° uv 233 (?) (pentaacetate 270 MHz  $CDCl_3$ ) 6.15 (H-1, s), 7.35 (H-3, s), 3.7 (H-5, dd, 9, 2.5), 6.3 (H-6, dd, 6, 2.5), 5.9 (H-7, dd, 6, 1.5), 3.0 (H-8, dd, 9, 1.5), 2.55 (H-9, t, 9), 4.2 (H-10, d, 12), 3.75 (COOMe), 4.3 (H-6', d, 12), 2.05–1.95 (OAc). *Ferretia apodanthera* (Rubiaceae) (215)

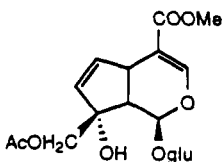
## 284. MONOTROPEIN METHYL ESTER

(Galioside)

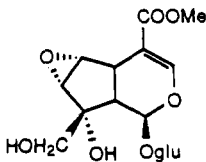


$C_{17}H_{24}O_{11}$  404.37  $[\alpha] -86.2^\circ$  (MeOH) uv 238 (MeOH) (90 MHz  $D_2O$ ) 5.72 (H-1, d, 1.9), 7.50 (H-3, d, 1.3), 3.5–3.0 (H-5, m), 6.32 (H-6, dd, 5.7, 3.0), 5.78 (H-7, dd, 5.7, 1.7), 2.78 (H-9, dd, 8.3, 1.9), 3.82 (OMe); ( $D_2O$ ) 94.4 (C-1), 151.2 (C-3), 110.3 (C-4), 37.1 (C-5), 137.0 (C-6), 132.1 (C-7), 84.7 (C-8), 44.1 (C-9), 69.6 (C-10), 169.3 (C-11), 51.8 (OMe), 98.4 (C-1'), 72.7 (C-2'), 76.3 (C-3'), 72.5 (C-4'), 75.7 (C-5'), 60.7 (C-6'). (154, 218)

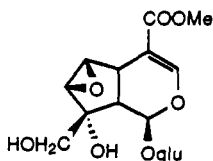
## 285. GALIOSIDE 10-ACETATE



$C_{19}H_{26}O_{12}$  446.41  $[\alpha] -63.6^\circ$  (MeOH) (90 MHz  $D_2O$ ) 4.25 (H-10, s), 2.17 (OAc); ( $D_2O$ ) 95.0 (C-1), 151.9 (C-3), 110.8 (C-4), 37.6 (C-5), 131.8 (C-6), 138.3 (C-7), 83.8 (C-8), 45.7 (C-9), 70.7 (C-10), 170.0 (C-11), 52.6 (OMe), 99.0 (C-1'), 73.4 (C-2'), 76.4 (C-3'), 70.3 (C-4'), 76.9 (C-5'), 61.4 (C-6'). *Fouquieria diguetii* (Fouquieriaceae) (185)

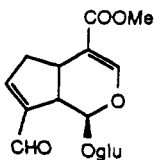
286. 6 $\alpha$ ,7 $\alpha$ -EPOXYSPLENDOSIDE

$C_{17}H_{24}O_{12}$  420.37 pentaacetate  $[\alpha] -6.5^\circ$  ( $CHCl_3$ ) (pentaacetate 90 MHz  $CDCl_3$ ) 5.31 (H-1, d, 9.0), 7.47 (H-3, d, 2.0), 3.09 (H-5, m), 3.8 (H-6), 3.49 (H-7, d, 3.0), 1.93 (H-9, t, 9.0), 4.11 (H-10), 3.76 (COOMe), 2.14–1.98 (OAc); (pentaacetate  $CDCl_3$ ) 98.6 (C-1), 152.5 (C-3), 104.5 (C-4), 36.4 (C-5), 60.0 (C-6), 56.1 (C-7), 79.3 (C-8), 39.4 (C-9), 67.3 (C-10), 166.6 (C-11), 51.4 (OMe), 99.2 (C-1'), 70.8 (C-2'), 72.4 (C-3'), 68.2 (C-4'), 72.4 (C-5'), 61.4 (C-6'). Oxidation of galioside pentaacetate (185)

287. 6 $\beta$ ,7 $\beta$ -EPOXYSPLENDOSIDE

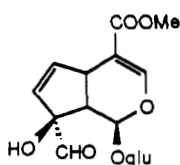
$C_{17}H_{24}O_{12}$  420.37 pentaacetate mp 182–183°  $[\alpha] -85.6^\circ$  ( $CHCl_3$ ) (90 MHz  $D_2O$ ) 5.66 (H-1, bs), 7.53 (H-3, d, 1.5), 4.00 (H-6, bd, 2.5), 3.48 (H-7, d, 2.5), 2.22 (H-9, bd, 8.5), 3.76 (COOMe); (pentaacetate  $CHCl_3$ ) 92.3 (C-1), 151.6 (C-3), 106.8 (C-4), 31.6 (C-5), 59.0 (C-6)<sup>a</sup>, 58.3 (C-7)<sup>a</sup>, 77.6 (C-8), 42.7 (C-9), 68.1 (C-10), 166.1 (C-11), 51.2 (OMe), 95.0 (C-1'), 70.3 (C-2'), 72.1 (C-3'), 67.8 (C-4'), 72.1 (C-5'), 61.4 (C-6'). *Fouquieria diguetii* (Fouquieriaceae) (185)

## 288. 10-DEHYDROGENIPOSIDE

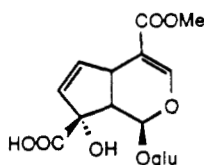


$C_{17}H_{22}O_{10}$  386.35 tetraacetate mp 128–130° (tetraacetate 200 MHz  $CDCl_3$ ) 6.17 (H-1, d, 2.1), 7.36 (H-3, s), 2.91, 2.72 (H-6, m's), 6.93 (H-7, m), 9.75 (H-10, s), 3.71 (COOMe), 2.13, 2.03, 2.00, 1.90 (OAc). Hydrolysis of gardenoside (207)

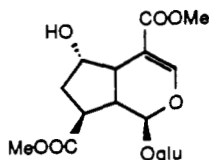
## 289. 10-DEHYDROGARDENOSIDE



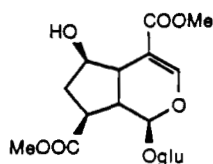
$C_{17}H_{22}O_{11}$  402.35 (pentaacetate 60 MHz  $CDCl_3$ ) 5.60 (H-1, d, 2.0), 7.30 (H-3, bs), 6.63 (H-6, dd, 7.0, 3.0), 6.03 (H-7, dd, 7.0, 2.0), 3.07 (H-9, dd, 9.5, 2.0), 9.44 (H-10, s), 3.77 (COOMe), 2.14–1.92 (OAc). *Randia canthioides* (Rubiaceae) (14)

290. MOLLUGOSIDE (8 $\alpha$ -Hydroxy-apodanthoside)

$C_{17}H_{22}O_{12}$  418.36 uv 230 (?) (? MHz  $D_2O$ ) 5.68 (H-1, d, 1.3), 7.46 (H-3, d, 1.3), 3.9–3.5 (H-5, m), 6.35 (H-6, dd, 6.0, 2.7), 5.74 (H-7, dd, 6.0, 1.7), 3.12 (H-9, dd, 9.0, 1.3), 3.78 (COOMe), 4.82 (H-1', d, 7.5); ( $D_2O$ ) 94.7 (C-1), 151.8 (C-3), 111.0 (C-4), 37.2 (C-5), 133.2 (C-6), 138.3 (C-7), 86.6 (C-8), 47.5 (C-9), 182.1 (C-10), 170.3 (C-11), 52.6 (OMe), 99.0 (C-1'), 73.4 (C-2'), 76.5 (C-3'), 70.4 (C-4'), 77.0 (C-5'), 61.5 (C-6'). *Galium mollugo* (Rubiaceae) (219)

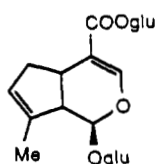
291.  $\alpha$ -DIHYDROGRISELINOSIDE

$C_{18}H_{26}O_{12}$  434.40 ( $D_2O$ ) 100.6 (C-1), 156.2 (C-3), 106.2 (C-4), 42.8 (C-5), 73.9 (C-6), 37.8 (C-7), 45.0 (C-8), 42.1 (C-9), 178.7 (C-10), 170.6 (C-11), 53.6, 52.8 (OMe), 100.2 (C-1'), 73.5 (C-2'), 76.6 (C-3'), 70.3 (C-4'), 77.1 (C-5'), 61.5 (C-6'). Reduction of griselinoside (2)

292.  $\beta$ -DIHYDROGRISELINOSIDE

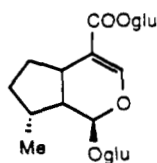
$C_{18}H_{26}O_{12}$  434.40 ( $D_2O$ ) 96.4 (C-1), 153.8 (C-3), 109.0 (C-4), 41.5 (C-5), 76.4 (C-6), 35.7 (C-7), 43.8 (C-8), 42.8 (C-9), 177.9 (C-10), 170.2 (C-11), 53.6, 52.8 (OMe), 99.4 (C-1'), 73.4 (C-2'), 76.4 (C-3'), 70.4 (C-4'), 77.2 (C-5'), 61.5 (C-6'). Reduction of griselinoside (2)

## 293. ASYSTASIOSIDE B



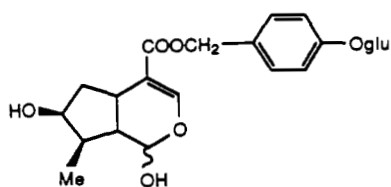
$C_{22}H_{32}O_{14}$  520.49 (500 MHz  $D_2O$ ) 5.51 (H-1, d, 4.8), 7.71 (H-3, bs), 3.23 (H-5, dt, 8, 5), 2.77 (H-6, bdd, 16, 7), 2.18 (H-6, bd, 16), 5.58 (H-7, m), 2.90 (H-9, m), 1.82 (H-10, bs), 4.84 (H-1', d, 8), 5.64 (H-1'', d, 8); ( $D_2O$ ) 97.2 (C-1), 155.6 (C-3), 110.5 (C-4), 35.6 (C-5), 38.6 (C-6), 127.9 (C-7), 139.1 (C-8), 49.8 (C-9), 15.5 (C-10), 168.2 (C-11), 99.4 (C-1'), 73.6 (C-2'), 76.5 (C-3'), 70.4 (C-4'), 77.2 (C-5'), 61.5 (C-6'), 94.6 (C-1''), 72.8 (C-2''), 76.4 (C-3''), 70.0 (C-4''), 77.6 (C-5''), 61.3 (C-6''). *Asystasia bella* (Acanthaceae) (41)

## 294. ASYSTASIOSIDE A



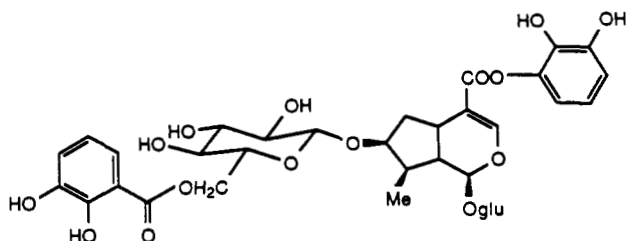
$C_{22}H_{34}O_{14}$  522.51 [ $\alpha$ ] -74° (MeOH) (500 MHz  $D_2O$ ) 5.58 (H-1, d, 3.6), 7.69 (H-3, s), 2.97 (H-5, bdt, 8.5, 5), 2.07 (H-6, dq, 13.2, 8), 1.64 (H-6, ddt, 13, 8, 5), 1.82 (H-7, m), 1.33 (H-7, dq, 12.6, 8), 2.35 (H-8, m), 2.44 (H-9, dt, 8.6, 3.7), 1.04 (H-10, d, 7.1), 4.83 (H-1', d, 8), 5.64 (H-1'', d, 8); ( $D_2O$ ) 97.1 (C-1), 154.7 (C-3), 112.7 (C-4), 32.5 (C-5), 31.5 (C-6), 33.1 (C-7), 36.1 (C-8), 43.4 (C-9), 16.3 (C-10), 168.4 (C-11), 99.2 (C-1'), 73.5 (C-2'), 76.5 (C-3'), 70.4 (C-4'), 77.1 (C-5'), 61.5 (C-6'), 94.5 (C-1''), 72.8 (C-2''), 76.4 (C-3''), 70.0 (C-4''), 77.6 (C-5''), 61.3 (C-6''). *Asystasia bella* (Acanthaceae) (41)

## 295. URCEOLATOSIDE D



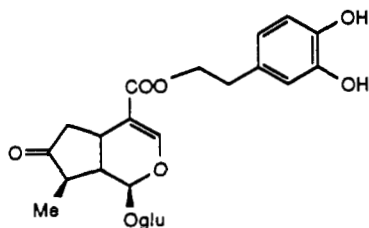
$C_{23}H_{30}O_{11}$  482.48 mp 153–161° [ $\alpha$ ]  $-42.5^\circ$  (MeOH) uv 236 (MeOH) (60 MHz  $Me_2CO-d_6$ ) 7.57 (H-3, s), 1.10 (H-10, d, 6), 5.15 (OCH<sub>2</sub>Ar, s), 7.19, 7.47 (H-2', H-3', d's, 9), 1.40–2.50 (4H). *Viburnum urceolatum* (Caprifoliaceae) (220)

## 296. DEPRESSOSIDE



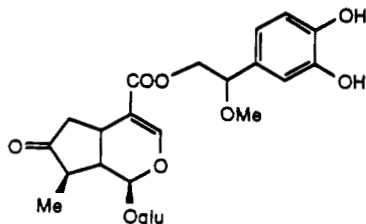
$C_{35}H_{42}O_{20}$  782.70 [ $\alpha$ ]  $-31^\circ$  (MeOH) uv 317, 277, 242, 217 (MeOH) (250 MHz  $CD_3OD$ ) 5.40 (H-1, bs), 7.52 (H-3, d, 1), 3.18 (H-5, m), 2.41 (H-6 $\alpha$ , bdd, 15, 8, 1.5), 1.86 (H-6 $\beta$ , bd, 15, 8, 5.5), 5.40 (H-7, bs), 2.23 (H-8, H-9, m), 1.13 (H-10, d, 6), 4.73 (H-1', d, 7.5)<sup>a</sup>, 3.62–3.24 (H-2'–H-5', H-2'''–H-5''', m), 3.93 (H-6', dd, 12, 1.5), 3.70 (H-6'', dd, 12, 5.5), 6.63 (H-4'', dd, 8, 1.5), 6.53 (H-5'', dd, 8, 8), 6.47 (H-6'', dd, 8, 1.5), 4.70 (H-1''', d, 8.5)<sup>a</sup>, 4.52 (H-6''', dd, 12, 1.5), 4.26 (H-6''', dd, 12, 7), 7.00 (H-4''', dd, 8, 1.5), 6.73 (H-5''', dd, 8, 8), 7.32 (H-6''', dd, 8, 1.5); ( $CD_3OD$ ) 97.3 (C-1), 152.3 (C-3), 114.1 (C-4), 32.3 (C-5), 40.3 (C-6), 80.1 (C-7), 41.0 (C-8), 47.1 (C-9), 13.5 (C-10), 168.6 (C-11), 100.2 (C-1'), 74.7 (C-2'), 78.3 (C-3')<sup>b</sup>, 71.5 (C-4'), 77.9 (C-5')<sup>b</sup>, 62.7 (C-6'), 136.5 (C-1''), 147.3 (C-2''), 147.1 (C-3''), 120.1 (C-4''), 109.9 (C-5''), 111.9 (C-6''), 104.0 (C-1'''), 74.7 (C-2'''), 77.5 (C-3'''), 71.9 (C-4'''), 75.5 (C-5'''), 64.5 (C-6'''), 171.2 (O=C), 113.1 (C-1'''), 151.3 (C-2'''), 147.0 (C-3'''), 121.7 (C-4'''), 120.0 (C-5'''), 121.1 (C-6'''). *Gentiana depressa* (Gentianaceae) (221)

## 297. SYRINGOPICROSIDE B



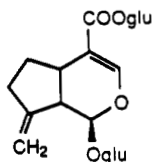
$C_{24}H_{30}O_{12}$  510.49 hexaacetate mp 76–78° [ $\alpha$ ]  $-81.1^\circ$  ( $CHCl_3$ ) (hexaacetate 60 MHz  $CDCl_3$ ) 5.43 (H-1, bs), 7.31 (H-3, bs), 1.14 (H-10, d, 6.2), 4.31 (H $\alpha$ , t, 6.8), 2.94 (H $\beta$ , t, 6.8), 7.15–6.83 (H-2'', H-5'', H-6''), 2.29 (ArOAc), 2.09, 2.03, 2.00, 1.80 (OAc); (hexaacetate  $CDCl_3$ ) 93.5 (C-1), 151.0 (C-3), 111.1 (C-4), 26.5 (C-5), 41.9 (C-6)<sup>a</sup>, 217.6 (C-7), 43.0 (C-8)<sup>a</sup>, 45.1 (C-9)<sup>a</sup>, 13.2 (C-10), 166.3 (C-11), 96.1 (C-1'), 70.7 (C-2'), 72.5 (C-3'), 68.5 (C-4'), 72.5 (C-5'), 61.8 (C-6'), 64.4 (C $\alpha$ ), 34.5 (C $\beta$ ), 136.8 (C-1''), 123.8 (C-2''), 142.4 (C-3''), 141.2 (C-4''), 124.1 (C-5''), 127.0 (C-6''), 20.6, 20.1 (O=CMe), 170.8, 170.4, 169.7, 169.3, 168.4 (O=CMe). *Syringa reticulata* (Oleaceae) (222)

## 298. SYRINGOPICOSIDE C



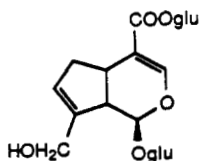
$C_{25}H_{32}O_{13}$  540.52 hexaacetate mp 74–76° [ $\alpha$ ] –86.9° (CHCl<sub>3</sub>) (hexaacetate 60 MHz CDCl<sub>3</sub>) 5.45 (H-1, bs), 7.35 (H-3, bs), 1.14 (H-10, d, 6.2), 7.30–7.00 (H-2'', H-5'', H-6''), 3.30 (OMe), 2.29 (ArOAc), 2.09, 2.03, 2.00, 1.85 (OAc); (hexaacetate CDCl<sub>3</sub>) 93.6 (C-1), 151.2 (C-3), 111.0 (C-4), 26.5 (C-5), 41.9 (C-6)<sup>a</sup>, 217.6 (C-7), 43.0 (C-8)<sup>a</sup>, 45.1 (C-9)<sup>a</sup>, 13.2 (C-10), 166.3 (C-11), 96.1 (C-1'), 70.7 (C-2'), 72.5 (C-3'), 68.5 (C-4'), 72.5 (C-5'), 61.8 (C-6'), 67.4 (C $\alpha$ ), 80.8 (C $\beta$ ), 127.0 (C-1''), 122.3 (C-2''), 142.7 (C-3''), 137.1 (C-4''), 124.0 (C-5''), 125.0 (C-6''), 57.4 (OMe), 20.6, 20.1 (O=CMe), 170.9, 170.4, 169.7, 169.4, 168.4 (O=CMe). *Syringa reticulata* (Oleaceae) (222)

## 299. ASYSTASIOSIDE C



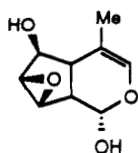
$C_{22}H_{32}O_{14}$  520.49 (500 MHz D<sub>2</sub>O) 5.59 (H-1, d, 4.6), 7.72 (H-3, d, 0.7), 3.11 (H-5, q, 6), 2.07, 1.82 (H-6, m's), 2.39 (H-7), 2.98 (H-9, m), 5.19, 5.17 (H-10, m's), 4.90 (H-1'', d, 8), 5.65 (H-1'', d, 8.1); (D<sub>2</sub>O) 97.2 (C-1), 155.2 (C-3), 112.2 (C-4), 31.0 (C-5), 30.5 (C-6), 34.2 (C-7), 150.6 (C-8), 45.8 (C-9), 109.9 (C-10), 168.4 (C-11), 99.5 (C-1'), 73.5 (C-2'), 76.5 (C-3'), 70.4 (C-4'), 77.2 (C-5'), 61.5 (C-6'), 94.6 (C-1''), 72.8 (C-2''), 76.4 (C-3''), 70.0 (C-4''), 77.6 (C-5''), 61.3 (C-6''). *Asystasia bella* (Acanthaceae) (41)

## 300. ASYSTASIOSIDE D

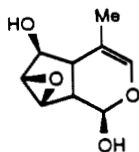


$C_{22}H_{32}O_{15}$  536.49 (250 MHz D<sub>2</sub>O) 5.30 (H-1, d, 6.8), 7.71 (H-3, d, 0.7), 3.22 (H-5, q, 7.5), 2.85, 2.16 (H-6, m's), 5.84 (H-7, m), 2.85 (H-9), 4.25, 4.22 (H-10, d's, 14), 4.80 (H-1'', d, 8), 5.60 (H-1'', d, 7.6); (D<sub>2</sub>O) 98.3 (C-1), 155.6 (C-3), 111.6 (C-4), 35.1 (C-5), 38.9 (C-6), 130.2 (C-7), 142.1 (C-8), 46.6 (C-9), 60.7 (C-10), 168.6 (C-11), 99.8 (C-1'), 73.7 (C-2'), 76.6 (C-3'), 70.4 (C-4'), 77.1 (C-5'), 61.5 (C-6'), 94.7 (C-1''), 72.9 (C-2''), 76.5 (C-3''), 70.1 (C-4''), 77.7 (C-5''), 61.4 (C-6''). *Asystasia bella* (Acanthaceae) (41)

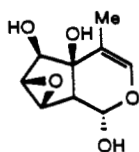
## Group 4 (iridoid aglycones)

301.  $\alpha$ -DEUTZIOGENIN

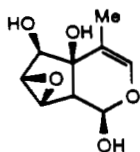
$C_9H_{12}O_4$  184.19 mp 145–153° (dec) (90 MHz D<sub>2</sub>O) 5.41 (H-1, d, 3.5), 5.98 (H-3, s, fine structure), 2.1–2.7 (H-5), 4.18 (H-6, d, 7.5), 3.7–3.5 (H-7, H-8), 2.72 (H-9, dd, 8.3, 3.5), 1.56 (H-11, s, fs); (D<sub>2</sub>O) 89.4 (C-1), 133.0 (C-3), 113.0 (C-4), 38.3 (C-5), 77.9 (C-6), 61.1 (C-7), 57.6 (C-8), 41.6 (C-9), 16.6 (C-11); *Deutzia scabra* (Saxifragaceae/Hydrangeaceae) (223)

302.  $\beta$ -DEUTZIOGENIN

$C_9H_{12}O_4$  184.19 mp 145–153° (dec) (90 MHz D<sub>2</sub>O) 4.60 (H-1, d, 10), 6.10 (H-3, s, fine structure), 1.96 (H-5, br, 7.7, 7.5), 4.05 (H-6, dd, 7.5, 1.5), 3.7–3.5 (H-7, H-8), 2.40 (H-9, dd, 10, 7.7), 1.56 (H-11, s, fs); (D<sub>2</sub>O) 93.5 (C-1), 135.9 (C-3), 113.0 (C-4), 41.1 (C-5), 78.5 (C-6), 59.5 (C-7), 56.7 (C-8), 44.1 (C-9), 16.1 (C-11). *Deutzia scabra* (Saxifragaceae/Hydrangeaceae) (223, 224)

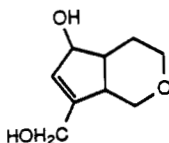
303.  $\alpha$ -SCABROGENIN

$C_9H_{12}O_5$  200.19 (90 MHz D<sub>2</sub>O) 5.54 (H-1, d, 3.8), 6.13 (H-3, s, fine structure), 4.30 (H-6), 3.8–3.6 (H-7, H-8), 2.78 (H-9, d, 3.8), 1.60 (H-11, s, fs); (D<sub>2</sub>O) 91.4 (C-1), 136.4 (C-3), 113.9 (C-4), 72.2 (C-5), 77.3 (C-6), 60.9 (C-7), 56.4 (C-8), 50.0 (C-9), 11.8 (C-11). *Deutzia scabra* (Saxifragaceae) (223)

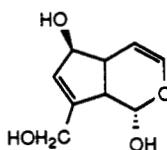
304.  $\beta$ -SCABROGENIN

$C_9H_{12}O_5$  200.19 (90 MHz  $D_2O$ ) 4.82 (H-1, d, 10.5), 6.20 (H-3, s, fine structure), 4.34 (H-6, d, 1.5), 3.8–3.6 (H-7, H-8), 2.52 (H-9, d, 10.5), 1.60 (H-11, s, fs); ( $D_2O$ ) 94.5 (C-1), 138.2 (C-3), 115.2 (C-4), 74.1 (C-5), 77.6 (C-6), 59.6 (C-7), 56.0 (C-8), 52.3 (C-9), 11.5 (C-11). *Deutzia scabra* (Saxifragaceae) (223)

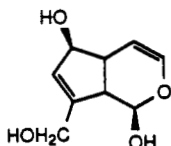
## 305. compound not named (1-DEHYDROXY-3,4-DIHYDROAUCUBIGENIN)



$C_9H_{14}O_3$  170.21 [ $\alpha$ ] +181.0° (MeOH) (diacetate, ? MHz  $CDCl_3$ ) 3.75 (H-1, dd, 14.4, 6.6), 3.67 (H-1, dd, 14.4, 6.4), 4.19 (H-3, m), 1.87–1.73 (H-4, m), 3.08 (H-5, m), 5.05 (H-6, d, 5.8), 5.75 (H-7, bs), 3.08 (H-9, m), 4.65 (H-10, d, 14), 4.59 (H-10, d, 14), 2.08, 2.07 (OAc); (pyridine- $d_5$ ) 61.8 (C-1)<sup>a</sup>, 60.5 (C-3)<sup>a</sup>, 28.5 (C-4), 43.6 (C-5), 87.3 (C-6), 126.2 (C-7), 150.5 (C-8), 49.6 (C-9), 67.4 (C-10). *Scrophularia ningpoensis* (Scrophulariaceae) (225)

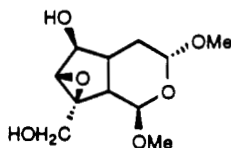
306.  $\alpha$ -AUCUBIGENIN

$C_9H_{12}O_4$  184.19 mp 110° ( $\alpha + \beta$ , 1:6) (300 MHz  $D_2O$ ) 5.30 (H-1, d, 3.3), 6.16 (H-3, dd), 4.47 (H-6, sext), 5.67 (H-7); ( $D_2O$ ) 92.2 (C-1), 140.2 (C-3), 105.3 (C-4), 43.7 (C-5), 81.4 (C-6), 131.0 (C-7), 147.4 (C-8), 47.2 (C-9), 60.7 (C-10). Hydrolysis of aucubin (226)

307.  $\beta$ -AUCUBIGENIN

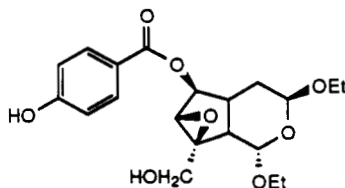
$C_9H_{12}O_4$  184.19 mp 110° ( $\beta + \alpha$ , 6:1) (300 MHz  $D_2O$ ) 4.71 (H-1, d, 6.7), 6.23 (H-3, dd, 6, 1.5), 5.03 (H-4, dd, 6, 3.5), 2.56 (H-5, m), 4.42 (H-6, sext), 5.69 (H-7, bs), 2.73 (H-9, br, 6.7), 4.15 (H-10, dd, 15); ( $D_2O$ ) 95.3 (C-1), 141.3 (C-3), 105.3 (C-4), 45.1 (C-5), 82.0 (C-6), 129.7 (C-7), 147.4 (C-8), 48.7 (C-9), 60.7 (C-10). Hydrolysis of aucubin (226, 227)

## 308. ECCREMOCARPOL A



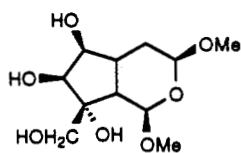
$C_{11}H_{18}O_6$  246.26 [ $\alpha$ ] -29° (MeOH) (400 MHz  $CD_3OD$ ) 4.94 (H-1, d, 4), 4.72 (H-3, dd, 7.5, 3), 1.92 (H-4, ddd, 14, 5, 3), 1.87 (H-4, dd, 14, 7.5), 1.98 (H-5, ddd, 8, 5, 1), 4.07 (H-6, dd, 8, 1), 2.77 (H-9, dd, 8, 4), 3.97/3.56 (H-10, d's, 13), 3.46, 3.40 (OMe); ( $CD_3OD$ ) 98.7 (C-1), 95.3 (C-3), 29.1 (C-4), 35.6 (C-5), 77.4 (C-6), 60.9 (C-7), 63.2 (C-8), 40.6 (C-9), 60.7 (C-10), 55.4, 54.4 (OMe). *Eccremocarpus scaber* (Bignoniaceae) (228)

## 309. SPECIONIN



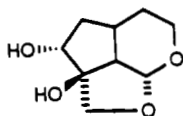
$C_{20}H_{26}O_8$  394.42 uv 254 (MeOH) (360 MHz  $CDCl_3$ ) 5.06 (H-1, d, 4), 4.89 (H-3, dd, 6.9, 3), 2.00/1.87 (H-4, m, 13.9, 7.2, 6.9, 5.1, 3), 2.45 (H-5, m, 8.4, 8.2, 7.2, 5.1), 5.37 (H-6, dd, 8.4, 1.4), 3.77 (H-7, d, 1.4), 2.81 (H-9, dd, 8.2, 4.0), 4.02/3.74 (H-10, d's, 12.5), 3.87/3.85 ( $OCH_2CH_3$ , d, 9.4), 3.51/3.48 ( $OCH_2CH_3$ , d, 8.5), 1.24/1.21 ( $OCH_2CH_3$ , 7), 7.98 (H-2', d, 8.7), 6.87 (H-3', d, 8.7); (? solv) 97.7 (C-1), 94.8 (C-3), 30.4 (C-4), 34.2 (C-5), 80.7 (C-6), 61.2 (C-7), 67.3 (C-8), 41.2 (C-9), 61.4 (C-10), 64.8, 64.0 ( $OCH_2CH_3$ ), 15.6, 15.5 ( $OCH_2CH_3$ ), 168.2 (O=C), 121.5 (C-1'), 132.8 (C-2'), 116.3 (C-3'), 164.0 (C-4'). *Catalpa speciosa* (Bignoniaceae) (229, 230)

## 310. ECCREMOCARPOL B



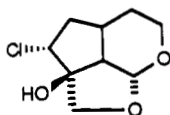
$C_{11}H_{20}O_7$  264.27  $[\alpha] - 18.5^\circ$  (MeOH) (400 MHz  $CD_3OD$ ) 5.14 (H-1, d, 3), 5.07 (H-3, dd, 3.5, 1), 2.38 (H-4, ddd, 14, 10, 1), 1.66 (H-4, dd, 14, 3.5), 2.57 (H-5, ddd, 14, 4.5, 1), 4.10 (H-6, d, 6.5), 3.99 (H-7, d, 6.5), 2.65 (H-9, dd, 4.5, 3), 3.84 (H-10), 3.50, 3.46 (OMe); ( $CD_3OD$ ) 97.0 (C-1), 91.1 (C-3), 35.0 (C-4), 36.7 (C-5), 76.9 (C-6), 75.9 (C-7), 81.2 (C-8), 37.3 (C-9), 63.8 (C-10), 55.4, 54.4 (OMe). *Eccremocarpus scaber* (Bignoniaceae) (228)

## 311. CISTANIN



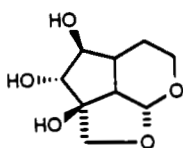
$C_9H_{14}O_4$  186.21 mp 123–124°  $[\alpha] + 62.6^\circ$  (MeOH) (400 MHz pyridine- $d_5$ ) 5.76 (H-1, d, 6), 4.18 (H-3 $\alpha$ , ddd, 12, 11, 2), 3.57 (H-3 $\beta$ , ddd, 11, 4, 2), 1.28 (H-4 $\alpha$ , bd, 14), 1.83 (H-4 $\beta$ , m), 2.38 (H-5, m), 1.96 (H-6 $\alpha$ , ddd, 12, 12, 6), 2.19 (H-6 $\beta$ , ddd, 12, 12, 12), 4.77 (H-7, ddd, 12, 6, 1.5), 2.51 (H-9, dd, 9, 6), 5.22 (H-10 $\alpha$ , d, 10), 3.99 (H-10 $\beta$ , dd, 10, 1.5); (pyridine- $d_5$ ) 101.4 (C-1), 55.5 (C-3), 25.0 (C-4), 26.9 (C-5), 37.0 (C-6), 79.2 (C-7), 88.7 (C-8), 47.1 (C-9), 71.5 (C-10). *Cistanche salsa* (Orobanchaceae) (231)

## 312. CISTACHLORIN



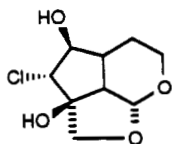
$C_9H_{13}ClO_3$  204.65 mp 66–67°  $[\alpha] + 59.1^\circ$  (MeOH) (400 MHz pyridine- $d_5$ ) 5.72 (H-1, d, 6), 4.03 (H-3 $\alpha$ , ddd, 12, 11, 2), 3.54 (H-3 $\beta$ , ddd, 11, 4, 2), 1.23 (H-4 $\alpha$ , bd, 14), 1.77 (H-4 $\beta$ , m), 2.35 (H-5, m), 2.00 (H-6 $\alpha$ , ddd, 12, 12, 6), 2.13 (H-6 $\beta$ , ddd, 12, 12, 12), 4.65 (H-7, ddd, 12, 6, 1.5), 2.52 (H-9, dd, 9, 6), 4.84 (H-10 $\alpha$ , d, 10), 3.99 (H-10 $\beta$ , dd, 10, 1.5); (pyridine- $d_5$ ) 101.6 (C-1), 55.4 (C-3), 24.4 (C-4), 28.8 (C-5), 38.8 (C-6), 67.7 (C-7), 88.8 (C-8), 47.2 (C-9), 73.5 (C-10). *Cistanche salsa* (Orobanchaceae) (231)

## 313. REHMAGLUTIN A



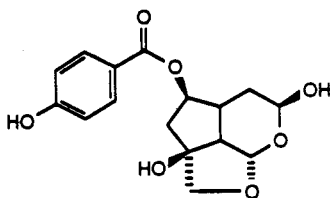
$C_9H_{14}O_5$  202.21 mp 134–136°  $[\alpha] + 43.6^\circ$  (MeOH) triacetate mp 128–130° (triacetate 500 MHz  $CDCl_3$ ) 5.34 (H-1, d, 5.2), 4.07 (H-3 $\alpha$ , ddd, 12.8, 11.9, 2.4), 3.63 (H-3 $\beta$ , ddd, 11.9, 4.9), 1.46 (H-4 $\alpha$ , bd, 14.6), 1.78 (H-4 $\beta$ , dddd, 14.6, 12.8, 5.2, 4.9), 2.64 (H-5, ddd, 11, 9.8, 5.2), 5.44 (H-6, dd, 11, 9.5), 5.85 (H-7, dd, 9.5, 1.5), 2.74 (H-9, dd, 9.8, 5.2), 4.59 (H-10 $\alpha$ , d, 10.5), 3.59 (H-10 $\beta$ , dd, 10.5, 1.5); ( $Me_2CO-d_6$ ) 101.0 (C-1), 56.4 (C-3), 22.4 (C-4), 34.9 (C-5), 75.4 (C-6), 85.0 (C-7), 85.2 (C-8), 44.9 (C-9), 71.0 (C-10); (triacetate  $Me_2CO-d_6$ ) 99.1 (C-1), 55.5 (C-3), 21.1 (C-4), 32.5 (C-5), 73.1 (C-6), 78.0 (C-7), 88.6 (C-8), 41.3 (C-9), 67.5 (C-10). *Rehmannia glutinosa* (Scrophulariaceae) (232)

## 314. REHMAGLUTIN D



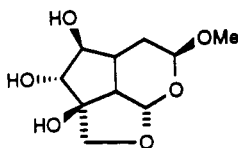
$C_9H_{13}ClO_4$  220.65 mp 132–133°  $[\alpha] + 60.6^\circ$  (MeOH) diacetate mp 96–97° (diacetate 500 MHz  $CDCl_3$ ) 5.46 (H-1, d, 5.2), 4.06 (H-3 $\alpha$ , ddd, 12.2, 12.0, 2.1), 3.62 (H-3 $\beta$ , dd, 12, 5.2), 1.47 (H-4 $\alpha$ , bd, 14.3), 1.77 (H-4 $\beta$ , dddd, 14.3, 12.2, 5.2, 4.6), 2.56 (H-5, ddd, 10.4, 9.8, 4.6), 5.39 (H-6, dd, 10.4, 10.4), 4.81 (H-7, dd, 10.4, 1.5), 2.85 (H-9, dd, 9.8, 5.2), 4.61 (H-10 $\alpha$ , d, 10.7), 3.74 (H-10 $\beta$ , dd, 10.7, 1.5); ( $Me_2CO-d_6$ ) 101.3 (C-1), 56.3 (C-3), 22.3 (C-4), 39.0 (C-5), 73.0 (C-6), 75.3 (C-7), 85.5 (C-8), 46.2 (C-9), 76.4 (C-10), (diacetate  $Me_2CO-d_6$ ) 101.2 (C-1), 56.3 (C-3), 21.1 (C-4), 35.8 (C-5), 75.6 (C-6), 67.5 (C-7), 90.5 (C-8), 42.7 (C-9), 69.5 (C-10). *Rehmannia glutinosa* (Scrophulariaceae) (232)

## 315. CATALPIN



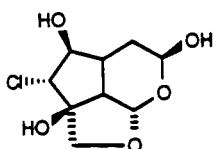
$C_{16}H_{18}O_7$  322.31 mp 93–94° uv 258 (MeOH) (400 MHz  $CD_3OD$ ) 5.51 (H-1, d, 5.4), 5.38 (H-3, dd, 7.5, 3.6), 1.92 (H-4 $\alpha$ , ddd, 11.5, 3.6, 3.6), 1.55 (H-4 $\beta$ , ddd, 11.5, 7.5, 3.6), 2.69 (H-5, dddd, 11.5, 6.5, 3.6, 3.6), 5.26 (H-6, ddd, 8.2, 7.8, 6.5), 2.54 (H-7 $\alpha$ , dd, 11.0, 7.8), 2.01 (H-7 $\beta$ , ddd, 11.0, 8.2, 1.5), 2.48 (H-9, dd, 11.5, 5.4), 3.90 (H-10 $\alpha$ , d, 10.8), 3.76 (H-10 $\beta$ , dd, 10.8, 1.5), 7.88 (H-2', d, 8.8), 6.82 (H-3', d, 8.8); (Me<sub>2</sub>CO-*d*<sub>6</sub>) 101.3 (C-1), 90.1 (C-3), 30.1 (C-4), 41.0 (C-5), 76.6 (C-6), 45.9 (C-7), 85.2 (C-8), 51.5 (C-9), 79.3 (C-10), 122.9 (C-1'), 133.6 (C-2'), 116.5 (C-3'), 163.2 (C-4'), 167.0 (C=O). *Catalpa ovata* (Bignoniaceae) (233)

## 316. JIOGLUTIN C

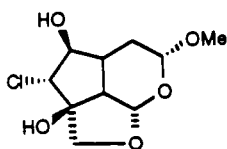


$C_{10}H_{16}O_6$  232.23 [ $\alpha$ ] +58.1° (MeOH) (500 MHz  $CD_3OD$ ) 5.43 (H-1, d, 5.3), 4.87 (H-3, dd, 8.1, 4.7), 2.01 (H-4, ddd, 14.1, 4.7, 2.6), 1.46 (H-4, ddd, 14.1, 8.1, 5.7), 2.15 (H-5, dddd, 10.4, 10.3, 5.7, 2.6), 3.61 (H-6, dd, 10.4, 8.9), 3.81 (H-7, dd, 8.9, 1.1), 2.29 (H-9, dd, 10.3, 5.3), 4.21 (H-10 $\alpha$ , d, 10.1), 3.52 (H-10 $\beta$ , 10.1, 1.1), 3.41 (OMe); ( $CD_3OD$ ) 101.2 (C-1), 97.6 (C-3), 27.7 (C-4), 36.5 (C-5), 77.6 (C-6), 84.9 (C-7), 86.0 (C-8), (C-9 under solv), 73.6 (C-10), 56.0 (OMe). *Rebmannia glutinosa* var. *bueichingensis* (Scrophulariaceae) (234)

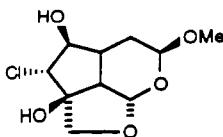
## 317. REHMAGLUTIN B



$C_9H_{13}ClO_5$  236.65 mp 152–153° [ $\alpha$ ] +33.8° (MeOH) diacetate mp 147–148° (diacetate 500 MHz  $CDCl_3$ ) 5.59 (H-1, d, 4.9), 6.41 (H-3, dd, 7.3, 6.4), 1.63 (H-4 $\alpha$ , ddd, 14.7, 7.3, 4.9), 2.11 (H-4 $\beta$ , ddd, 14.7–6.4, 3.8), 2.47 (H-5, dddd, 10.5, 10.1, 4.9, 3.8), 5.20 (H-6, dd, 10.1, 10.1), 4.25 (H-7, d, 10.1), 2.71 (H-9, dd, 10.5, 4.9), 4.34 (H-10 $\alpha$ , d, 11), 3.86 (H-10 $\beta$ , d, 11); (Me<sub>2</sub>CO-*d*<sub>6</sub>) 102.1 (C-1), 85.8 (C-3), 32.4 (C-4), 38.9 (C-5), 74.8 (C-6), 78.1 (C-7), 89.9 (C-8), 48.4 (C-9), 74.3 (C-10), (diacetate Me<sub>2</sub>CO-*d*<sub>6</sub>) 100.6 (C-1), 86.2 (C-3), 26.7 (C-4), 36.4 (C-5), 79.0 (C-6), 70.1 (C-7), 90.8 (C-8), 52.8 (C-9), 76.6 (C-10). *Rebmannia glutinosa* (Scrophulariaceae) (232)

318. JIOGLUTIN B (3-*epi*-Jio glutin A)

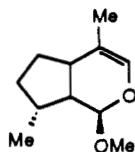
$C_{10}H_{15}ClO_5$  250.68 [ $\alpha$ ] –63.2° (MeOH) (500 MHz  $CD_3OD$ ) 5.48 (H-1, d, 6.6), 4.72 (H-3, dd, 4.4, 2.6), 1.87 (H-4, ddd, 14.7, 2.6, 1.8), 1.77 (H-4, ddd, 14.7, 7.2, 4.4), 2.11 (H-5, dddd, 11.5, 10, 7.2, 1.8), 4.23 (H-6, dd, 10, 9.6), 3.92 (H-7, dd, 9.6, 0.8), 2.51 (H-9, dd, 11.5, 6.6), 4.10 (H-10 $\alpha$ , d, 10.1), 3.63 (H-10 $\beta$ , dd, 10.1, 0.8), 3.39 (OMe); ( $CD_3OD$ ) 101.3 (C-1), 98.5 (C-3), 26.8 (C-4), 35.4 (C-5), 80.4 (C-6), 72.5 (C-7), 87.8 (C-8), 46.7 (C-9), 75.4 (C-10), 55.7 (OMe). *Rebmannia glutinosa* var. *bueichingensis* (Scrophulariaceae) (234)

319. JIOGLUTIN A (3-*O*-Methylrehmaglutin B)

$C_{10}H_{15}ClO_5$  250.68 [ $\alpha$ ] +63.3° (MeOH) (500 MHz  $CD_3OD$ ) 5.46 (H-1, d, 5.3), 4.87 (H-3, dd, 7.6, 5.4), 2.07 (H-4, ddd, 14.5, 5.4, 2.6), 1.51 (H-4, ddd, 14.5, 7.6, 5.7), 2.21 (H-5, dddd, 10.3, 10.1, 5.7, 2.6), 3.75 (H-6, dd, 10.1, 9.8), 3.96 (H-7, dd, 9.8, 0.8), 2.45 (H-9, dd, 10.3, 5.3), 4.16 (H-10 $\alpha$ , d, 10.4), 3.67 (H-10 $\beta$ , dd, 10.4, 0.8), 3.40 (OMe); ( $CD_3OD$ ) 100.6 (C-1), 97.9 (C-3), 27.4 (C-4), 38.1



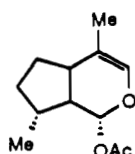
**320. (1R)-1-METHOXYMYODESERT-3-ENE (Myodesertin)**



(C-5), 78.8 (C-6), 73.3 (C-7), 86.1 (C-8), 50.7 (C-9), 75.7 (C-10), 55.9 (OMe). *Rebmannia glutinosa* var. *bueichingensis* (Scrophulariaceae) (234)

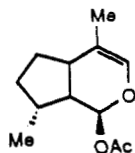
$C_{11}H_{18}O_2$  182.26 bp 67° (2mm Hg)  $[\alpha] -165^\circ$  (EtOH/CHCl<sub>3</sub>) uv 220 (EtOH) (100 MHz CDCl<sub>3</sub>) 5.97 (H-1, m), 4.57 (H-3, d, 3.8), 1.03 (H-10, d, 7), 1.50 (H-11, m), 3.42 (OMe). *Myoporum deserti* (Myoporaceae) (235, 236)

**321. (1R)-1-ACETOXYMYODESERT-3-ENE**



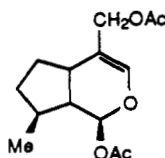
$C_{12}H_{18}O_3$  210.27 mp 17°  $[\alpha] +273^\circ$  (CHCl<sub>3</sub>) (100 MHz CDCl<sub>3</sub>) 5.96 (H-1, q, 1.5), 6.19 (H-3, dd, 2.4, 0.5), 2.38–2.28, 2.28–2.19, 2.10–1.97, 1.92–1.78, 1.73–1.60, 1.43–1.29 (H-5–H-9, m's), 1.01 (H-10, d, 7), 1.60 (H-11, m), 2.06 (OAc); (CDCl<sub>3</sub>) 89.7 (C-1), 132.7 (C-3), 114.2 (C-4), 39.0 (C-5), 32.3 (C-6), 30.7 (C-7), 36.5 (C-8), 42.7 (C-9), 17.1 (C-10)<sup>a</sup>, 15.0 (C-11)<sup>a</sup>, 169.7 (O=CMe), 21.5 (O=CMe). *Myoporum deserti* (Myoporaceae) (237)

**322. (1S)-1-ACETOXYMYODESERT-3-ENE**



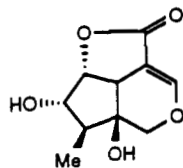
$C_{12}H_{18}O_3$  210.27  $[\alpha] -183^\circ$  (CHCl<sub>3</sub>) (100 MHz CDCl<sub>3</sub>) 6.04 (H-1, d, 3.8), 6.00 (H-3, q, 1.5), 2.53–2.44, 2.29–2.18, 1.80–1.58, 1.35–1.18 (H-5–H-9, m's), 1.02 (H-10, d, 7.1), 1.54 (H-11, m), 2.07 (OAc); (CDCl<sub>3</sub>) 90.8 (C-1), 134.7 (C-3), 113.4 (C-4), 37.0 (C-5), 32.8 (C-6), 29.1 (C-7), 35.3 (C-8), 42.7 (C-9), 16.3 (C-10)<sup>a</sup>, 16.0 (C-11)<sup>a</sup>, 169.8 (O=CMe), 21.2 (O=CMe). *Myoporum deserti* (Myoporaceae) (237)

**323. TEUCREIN**



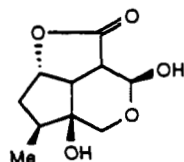
$C_{14}H_{20}O_5$  268.31 bp 125–130° (0.5 mm Hg)  $[\alpha] -73.5^\circ$  (C<sub>6</sub>H<sub>6</sub>) (? MHz CDCl<sub>3</sub>) 5.87 (H-1, d, 4.3), 6.30 (H-3, s), 2.66 (H-5, m), 1.07 (H-10, d, 5.5), 4.66, 4.24 (H-11, d's, 11.9), 2.10, 2.04 (OAc); (CDCl<sub>3</sub>) 91.5 (C-1), 140.0 (C-3), 112.8 (C-4), 48.0 (C-5), 32.9 (C-6), 30.0 (C-7), 35.0 (C-8), 35.0 (C-9), 20.2 (C-10), 63.9 (C-11), 170.2, 169.2 (O=CMe), 20.9, 20.8 (O=CMe). *Teucrium marum* (Labiatae) (238)

**324. GELSEMIDE**



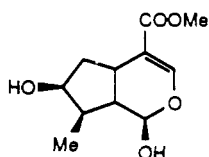
$C_{10}H_{12}O_5$  212.20 mp 179–180°  $[\alpha] -343^\circ$  (MeOH) (270 MHz D<sub>2</sub>O) 4.25/3.95 (H-1, 11.9), 7.53 (H-3, d, 2.5), 3.44 (H-5, dd, 7.3, 2.5), 5.12 (H-6, t, 7.2), 4.14 (H-7, dd, 10.5, 7.2), 1.98 (H-8, dq, 10.5, 6.8), 1.11 (H-10, d, 6.8); (D<sub>2</sub>O) 67.3 (C-1), 154.0 (C-3), 102.5 (C-4), 47.5 (C-5), 80.3 (C-6), 78.8 (C-7), 42.1 (C-8), 72.3 (C-9), 9.7 (C-10), 174.5 (C-11). *Gelsemium sempervirens* (Loganiaceae) (239)

**325. 9-HYDROXYSEMPEOSIDE AGLUCONE**



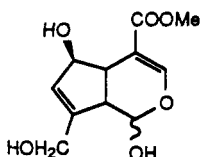
$C_{10}H_{14}O_5$  214.22 (90 MHz CDCl<sub>3</sub>) 3.91/3.47 (H-1, 13), 5.52 (H-3, bs), 2.98 (H-4, H-5, d-like), 5.06 (H-6, q-like, 4.5), 2.35–1.75 (H-7, H-8), 0.98 (H-10, d, 5.5); (CDCl<sub>3</sub>/CD<sub>3</sub>OD) 57.9 (C-1), 89.0 (C-3), 43.7 (C-4), 46.0 (C-5), 82.9 (C-6), 37.4 (C-7), 35.2 (C-8), 72.7 (C-9), 9.1 (C-10), 176.0 (C-11). Enzymatic hydrolysis of 9-hydroxysempeoside (239)

## 326. LOGANETIN

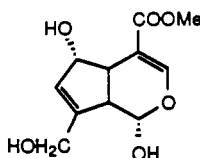


$C_{11}H_{16}O_5$  228.24 uv 230 (MeOH) (200 MHz  $CDCl_3$ ) 4.96 (H-1 and OH, m), 7.44 (H-3, s), 3.16 (H-5, bq, 8), 1.57 (H-6 $\alpha$ , m, 14, 8.5, 4), 2.58 (H-6 $\beta$ , dd, 13, 7.5), 4.15 (H-7, m), 1.95 (H-8, H-9, m), 1.14 (H-10, d, 7.5), 3.74 (OMe); ( $D_2O$ ) 96.3 (C-1), 153.4 (C-3), 112.2 (C-4), 32.1 (C-5), 41.5 (C-6), 74.8 (C-7), 41.5 (C-8), 46.8 (C-9), 13.7 (C-10), 170.9 (C-11), 52.6 (OMe). Hydrolysis of loganin, *Gentiana verna* (Gentianaceae) (240, 241)

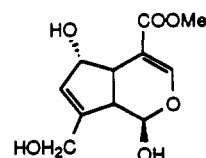
## 327. DEACETYLASPERULOSIDIC ACID METHYL ESTER AGLYCONE



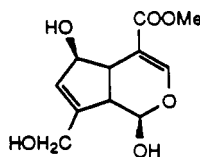
$C_{11}H_{14}O_6$  242.23 triacetate [ $\alpha$ ] +118.0° ( $CHCl_3$ ) uv 234 (MeOH) (triacetate 60 MHz  $CDCl_3$ ) 5.68 (H-1, d, 10), 7.57 (H-3, d, 2), 3.19 (H-5, ddd, 8, 6.4, 2), 5.73 (H-6, dd, 6.4, 3), 6.15 (H-7, bs), 2.75 (H-9, d, 10, 8), 4.68 (H-10, bs), 3.71 (COOMe), 2.17-1.94 (OAc). *Randia canthioides* (Rubiaceae) (242)

328. 6 $\alpha$ -HYDROXY-1-*epi*-GENIPIN

$C_{11}H_{14}O_6$  242.23 from 1 $\alpha$ ,1 $\beta$ -mixture (100 MHz  $CD_3OD$ ) 4.82 (H-1, d, 7), 7.62 (H-3, s), 2.95 (H-5, br, 7), 5.96 (H-7, bs), 2.37 (H-9, br, 8), 4.46 (H-10, m), 3.70 (COOMe); ( $CD_3OD$ ) 90.8 (C-1), 154.7 (C-3), 108.1 (C-4), 39.4 (C-5), 75.3 (C-6), 130.3 (C-7), 150.1 (C-8), 45.6 (C-9), 61.8 (C-10), 169.8 (C-11). Enzymatic hydrolysis of 6 $\alpha$ -hydroxygeniposide (243)

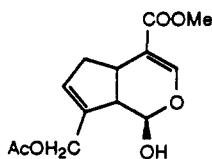
329. 6 $\alpha$ -HYDROXYGENIPIN

$C_{11}H_{14}O_6$  242.23 from 1 $\alpha$ ,1 $\beta$ -mixture (100 MHz  $CD_3OD$ ) 5.50 (H-1, d, 4), 7.51 (H-3, s), 2.95 (H-5, br, 7), 5.96 (H-7, bs), 2.37 (H-9, br, 8), 4.46 (H-10, m), 3.70 (COOMe); ( $CD_3OD$ ) 100.6 (C-1), 156.4 (C-3), 107.4 (C-4), 43.0 (C-5), 75.6 (C-6), 129.7 (C-7), 151.8 (C-8), 47.8 (C-9), 61.4 (C-10), 169.4 (C-11). Enzymatic hydrolysis of 6 $\alpha$ -hydroxygeniposide (243)

330. 6 $\beta$ -HYDROXYGENIPIN (Scandoside methyl ester aglucone)

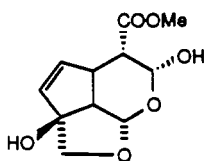
$C_{11}H_{14}O_6$  242.23 [ $\alpha$ ] +396° (MeOH) uv 239 (MeOH) (100 MHz  $CD_3OD$ ) 4.74 (H-1, d, 8), 7.54 (H-3, s), 2.90 (H-5, m), 5.80 (H-7, bs), 2.90 (H-9, m), 4.22 (H-10, m), 3.76 (COOMe); ( $CD_3OD$ ) 98.5 (C-1), 155.0 (C-3), 110.0 (C-4), 47.0 (C-5), 83.0 (C-6), 130.1 (C-7), 148.0 (C-8), 47.0 (C-9), 61.5 (C-10), 171.0 (C-11). Enzymatic hydrolysis of 6 $\beta$ -hydroxygeniposide (243)

## 331. 10-O-ACETYLGENIPIN

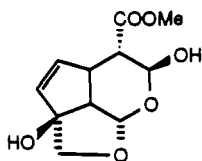


$C_{13}H_{16}O_6$  268.27 [ $\alpha$ ] +48.2° ( $CHCl_3$ ) uv 240 (MeOH) (60 MHz  $CDCl_3$ ) 7.52 (H-3, d, 1.0), 5.75 (H-7, m), 3.71 (COOMe), 2.10 (OAc). Enzymatic hydrolysis of 10-O-acetylgeniposide (205)

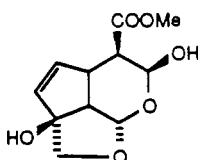
## 332. GARDENOGENIN A



$C_{11}H_{14}O_6$  242.23 mp 141–143°  $[\alpha] +117.5^\circ$  (MeOH) (360 MHz  $CD_3OD$ ) 5.50 (H-1, d, 5.8), 5.38 (H-3, d, 2.6), 2.69 (H-4, dd, 9.4, 2.6), 3.54 (H-5, tt, 9.4, 9.4, 2.2, 2), 5.92 (H-6, dd, 5.4, 2.2), 5.74 (H-7, dd, 5.4, 2), 2.67 (H-9, dd, 9.4, 5.8), 3.79, 3.54 (H-10, d's, 9.3), 3.72 (COOMe); ( $CD_3OD$ ) 90.3 (C-1), 101.1 (C-3), 49.5 (C-4), 48.3 (C-5), 138.0 (C-6), 135.5 (C-7), 93.9 (C-8), 40.5 (C-9), 74.7 (C-10), 172.9 (C-11), 52.5 (OMe). Enzymatic hydrolysis of gardenoside (244)

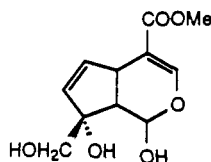
333. GARDENOGENIN B ( $\alpha$ -Gardiol)

$C_{11}H_{14}O_6$  242.23  $[\alpha] +152^\circ$  (MeOH) (360 MHz  $CD_3OD$ ) 5.55 (H-1, d, 5.7), 5.18 (H-3, d, 8.6), 2.71 (H-4, dd, 8.6, 5.4), 3.54 (H-5, m, 8.5, 5.4), 5.81 (H-6, d, 5.8), 5.79 (H-7, d, 5.8), 2.64 (H-9, d, 8.5, 5.7), 3.94/3.78 (H-10, d's, 9.8), 3.74 (COOMe); ( $D_2O$ ) 101.2 (C-1), 90.3 (C-3), 47.3 (C-4), 43.4 (C-5), 135.7 (C-6, C-7), 93.0 (C-8), 51.1 (C-9), 75.8 (C-10), 174.4 (C-11), 53.6 (OMe). Enzymatic hydrolysis of gardenoside, *Rotbmannia globosa* (Rubiaceae). Artifact from gardenoside? (244, 245)

334.  $\beta$ -GARDIOL

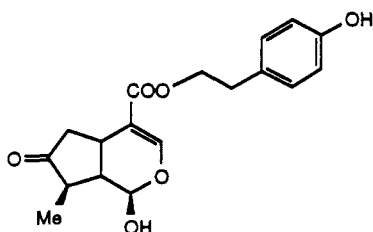
$C_{11}H_{14}O_6$  242.23 mp 122–124°  $[\alpha] +211^\circ$  (MeOH) (100 MHz  $CDCl_3$ ) 5.62 (H-1, d, 6.3), 5.37 (H-3, dd, 7.4, 2.1), 2.82 (H-4, dd, 6.4, 2), 3.7 (H-5, m), 5.97 (H-6, dd, 5.1, 1.8), 5.87 (H-7, dd, 5.4, 2.1), 2.70 (H-9, dd, 8.9, 6.3), 3.92/3.67 (H-10, 9.5), 3.82 (COOMe); ( $D_2O$ ) 101.5 (C-1), 89.2 (C-3), 46.9 (C-4), 41.7 (C-5), 138.5 (C-6), 134.1 (C-7), 93.4 (C-8), 46.9 (C-9), 73.0 (C-10), 173.8 (C-11), 53.4 (OMe). *Rotbmannia globosa* (Rubiaceae). Artifact from gardenoside? (245)

## 335. GALIOSIDE AGLUCONE



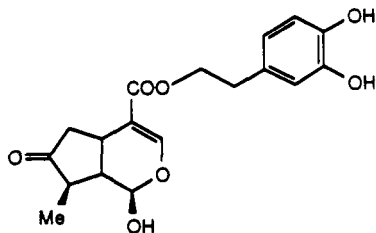
$C_{11}H_{14}O_6$  242.23 mp 110–115°  $[\alpha] +52.9^\circ$  (MeOH) (200 MHz  $CD_3OD$ ) (H-1 under HDO), 7.45 (H-3, d, 1.4), 3.53 (H-5, m), 6.08 (H-6, dd, 5.6, 2.3), 5.61 (H-7, dd, 5.6, 2.3), 3.55 (H-10, m), 3.72 (COOMe). Enzymatic hydrolysis of galioside (244)

## 336. SYRINGOPICROGENIN A



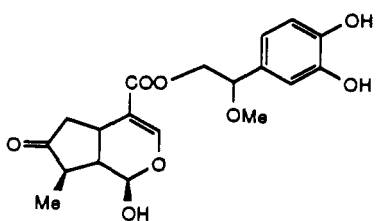
$C_{18}H_{20}O_6$  332.35 diacetate  $[\alpha] -75.0^\circ$  ( $CHCl_3$ ) (60 MHz  $CDCl_3$ ) 6.29 (H-1, d, 2.1), 7.38 (H-3, d, 1.6), 1.18 (H-10, d, 6.6), 4.43 (H $\alpha$ , t, 6.7), 2.95 (H $\beta$ , t, 6.7), 7.11 (H-2', H-3', q, 8.8), 2.29 (ArOAc), 2.13 (C-1 OAc); ( $CDCl_3$ ) 89.5 (C-1), 151.6 (C-3), 110.2 (C-4), 26.6 (C-5), 42.2 (C-6)<sup>a</sup>, 217.1 (C-7), 43.2 (C-8)<sup>a</sup>, 44.6 (C-9)<sup>a</sup>, 13.1 (C-10), 166.3 (C-11), 64.8 (C $\alpha$ ), 34.6 (C $\beta$ ), 135.6 (C-1'), 130.0 (C-2'), 121.9 (C-3'), 149.8 (C-4'), 169.7, 169.5 (O=CMe), 21.1, 20.9 (O=CMe). *Syringa reticulata* (Oleaceae) (222)

## 337. SYRINGOPICROGENIN B



$C_{18}H_{20}O_7$  348.35 triacetate  $[\alpha] -65.2^\circ$  ( $CHCl_3$ ) (60 MHz  $CDCl_3$ ) 6.29 (H-1, d, 2.1), 7.38 (H-3, d, 1.5), 1.17 (H-10, d, 6.4), 4.34 (H $\alpha$ , t, 6.7), 2.95 (H $\beta$ , t, 6.7), 7.17–7.00 (H-2', H-5', H-6'), 2.28 (ArOAc), 2.13 (C-1 OAc); ( $CDCl_3$ ) 89.5 (C-1), 151.8 (C-3), 110.0 (C-4), 26.6 (C-5), 42.1 (C-6)<sup>a</sup>, 217.2 (C-7), 43.2 (C-8)<sup>a</sup>, 44.5 (C-9)<sup>a</sup>, 13.1 (C-10), 166.3 (C-11), 64.5 (C $\alpha$ ), 34.5 (C $\beta$ ), 136.9 (C-1'), 123.6 (C-2'), 142.3 (C-3'), 141.1 (C-4'), 124.1 (C-6'), 127.1 (C-6'), 169.5, 168.6 (O=CMe), 20.8, 20.6 (O=CMe). *Syringa reticulata* (Oleaceae) (222)

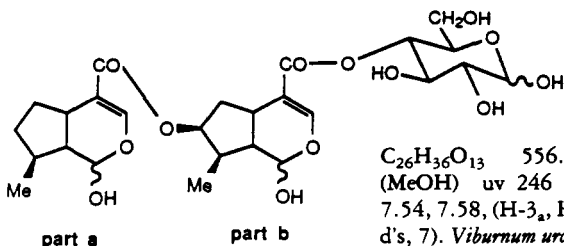
## 338. SYRINGOPICROGENIN C



$C_{19}H_{22}O_8$  378.38 triacetate  $[\alpha] -36.3^\circ$  ( $CHCl_3$ ) (triacetate 60 MHz  $CDCl_3$ ) 6.30 (H-1, d, 2.1), 7.42 (H-3, d, 1.2), 1.18 (H-10, d, 6.6), 4.27 (H $\alpha$ , m), 3.80 (H $\beta$ , q, 5.1, 2.1), 7.30–7.00 (H-2', H-5', H-6'), 3.32 (OMe), 2.28 (ArOAc), 2.13 (C-1 OAc); (triacetate  $CDCl_3$ ) 89.5 (C-1), 152.1 (C-3), 110.0 (C-4), 26.6 (C-5), 42.2 (C-6)<sup>a</sup>, 217.2 (C-7), 43.2 (C-8)<sup>a</sup>, 44.6 (C-9)<sup>a</sup>, 13.1 (C-10), 166.3 (C-11), 67.4 (C $\alpha$ ), 80.9 (C $\beta$ ), 57.5 (OMe), 127.2 (C-1'), 122.2 (C-2'), 142.6 (C-3'), 137.2 (C-4'), 123.9 (C-5'), 125.1 (C-6'), 169.6, 168.4 (O=CMe), 20.8, 20.6 (O=CMe). *Syringa reticulata* (Oleaceae) (222)

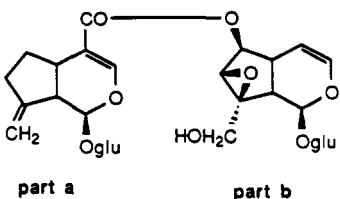
## Group 5 (bis-iridoids and bis-iridoid aglycones)

## 339. URCEOLATOSIDE B



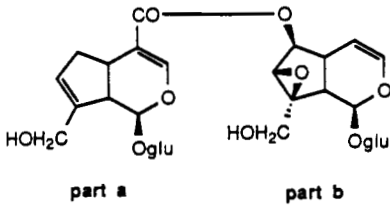
$C_{26}H_{36}O_{13}$  556.56 mp 148–152°  $[\alpha] -15^\circ$  (MeOH) uv 246 (MeOH) (100 MHz pyridine-*d*<sub>5</sub>) 7.54, 7.58, (H-3<sub>a</sub>, H-3<sub>b</sub>, s's), 0.8, 0.94 (H-10<sub>a</sub>, H-10<sub>b</sub>, d's, 7). *Viburnum urceolatum* (Caprifoliaceae) (220)

## 340. RADIATOSIDE C



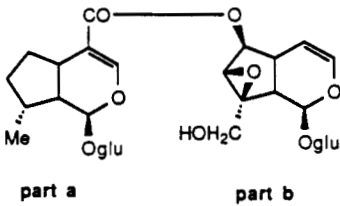
$C_{31}H_{42}O_{18}$  702.66  $[\alpha] -125.3^\circ$  (MeOH) uv 234 (MeOH) (400 MHz  $D_2O$ ) 5.12 (H-1<sub>a</sub>, d, 5.8), 7.38 (H-3<sub>a</sub>, d, 1), 2.78 (H-5<sub>a</sub>, m), 2.24–1.55 (H-6<sub>a</sub>, H-7<sub>a</sub>), 2.92 (H-9<sub>a</sub>, dd, 8, 5.8), 5.00 (H-10<sub>a</sub>, bdd, 6.3, 1.9), 4.78 (H-1'<sub>a</sub>, d, 7.9), 4.97 (H-1<sub>b</sub>, d, 9.5), 6.19 (H-3<sub>b</sub>, dd, 6, 1.9), 4.82 (H-4<sub>b</sub>, dd, 6, 3.5), 2.48 (H-5<sub>b</sub>, m), 4.83 (H-6<sub>b</sub>, dd, 7.9, 1), 3.73 (H-7<sub>b</sub>, bs), 2.62 (H-9<sub>b</sub>, dd, 9.5, 8), 3.89, 3.79 (H-10<sub>b</sub>, 13.2), 4.68 (H-1'<sub>b</sub>, d, 7.9); ( $CD_3OD$ ) 96.6 (C-1<sub>a</sub>), 150.4 (C-3<sub>a</sub>), 111.0 (C-4<sub>a</sub>), 31.1 (C-5<sub>a</sub>), 30.9 (C-6<sub>a</sub>), 36.1 (C-7<sub>a</sub>), 154.4 (C-8<sub>a</sub>), 45.7 (C-9<sub>a</sub>), 110.0 (C-10<sub>a</sub>), 169.4 (C-11<sub>a</sub>), 99.4 (C-1'<sub>a</sub>), 73.5 (C-2'<sub>a</sub>), 77.4 (C-3'<sub>a</sub>), 70.3 (C-4'<sub>a</sub>), 76.5 (C-5'<sub>a</sub>), 61.5 (C-6'<sub>a</sub>), 95.0 (C-1<sub>b</sub>), 141.7 (C-3<sub>b</sub>), 103.2 (C-4<sub>b</sub>), 34.3 (C-5<sub>b</sub>), 80.4 (C-6<sub>b</sub>), 60.3 (C-7<sub>b</sub>), 67.2 (C-8<sub>b</sub>), 42.2 (C-9<sub>b</sub>), 60.4 (C-10<sub>b</sub>), 99.1 (C-1'<sub>b</sub>), 73.5 (C-2'<sub>b</sub>), 77.0 (C-3'<sub>b</sub>), 70.3 (C-4'<sub>b</sub>), 76.5 (C-5'<sub>b</sub>), 61.5 (C-6'<sub>b</sub>). *Argylia radiata* (Bignoniaceae) (246)

341. RADIATOSIDE B



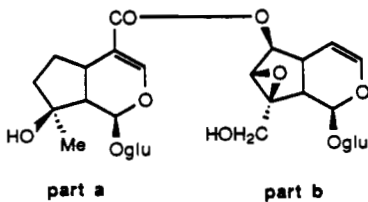
$C_{31}H_{42}O_{19}$  718.66  $[\alpha] -138.6^\circ$  (MeOH) uv 234 (MeOH) [400 MHz  $CD_3OD-CDCl_3$  (2:8)] 5.09 (H-1<sub>a</sub>, d, 7.2), 7.47 (H-3<sub>a</sub>, d, 0.5), 2.72 (H-5<sub>a</sub>, m), 1.98 (H-6<sub>a</sub>, m), 5.68 (H-7<sub>a</sub>, bs), 2.48 (H-9<sub>a</sub>, t, 7.2), 4.19, 4.07 (H-10<sub>a</sub>, 14), 4.99 (H-1<sub>b</sub>, d, 9.5), 6.19 (H-3<sub>b</sub>, dd, 6, 1.9), 4.82 (H-4<sub>b</sub>, dd, 6, 3.5), 2.48 (H-5<sub>b</sub>, m), 4.84 (H-6<sub>b</sub>, dd, 7.9, 1), 3.73 (H-7<sub>b</sub>, bs), 2.64 (H-9<sub>b</sub>, dd, 9.5, 8), 3.91, 3.70 (H-10<sub>b</sub>, 13.2); ( $CD_3OD$ ) 98.0 (C-1<sub>a</sub>), 154.2 (C-3<sub>a</sub>), 109.9 (C-4<sub>a</sub>), 35.0 (C-5<sub>a</sub>), 36.2 (C-6<sub>a</sub>), 130.0 (C-7<sub>a</sub>), 141.6 (C-8<sub>a</sub>), 46.9 (C-9<sub>a</sub>), 61.4 (C-10<sub>a</sub>), 169.3 (C-11<sub>a</sub>), 99.4 (C-1'<sub>a</sub>), 73.7 (C-2'<sub>a</sub>), 77.1 (C-3'<sub>a</sub>)<sup>a</sup>, 70.4 (C-4'<sub>a</sub>), 76.6 (C-5'<sub>a</sub>)<sup>a</sup>, 61.5 (C-6'<sub>a</sub>), 96.4 (C-1<sub>b</sub>), 141.2 (C-3<sub>b</sub>), 102.5 (C-4<sub>b</sub>), 33.8 (C-5<sub>b</sub>), 80.5 (C-6<sub>b</sub>), 60.7 (C-7<sub>b</sub>), 67.2 (C-8<sub>b</sub>), 42.3 (C-9<sub>b</sub>), 60.5 (C-10<sub>b</sub>), 99.4 (C-1'<sub>b</sub>), 73.7 (C-2'<sub>b</sub>), 77.2 (C-3'<sub>b</sub>)<sup>a</sup>, 70.4 (C-4'<sub>b</sub>), 76.6 (C-5'<sub>b</sub>)<sup>a</sup>, 61.5 (C-6'<sub>b</sub>). *Argylia radiata* (Bignoniaceae) (246)

342. ARGYLIOSIDE



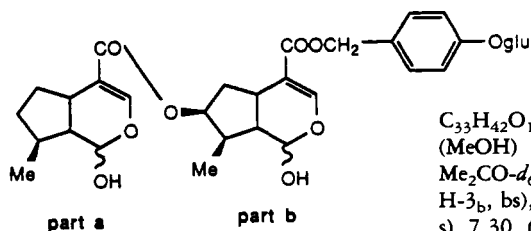
$C_{31}H_{44}O_{18}$  704.68  $[\alpha] -126^\circ$  (MeOH) uv 234 (MeOH) (400 MHz  $CD_3OD$ ) 5.43 (H-1<sub>a</sub>, d, 5.1), 7.43 (H-3<sub>a</sub>, bs), 2.92 (H-5<sub>a</sub>, bq, 8.3, 8.3, 8.3), 1.59 (H-6<sub>a</sub>α), dddd, 12.6, 9, 8.3), 2.07 (H-6<sub>a</sub>β), dddd, 12.6, 8.3, 8.3, 8.3), 1.76 (H-7<sub>a</sub>α), dddd, 12.4, 8.3), 1.36 (H-7<sub>a</sub>β), dddd, 12.4, 9, 8.3, 8.3), 2.23 (H-8<sub>a</sub>, H-9<sub>a</sub>, m, 8.3, 7.3, 5.1), 1.06 (H-10<sub>a</sub>, d, 7.3), 4.71 (H-1'<sub>a</sub>, d, 7.2), 5.08 (H-1<sub>b</sub>, d, 9.3), 6.32 (H-3<sub>b</sub>, dd, 6.5, 1.8), 4.74 (H-4<sub>b</sub>, dd, 6.5, 4), 2.48 (H-5<sub>b</sub>, m, 7.5, 7.2, 4, 1.8), 4.66 (H-6<sub>b</sub>, dd, 7.2, 2.2), 3.64 (H-7<sub>b</sub>, bs, 2.2), 2.54 (H-9<sub>b</sub>, dd, 9.3, 7.5), 3.64, 4.08 (H-10<sub>b</sub>, d, 13.2), 4.65 (H-1'<sub>b</sub>, d, 7.2); ( $CD_3OD$ ) 95.1 (C-1<sub>a</sub>), 152.5 (C-3<sub>a</sub>), 112.1 (C-4<sub>a</sub>), 32.2 (C-5<sub>a</sub>), 31.0 (C-6<sub>a</sub>)<sup>a</sup>, 33.3 (C-7<sub>a</sub>)<sup>a</sup>, 34.3 (C-8<sub>a</sub>), 43.5 (C-9<sub>a</sub>), 15.7 (C-10<sub>a</sub>), 167.9 (C-11<sub>a</sub>), 98.7 (C-1'<sub>a</sub>), 73.7 (C-2'<sub>a</sub>), 77.3 (C-3'<sub>a</sub>)<sup>b</sup>, 69.6 (C-4'<sub>a</sub>), 77.1 (C-5'<sub>a</sub>)<sup>b</sup>, 61.9 (C-6'<sub>a</sub>), 94.1 (C-1<sub>b</sub>), 141.3 (C-3<sub>b</sub>), 102.1 (C-4<sub>b</sub>), 36.4 (C-5<sub>b</sub>), 80.5 (C-6<sub>b</sub>), 59.2 (C-7<sub>b</sub>), 65.2 (C-8<sub>b</sub>), 42.0 (C-9<sub>b</sub>), 60.1 (C-10<sub>b</sub>), 98.7 (C-1'<sub>b</sub>), 73.7 (C-2'<sub>b</sub>), 77.1 (C-3'<sub>b</sub>)<sup>b</sup>, 69.6 (C-4'<sub>b</sub>), 76.6 (C-5'<sub>b</sub>)<sup>b</sup>, 61.9 (C-6'<sub>b</sub>). *Argylia radiata* (Bignoniaceae) (247)

343. RADIATOSIDE



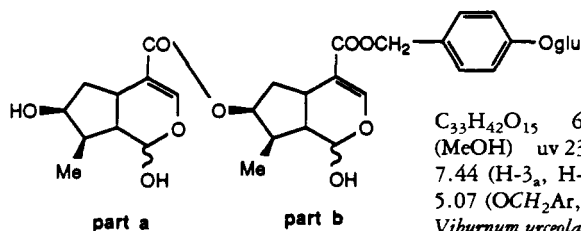
$C_{31}H_{44}O_{91}$  720.68  $[\alpha] -48.9^\circ$  (MeOH) uv 234 (MeOH) (400 MHz  $CD_3OD$ ) 5.09 (H-1<sub>a</sub>, d, 9.5), 6.33 (H-3<sub>a</sub>, dd, 6.5, 1.8), 4.68 (H-4<sub>a</sub>, dd, 6.5, 4), 2.57 (H-5<sub>a</sub>, m), 4.88 (H-6<sub>a</sub>, dd, 8, 1), 3.64 (H-7<sub>a</sub>, m), 2.60 (H-9<sub>a</sub>, dd, 9.5, 7.5), 4.09, 3.79 (H-10<sub>a</sub>, 13.2), 4.59 (H-1'<sub>a</sub>, d, 8), 5.45 (H-1<sub>b</sub>, d, 3.5), 7.49 (H-3<sub>b</sub>, s), 1.6-2.4 (H-5<sub>b</sub>, H-6<sub>b</sub>, H-7<sub>b</sub>), 3.10 (H-9<sub>b</sub>, m), 1.40 (H-10<sub>b</sub>, s), 4.75 (H-1'<sub>b</sub>, d, 8); ( $CD_3OD$ ) 94.1 (C-1<sub>a</sub>)<sup>a</sup>, 141.5 (C-3<sub>a</sub>), 102.0 (C-4<sub>a</sub>), 35.5 (C-5<sub>a</sub>), 80.2 (C-6<sub>a</sub>), 58.7 (C-7<sub>a</sub>), 65.8 (C-8<sub>a</sub>), 42.1 (C-9<sub>a</sub>), 59.4 (C-10<sub>a</sub>), 98.8 (C-1'<sub>a</sub>), 73.7 (C-2'<sub>a</sub>), 77.5 (C-3'<sub>a</sub>)<sup>b</sup>, 70.7 (C-4'<sub>a</sub>), 76.8 (C-5'<sub>a</sub>)<sup>b</sup>, 61.6 (C-6'<sub>a</sub>), 94.6 (C-1<sub>b</sub>)<sup>a</sup>, 151.8 (C-3<sub>b</sub>), 113.2 (C-4<sub>b</sub>), 30.7 (C-5<sub>b</sub>), 29.7 (C-6<sub>b</sub>), 39.8 (C-7<sub>b</sub>), 80.1 (C-8<sub>b</sub>), 51.1 (C-9<sub>b</sub>), 23.7 (C-10<sub>b</sub>), 169.3 (C-11<sub>b</sub>), 98.8 (C-1'<sub>b</sub>), 73.8 (C-2'<sub>b</sub>), 77.3 (C-3'<sub>b</sub>)<sup>b</sup>, 70.7 (C-4'<sub>b</sub>), 77.0 (C-5'<sub>b</sub>)<sup>b</sup>, 61.8 (C-6'<sub>b</sub>). *Argylia radiata* (Bignoniaceae) (248)

## 344. URCEOLATOSIDE A



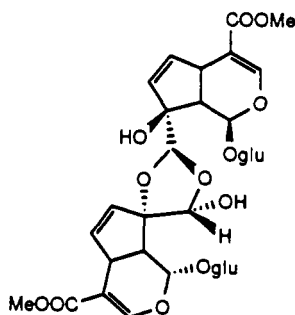
$C_{33}H_{42}O_{14}$  662.69 mp 136–140°  $[\alpha] -56^\circ$   
(MeOH) uv 240, 228, 204 (MeOH) (60 MHz  
 $Me_2CO-d_6$ ) 4.93 (H-1<sub>a</sub>, H-1<sub>b</sub>, H-1'<sub>b</sub>, m), 7.38 (H-3<sub>a</sub>,  
H-3<sub>b</sub>, bs), 1.08 (H-10<sub>a</sub>, H-10<sub>b</sub>, d, 7), 5.02 (OCH<sub>2</sub>Ar,  
s), 7.30, 6.99 (H-2'<sub>b</sub>, H-3'<sub>b</sub>, d's, 10). *Viburnum urceolatum* (Caprifoliaceae) (220)

## 345. URCEOLATOSIDE C



$C_{33}H_{42}O_{15}$  678.69 mp 134–138°  $[\alpha] -42.1^\circ$   
(MeOH) uv 238, 228 (MeOH) (60 MHz  $Me_2CO-d_6$ )  
7.44 (H-3<sub>a</sub>, H-3<sub>b</sub>, bs), 1.07 (H-10<sub>a</sub>, H-10<sub>b</sub>, bd, 6),  
5.07 (OCH<sub>2</sub>Ar, s), 7.36, 7.00 (H-2'<sub>b</sub>, H-3'<sub>b</sub>, d's, 9).  
*Viburnum urceolatum* (Caprifoliaceae) (220)

## 346. 10-DEHYDROGARDENOSIDE DIMER



$C_{34}H_{44}O_{22}$  804.71 mp 168–170°  $[\alpha] -113.9^\circ$   
(H<sub>2</sub>O) uv 235 (MeOH) (200 MHz D<sub>2</sub>O) 5.87 (H-1,  
d, 2), 7.46 (H-3, bs), 6.40 (H-6, dd, 6, 3), 5.74 (H-7,  
dd, 6, 2), 2.77 (H-9, dd, 8, 2), 5.23 (H-10, s), 5.94 (H-1',  
d, 1.2), 7.50 (H-3', bs), 6.46 (H-6', dd, 6.4, 3.2),  
5.84 (H-7', dd, 6.4, 1), 2.99 (H-9', dd, 9.2, 1.2), 5.58  
(H-10', s), 3.77 (COOMe); (nonacetate CDCl<sub>3</sub>), 92.9,  
92.7 (C-1, C-1'), 149.5, 149.4 (C-3, C-3'), 111.7,  
111.5 (C-4, C-4'), 37.2 (C-5, C-5'), 133.5, 128.9 (C-6,  
C-6'), 138.8, 136.0 (C-7, C-7'), 96.1, 84.3 (C-8, C-8'),  
51.7, 49.9 (C-9, C-9'), 105.7, 94.1 (C-10, C-10'),  
166.6, 166.5 (C-11, C-11'), 51.3 (OMe). *Randia canthioides* (Rubiaceae) (14)

TABLE 2. Alphabetical Compound Index

(1R)-1-Acetoxydesert-3-ene	321	8-O-Acetylmussaenosidic acid	184
(1S)-1-Acetoxydesert-3-ene	322	6-O-Acetylscandoside	193
Acetylbarlerin	245	6-O-Acetylshanzhiside methyl ester	243
6-O-(2,3,4-Acetylcinnamoyl)-p-methoxycinnamoyl)rhannosylcatalpol	106	8-O-Acetylshanzhiside methyl ester	244
6'-O-Acetyldeutzioside	5	10-O-Acetylsplendoside	275
7-O-Acetyl-8- <i>epi</i> -loganic acid	171	Adoxoside	270
10-O-Acetylgenipin	331	Adoxosidic acid	191
10-O-Acetylgeniposide	260	Agnuside	76
8-O-Acetylharpagide	44	Ajugol	35
10-O-Acetyl-6β-hydroxymonogolioside	139	Ajugoside	36
7-O-Acetylloganic acid	178	Allobetonicoside	19
6-O-(2''-O-Acetyl-3''-O-p-methoxy-trans-cinnamoyl)rhannopyranosylaucubin	72	Allosyldecaloside	8
6-O-Acetylmioporoside	32	Allosylepoxydecaloside	12
8-O-Acetylmioporoside	33	Amareloside	75
		Andromedoside	197
		6-O-Angeloylantirinoside	26

- Apodantheroside **283**  
 Arbortristoside A **238**  
 Arbortristoside B **278**  
 Argylioside **342**  
 Asperulosidol **143**  
 Asystasioside A **294**  
 Asystasioside B **293**  
 Asystasioside C **299**  
 Asystasioside D **300**  
 Asystasioside E **127**  
 $\alpha$ -Aucubigenin **306**  
 $\beta$ -Aucubigenin **307**  
 Aucubigenin-1-*O*- $\beta$ -cellobioside **60**  
 Aucubigenin-1-*O*- $\beta$ -gentiobioside **61**  
 Aucubigenin-1-*O*- $\beta$ -serotinoside **62**  
 Avicennioside **55**  
 Barbatoside **235**  
 Barlerin **244**  
 Bartsioside **58**  
 6-*O*-Benzoyl-6'-*O*-acetylshanzhiside methyl ester **248**  
 2'-*O*-Benzoylaucubin **63**  
 8-*O*-Benzoylharpagide **45**  
 6-*O*-Benzoylshanzhiside methyl ester **246**  
 8-*O*-Benzoylshanzhiside methyl ester **247**  
 7-*O*-Benzoyltecomoside **152**  
 5,7-Bisdeoxycynanchoside **122**  
 Boschnaside **132**  
 Cachineside I **149**  
 Cachineside III **165**  
 Cachineside IV **163**  
 Cachineside V **161**  
 10-*O*-Caffeoyldeacetyldaphylloside **264**  
 2'-*O*-*cis*-Caffeoylloganin **222**  
 2'-*O*-*trans*-Caffeoylloganin **223**  
 6-*O*-Caffeoylnyctanthoside **278**  
 6-*O*-(2''-*O*-Caffeoylrhamnopyranosyl)catalpol **94**  
 6-*O*-(3''-*O*-Caffeoylrhamnopyranosyl)catalpol **95**  
 Calycinoside **119**  
 Campenoside **150**  
 Campsioside **162**  
 Capenoside **120**  
 Caprarioside **45**  
 Catalpin **315**  
 Catalpolgenin-1-*O*- $\alpha$ -L-arabinofuranoside **88**  
 6'-*O*-Cinnamoylantirrinoside **25**  
 10-*O*-Cinnamoylaucubin **77**  
 10-*O*-*cis*-Cinnamoylcatalpol **117**  
 7-*O*-Cinnamoyl-8-*epi*-Loganic acid **173**  
 8-*O*-*cis*-Cinnamoylharpagide **46**  
 10-*O*-*trans*-Cinnamoylmelittoside **82**  
 2'-*O*-Cinnamoylmussaenosidic acid **187**  
 6-*O*-(2''-*O*-Cinnamoyl- $\alpha$ -L-rhamnopyranosyl)aucubin **69**  
 6-*O*-(3''-*O*-Cinnamoyl- $\alpha$ -L-rhamnopyranosyl)aucubin **70**  
 7-*O*-Cinnamoyltecomoside **154**  
 Cistachlorin **312**  
 Cistanin **311**  
 6-*O*-*p*-Coumaroylajugol **40**  
 10-*O*-*cis*-*p*-Coumaroylaucubin **78**  
 10-*O*-*trans*-*p*-Coumaroylaucubin **79**  
 6-*O*-*p*-Coumaroylcatalpol **110**  
 4'-*O*-*p*-Coumaroyl-7,8-dihydro-8-dehydroxy-methylbartsioside **1**  
 6''-*O*-*p*-Coumaroylgenipin gentiobioside **261**  
 6'-*O*-*p*-Coumaroylharpagide **48**  
 8-*O*-*p*-Coumaroylharpagide **47**  
 6-*O*-*trans*-*p*-Coumaroyl-6 $\beta$ -hydroxyloganin **237**  
 4'-*O*-*cis*-*p*-Coumaroylloganic acid **176**  
 4'-*O*-*trans*-*p*-Coumaroylloganic acid **177**  
 2'-*O*-*cis*-Coumaroylloganin **218**  
 2'-*O*-*trans*-Coumaroylloganin **219**  
 4'-*O*-*cis*-*p*-Coumaroylloganin **220**  
 4'-*O*-*trans*-*p*-Coumaroylloganin **221**  
 7-*O*-*p*-Coumaroylloganin **227**  
 6'-*O*-*p*-Coumaroylprocumbide **24**  
 6-*O*-(3''-*O*-*p*-Coumaroyl- $\alpha$ -L-rhamnopyranosyl)aucubin **71**  
 6-*O*-(2''-*O*-*p*-Coumaroyl- $\alpha$ -L-rhamnopyranosyl)catalpol **91**  
 6-*O*-(3''-*O*-*p*-Coumaroyl- $\alpha$ -L-rhamnopyranosyl)catalpol **92**  
 6-*O*-*p*-Coumaroylscandoside methyl ester **266**  
 3''-*O*-*p*-Coumaroylsinuatoal **71**  
 7-*O*-*p*-Coumaroyltecomoside **155**  
 Cynanchoside **129**  
 Daunoside **51**  
 Deacetylasperulosidic acid methyl ester **262**  
 Deacetylasperulosidic acid methyl ester aglycone **327**  
 Deacetyldaphylloside **262**  
 Decapetaloside **138**  
 Decumbeside A **23**  
 Decumbeside B **22**  
 Decumbeside C **50**  
 Decumbeside D **49**  
 10-Dehydrogardenoside **289**  
 10-Dehydrogardenoside dimer **346**  
 10-Dehydrogeniposide **288**  
 7-Dehydrologanin **229**  
 1-Dehydroxy-3,4-dehydroaucubigenin **305**  
 6-Deoxycatalpol **86**  
 7-Deoxy-8-*epi*-loganic acid **169**  
 7-Deoxy-8-*epi*-loganin **209**  
 7-Deoxygardsoside **189**  
 10-Deoxygeniposide **208**  
 5-Deoxylamiol **134**  
 5-Deoxylamioside **135**  
 6-Deoxylamioside **136**  
 10-Deoxymelittoside **16**  
 5-Deoxypulchelloside I **234**  
 5-Deoxystansioside **144**  
 Depressoside **296**  
 10-Descinnamoylglobularimin **124**  
 10-Descinnamoylglobularinin **125**  
 6-Desoxy-8-*O*-isoferuloylharpagide **30**  
 $\alpha$ -Deutzigenin **301**  
 $\beta$ -Deutzigenin **302**  
 6,8-Di-*O*-acetylshanzhiside methyl ester **245**  
 6,6'-Di-*O*-benzoylshanzhiside methyl ester **249**  
 2',8-Di-*O*-foliamenthoyleuphoroside **160**

- 6,7-Dihydroapodantheroside **270**  
 3,4-Dihydroaucubin **56**  
 (8*S*)-7,8-Dihydroaucubin **121**  
 Dihydrobrasoside **198**  
 Dihydrocatalpol **87**  
 8 $\alpha$ -Dihydrogeniposide **269**  
 8 $\beta$ -Dihydrogeniposide **270**  
 $\alpha$ -Dihydrogriselinoside **291**  
 $\beta$ -Dihydrogriselinoside **292**  
 $\alpha$ -Dihydrohastatoside **231**  
 $\beta$ -Dihydrohastatoside **232**  
 $\alpha$ -Dihydroverbenol **140**  
 $\beta$ -Dihydroverbenol **141**  
 5 $\beta$ ,7 $\alpha$ -Dihydroxydeutzol **6**  
 7 $\alpha$ ,10-Dihydroxyharpagide **129**  
 Durantoside 4 **255**  
 Eccremocarpol A **308**  
 Eccremocarpol B **310**  
 6-*epi*-Aucubin **59**  
 8-*epi*-Boschnaloside **144**  
 8-*epi*-Caryptoside **252**  
 1,5,9-*epi*-Deoxyloganic acid **168**  
 6-*epi*-Dihydrocornin **210**  
 7-*epi*-(*Di-m*-hydroxybenzoyl)loganic acid **182**  
 7-*epi*-(*m*-Hydroxybenzoyl)loganic acid **180**  
 8-*epi*-Iridodial glucoside **132**  
 3-*epi*-Jioglutin A **318**  
 8-*epi*-Loganic acid **170**  
 7-*epi*-Loganin **212**  
 8-*epi*-Loganin **214**  
 7-*epi*-*O*-(*m*-Methoxybenzoyl)loganin **213**  
 6-*epi*-Monomelittoside **80**  
 8-*epi*-Splendoside **273**  
 6-*epi*-Stilbericoside **2**  
 Epoxydecaloside **11**  
 5,6- $\beta$ -Epoxy-7 $\beta$ -hydroxy-8 $\beta$ -methyl-1- $\beta$ -D-  
 rhamnosidal iridoid **20**  
 6 $\alpha$ ,7 $\alpha$ -Epoxy splendoside **286**  
 6 $\beta$ ,7 $\beta$ -Epoxy splendoside **287**  
 Eranthemoside **130**  
 Euphroside **158**  
*cis*-Eurostoside **78**  
*trans*-Eurostoside **79**  
 6-*O*-*cis*-Feruloylajugol **41**  
 6-*O*-*trans*-Feruloylajugol **42**  
 6-*O*-*cis*-Feruloylcatalpol **112**  
 6-*O*-*trans*-Feruloylcatalpol **113**  
 2'-*O*-*cis*-Feruloylloganin **224**  
 2'-*O*-*trans*-Feruloylloganin **225**  
 6-*O*-Feruloylscandoside methyl ester **268**  
 6-*O*-Feruloylshanzhiside **188**  
 6-*O*-Foliamenthoylajugol **43**  
 6-*O*-Foliamenthoylcatalpol **116**  
 6-*O*-Foliamenthoyl-6-*epi*-aucubin **75**  
 8-*O*-Foliamenthoyleuphroside **159**  
 Galioside **284**  
 Galioside 10-acetate **285**  
 Galioside aglucone **335**  
 Gardenogenin A **332**  
 Gardenogenin B **333**  
 Gardenosidic acid **195**  
 $\alpha$ -Gardiol **333**  
 $\beta$ -Gardiol **334**  
 Gardoside methyl ester **258**  
 Gelsemide **324**  
 Gelsemide 7-glucoside **202**  
 Globularicisin **117**  
 Globularin **118**  
 6-*O*-Glucopyranosylaucubin **65**  
 6'-*O*-Glucosylaucubin **61**  
 6-*O*-Glucosyl-2'-*O*-benzoylaurubin **64**  
 Glucosyldecaloside **9**  
 Glucosylepoxydecaloside **13**  
 5-*O*-Glucosylmacfadienoside **119**  
 Glutinoside **128**  
 6 $\beta$ -Hydroxyadoxoside **271**  
 8 $\alpha$ -Hydroxyapodanthoside **290**  
 6-*O*-*p*-Hydroxybenzoylajugol **37**  
 10-*O*-*p*-Hydroxybenzoylaurubin **76**  
 6-*O*-*p*-Hydroxybenzoyl-6-*epi*-aucubin **73**  
 7-*O*-*p*-Hydroxybenzoyl-8-*epi*-loganic acid **172**  
 6-*O*-*p*-Hydroxybenzoyl-6-*epi*-monomelitto-  
 side **84**  
 7-*O*-*p*-Hydroxybenzoylgardoside **190**  
 4'-*O*-*m*-Hydroxybenzoylloganin **216**  
 6'-*O*-*m*-Hydroxybenzoylloganin **217**  
 2'-*O*-*p*-Hydroxybenzoylmussaenosidic acid **185**  
 6'-*O*-*p*-Hydroxybenzoylmussaenosidic acid **186**  
 7-*O*-*p*-Hydroxybenzoyltecomoside **153**  
 5-Hydroxycampenoside **154**  
 5-Hydroxycampsiside **164**  
 10-Hydroxycornin **276**  
 11-Hydroxydecapetaloside **142**  
 11-Hydroxydeutzioside **11**  
 6 $\alpha$ -Hydroxy-1-*epi*-genipin **328**  
 7 $\beta$ -Hydroxy-8-*epi*-iridodial glucoside **133**  
 5-Hydroxy-8-*epi*-loganin **233**  
 6 $\alpha$ -Hydroxygenipin **329**  
 6 $\beta$ -Hydroxygenipin **330**  
 6 $\alpha$ -Hydroxygeniposide **262**  
 6 $\beta$ -Hydroxygeniposide **265**  
 6 $\beta$ -Hydroxyipolamiide **253**  
 6 $\beta$ -Hydroxyloganin **236**  
 10-Hydroxyloganin **272**  
 9-Hydroxysemperoside **201**  
 9-Hydroxysemperoside aglucone **325**  
 6 $\beta$ -Hydroxysplendoside **279**  
 7 $\alpha$ -Hydroxysplendoside **281**  
 7 $\beta$ -Hydroxysplendoside **282**  
 6 $\beta$ -Hydroxysplendoside 10-acetate **280**  
 7 $\beta$ -Hydroxystanside **149**  
 Hygrophiloside **131**  
 Ipolamiide **240**  
 6-*O*-(2''-*O*-Isoferuloylrhamnopyranosyl)  
 catalpol **96**  
 6-*O*-(3''-*O*-Isoferuloylrhamnopyranosyl)  
 catalpol **97**  
 Isoscrophularioside **77**  
 6-*O*-Isovanilloylcatalpol **108**  
 Jaranidoside **54**  
 Jioglutin A **319**  
 Jioglutin B **318**



- Jioglutin C **316**  
 Jioglutoside A **88**  
 Jioglutoside B **257**  
 7-Ketologanin **229**  
 Kickxioside **28**  
 Lamiide **254**  
 Lamourouxide I **167**  
 Leonuride **36**  
 Linarioside **55**  
 Loganetin **326**  
 Loganic acid **175**  
 Loganin **215**  
 Lychnitoside **7**  
 Lytanthosalin **77**  
 Melittoside **81**  
 Mentzelosylepoxydecaloside **14**  
 6-*O*-*p*-Methoxybenzoyl-6-*epi*-monomelittoside **85**  
 6-*O*-*p*-Methoxycinnamoylaucubin **74**  
 6-*O*-*p*-Methoxycinnamoylcatalposide **111**  
 6-*O*-*p*-Methoxycinnamoylscandoside methyl ester **267**  
 7-*O*-*p*-Methoxycinnamoylrecomoside **156**  
 (1*R*)-1-Methoxymyodesert-3-ene **320**  
 4-Methylantirrinoside **137**  
 10-Methylxioside **207**  
 Methyl paederoside **263**  
 3-*O*-Methylrehmaglutin B **319**  
 6'-*O*-[2(*R*)-Methyl-3-veratroxyloxypropanoyl]loganin **226**  
 Mollugoside **290**  
 Monotropein **196**  
 Monotropein methyl ester **284**  
 MS-5 **184**  
 MS-6 **171**  
 Mussaenoside **239**  
 Mussaenosidic acid **183**  
 Myodesertin **320**  
 Myoporoside **31**  
 Negundoside **185**  
 Nemoroside **116**  
 Nemorososide **43**  
 6-*O*-Nerol-8-oylantirrinoside **29**  
 Nigroside 1 **70**  
 Nigroside 2 **69**  
 Nishindaside **57**  
 Nyctanthoside **277**  
 Oldenlandoside I **266**  
 Oldenlandoside II **268**  
 Paederoside **203**  
 Paulownioside **123**  
 Penstemonoside **211**  
 Penstemoside **230**  
 Periclymenoside **228**  
 Periclymenosidic acid **179**  
 7-*O*-(5-Phenyl-2,4-pentadienoyl)-8-*epi*-loganic acid **174**  
 10-*O*-(5-Phenyl-2,4-pentadienoyl)geniposidic acid **192**  
 Physoside **53**  
 Pinifolin **157**  
 Plantarenaloside **145**  
 Plantarenalosisigenin-1-*O*- $\beta$ -gentiobioside **146**  
 Ponderanoside **164**  
 Premnoside A **100**  
 Premnoside B **101**  
 Premnoside C **102**  
 Premnoside D **103**  
 Procumboside **21**  
 Pulverulentoside I **98**  
 Pulverulentoside II **99**  
 Quinovosyldecaloside **10**  
 Radiatoside **343**  
 Radiatoside B **341**  
 Radiatoside C **340**  
 Randioside **15**  
 Rehmaglutin A **313**  
 Rehmaglutin B **317**  
 Rehmaglutin D **314**  
 Rehmannioside A **89**  
 Rehmannioside B **90**  
 Rehmannioside C **34**  
 Rehmannioside D **83**  
 6-*O*- $\alpha$ -L-Rhamnopyranosylaucubin **68**  
 6-*O*-(4''-*O*- $\alpha$ -L-Rhamnopyranosylvanilloyl)ajugol **39**  
 Saccaroside **91**  
 $\alpha$ -Scabrogenin **303**  
 $\beta$ -Scabrogenin **304**  
 Scabrosidol **6**  
 Scandoside methyl ester **265**  
 Scandoside methyl ester aglucone **330**  
 Scropolioside A **104**  
 Scropolioside B **105**  
 Semperoside **199**  
 Senburiside I **181**  
 Senburiside II **182**  
 6-*O*-Seneciolylantirrinoside **27**  
 Sesamoside **256**  
 Shanzhiside methyl ester **241**  
 Shanzhisin methyl ester gentiobioside **242**  
 Sinuatol **68**  
 Sinuatoside **67**  
 6-*O*-Sinuatosylaucubin **67**  
 Sophorosylmonomelittoside **83**  
 Specionin **309**  
 Specioside **110**  
 Speedoside **115**  
 Splendoside **274**  
 Splendoside 10-acetate **275**  
 Stanside **144**  
 Stansioside **147**  
 Stansiosigenin 1-*O*- $\beta$ -gentiobioside **148**  
 Strilbericoside **3**  
 Strictoloside **259**  
 Swertiaside **180**  
 Syringopicrogenin A **336**  
 Syringopicrogenin B **337**  
 Syringopicrogenin C **338**  
 Syringopicroside B **297**  
 Syringopicroside C **298**

6- <i>O</i> -Syringyl-8- <i>O</i> -acetylshanzhiside methyl ester	<b>251</b>	Urceolatoside C	<b>345</b>
6- <i>O</i> -Syringylshanzhiside methyl ester	<b>250</b>	Urceolatoside D	<b>295</b>
Tarennine	<b>188</b>	V1	<b>204</b>
Tarphetalin	<b>240</b>	V2	<b>205</b>
Tecoside	<b>151</b>	V3	<b>206</b>
Teucardoside	<b>18</b>	6- <i>O</i> -Vanilloylajugol	<b>38</b>
Teucrein	<b>323</b>	Vebraside	<b>200</b>
Teuhircoside	<b>17</b>	6- <i>O</i> -Veratroylcatalposide	<b>109</b>
Thunbergioside	<b>4</b>	Verbascoside A	<b>93</b>
Ugandoside	<b>166</b>	Verbascoside B	<b>126</b>
Undulatin	<b>1</b>	Verproside	<b>107</b>
Unedide	<b>194</b>	Virginioside	<b>52</b>
Urceolatoside A	<b>344</b>	Welloside	<b>114</b>
Urceolatoside B	<b>339</b>	6- <i>O</i> - $\beta$ -D-Xylopyranosylaucubin	<b>66</b>
		Yuheinoside	<b>145</b>

TABLE 3. Molecular Formula Index

$C_9H_{12}O_4$	<b>306</b> $\alpha$ -Aucubigenin	$C_{11}H_{16}O_5$	<b>326</b> Loganetin
	<b>307</b> $\beta$ -Aucubigenin	$C_{11}H_{18}O_2$	<b>320</b> (1 <i>R</i> )-1-Methoxymyodesert-3-ene (Myodesertin)
	<b>301</b> $\alpha$ -Deutzigenin	$C_{11}H_{18}O_6$	<b>308</b> Eccremocarpol A
	<b>302</b> $\beta$ -Deutzigenin	$C_{11}H_{20}O_7$	<b>310</b> Eccremocarpol B
$C_9H_{12}O_5$	<b>303</b> $\alpha$ -Scabrogenin	$C_{12}H_{18}O_3$	<b>321</b> (1 <i>R</i> )-1-Acetoxydesert-3-ene
	<b>304</b> $\beta$ -Scabrogenin	$C_{12}H_{18}O_4$	<b>322</b> (1 <i>S</i> )-1-Acetoxydesert-3-ene
$C_9H_{13}ClO_3$	<b>312</b> Cistachlorin	$C_{13}H_{16}O_6$	<b>331</b> 10- <i>O</i> -Acetylgenipin
$C_9H_{13}ClO_4$	<b>314</b> Rehmaglutin D	$C_{14}H_{20}O_5$	<b>323</b> Teucrein
$C_9H_{13}ClO_5$	<b>317</b> Rehmaglutin B	$C_{14}H_{20}O_9$	<b>88</b> Jioglutoside A (Catalpogenin-1- <i>O</i> - $\alpha$ -L-arabinofuranoside)
$C_9H_{14}O_3$	<b>305</b> 1-Dehydroxy-3,4-dihydroaucubigenin	$C_{14}H_{20}O_{10}$	<b>2</b> 6- <i>epi</i> -Stilbericoside
$C_9H_{14}O_4$	<b>311</b> Cistanin		<b>3</b> Stilbericoside
$C_9H_{14}O_5$	<b>313</b> Rehmaglutin A	$C_{14}H_{21}ClO_{10}$	<b>4</b> Thunbergioside
$C_{10}H_{12}O_5$	<b>324</b> Gelsemide	$C_{15}H_{20}O_9$	<b>131</b> Hygrophiloside
$C_{10}H_{14}O_5$	<b>325</b> 9-Hydroxysemperoside aglucone		<b>17</b> Teuhircoside
$C_{10}H_{15}ClO_5$	<b>319</b> Jioglutin A (3- <i>O</i> -methylrehmaglutin B)	$C_{15}H_{22}O_8$	<b>58</b> Bartsioside
	<b>318</b> Jioglutin B (3- <i>epi</i> -Jioglutin A)		<b>20</b> 5,6- $\beta$ -Epoxy-7 $\beta$ -hydroxy-8 $\beta$ -methyl- 1- $\beta$ -D-rhamnosidal iridoid
$C_{10}H_{16}O_6$	<b>316</b> Jioglutin C		<b>7</b> Lychnitoside
$C_{11}H_{14}O_6$	<b>327</b> Deacetylasperulosidic acid methyl ester aglycone	$C_{15}H_{22}O_9$	<b>86</b> 6-Deoxycatalpol
	<b>335</b> Galioside aglucone		<b>59</b> 6- <i>epi</i> -Aucubin
	<b>332</b> Gardenogenin A		<b>130</b> Eranthemside
	<b>333</b> Gardenogenin B ( $\alpha$ -Gardiol)	$C_{15}H_{22}O_{10}$	<b>80</b> 6- <i>epi</i> -Monomelirtoside
	<b>334</b> $\beta$ -Gardiol		<b>11</b> Epoxydecaloside (11-Hydroxydeutzio- side)
	<b>328</b> 6 $\alpha$ -Hydroxy-1- <i>epi</i> -genipin		
	<b>329</b> 6 $\alpha$ -Hydroxygenipin		
	<b>330</b> 6 $\beta$ -Hydroxygenipin (Scandoside methyl ester aglucone)		

- 21** Procumboside  
**52** Virginioside  
 $C_{15}H_{23}ClO_{10}$   
**127** Asystasioside E  
**128** Glutinoside  
**55** Linarioside  
 $C_{15}H_{24}O_8$   
**120** Capensioside  
 $C_{15}H_{24}O_9$   
**35** Ajugol  
**56** 3,4-Dihydroaucubin  
**121** (8*S*)-7,8-Dihydroaucubin  
**31** Myoporoside  
 $C_{15}H_{24}O_{10}$   
**122** 5,7-Bisdeoxycynanchoside  
**51** Daunoside  
**87** Dihydrocatalpol  
**53** Physoside  
 $C_{15}H_{24}O_{11}$   
**124** 10-Descinnamoylglobularimin  
**125** 10-Descinnamoylglobularinin  
**123** Paulownioside  
**6** Scabrosidol (5 $\beta$ ,7 $\alpha$ -Dihydroxydeutzol)  
 $C_{15}H_{24}O_{12}$   
**129** Cynanchoside (7 $\alpha$ ,10-Dihydroxy-harpagide)  
 $C_{16}H_{18}O_7$   
**315** Catalpin  
 $C_{16}H_{20}O_{10}$   
**15** Randioside  
 $C_{16}H_{22}O_9$   
**189** 7-Deoxygardoside  
**166** Ugandoside  
 $C_{16}H_{22}O_{10}$   
**202** Gelsemide 7-glucoside  
 $C_6H_{22}O_{11}$   
**195** Gardenosidic acid  
**196** Monotropein  
 $C_{16}H_{24}O_8$   
**144** 5-Deoxystansioside (Stanside, 8-*epi*-Boschnaloside)  
 $C_{16}H_{24}O_9$   
**149** Cachinoside I (7 $\beta$ -Hydroxystanside)  
**169** 7-Deoxy-8-*epi*-Loganic acid  
**198** Dihydrobrasoside  
**168** 1,5,9-*epi*-Deoxyloganic acid  
**145** Plantarenaloside (Yuheinoside)  
**199** Semperoside  
**147** Stansioside  
 $C_{16}H_{24}O_{10}$   
**191** Adoxosidic acid  
**143** Asperulosidol  
**161** Cachinoside V  
**170** 8-*epi*-Loganic acid  
**158** Euphroside  
**201** 9-Hydroxysemperoside  
**175** Loganic acid  
**137** 4-Methylantirrinoside  
**183** Mussaenosidic acid  
**151** Tecomoside  
**200** Vebraside  
 $C_{16}H_{24}O_{11}$   
**163** Cachinoside IV  
 $C_{16}H_{24}O_{12}$   
**194** Unedide  
 $C_{16}H_{26}O_7$   
**132** Boschnaside (8-*epi*-Iridodial glucoside)  
 $C_{16}H_{26}O_8$   
**138** Decapetaloside  
**133** 7 $\beta$ -Hydroxy-8-*epi*-iridodial glucoside  
 $C_{16}H_{26}O_9$   
**134** 5-Deoxylamiol  
**140**  $\alpha$ -Dihydroverbenol  
**141**  $\beta$ -Dihydroverbenol  
**142** 11-Hydroxydecapetaloside  
 $C_{17}H_{22}O_{10}$   
**288** 10-Dehydrogeniposide  
 $C_{17}H_{22}O_{11}$   
**289** 10-Dehydrogardenoside  
**207** 10-Methylxoside  
 $C_{17}H_{22}O_{12}$   
**290** Mollugoside (8 $\alpha$ -Hydroxyapodanthoside)  
 $C_{17}H_{24}O_9$   
**208** 10-Deoxygeniposide  
 $C_{17}H_{24}O_{10}$   
**5** 6'-*O*-Acetyldeutzioside  
**283** Apodantheroside  
**258** Gardoside methyl ester  
**229** 7-Ketologanin (7-Dehydrologanin)  
 $C_{17}H_{24}O_{11}$   
**276** 10-Hydroxycornin  
**262** 6 $\alpha$ -Hydroxygeniposide (Deacetyl-daphylloside, Deacetylasperulosidic acid methyl ester)  
**265** 6 $\beta$ -Hydroxygeniposide (Scandoside methyl ester)  
**284** Monotropein methyl ester (Galioside)  
**259** Strictoloside  
 $C_{17}H_{24}O_{12}$   
**286** 6 $\alpha$ ,7 $\alpha$ -Epoxy Splendoside  
**287** 6 $\beta$ ,7 $\beta$ -Epoxy Splendoside  
**256** Sesamoside  
 $C_{17}H_{26}O_9$   
**209** 7-Deoxy-8-*epi*-Loganin  
**157** Pinifolin  
 $C_{17}H_{26}O_{10}$   
**32** 6-*O*-Acetylmiporoside  
**33** 8-*O*-Acetylmiporoside  
**270** Adoxoside (8 $\beta$ -Dihydrogeniposide, 6,7-Dihydroapodantheroside)  
**36** Ajugoside (Leonuride)  
**269** 8 $\alpha$ -Dihydrogeniposide  
**210** 6-*epi*-Dihydrocornin  
**212** 7-*epi*-Loganin  
**214** 8-*epi*-Loganin  
**215** Loganin  
**239** Mussaenoside  
**211** Penstemonoside  
 $C_{17}H_{26}O_{11}$   
**44** 8-*O*-Acetylharpagide  
**234** 5-Deoxypulchelloside I

- 231**  $\alpha$ -Dihydrohastatoside  
**232**  $\beta$ -Dihydrohastatoside  
**252** 8-*epi*-Caryptoside  
**273** 8-*epi*-Splendoside  
**271** 6 $\beta$ -Hydroxyadoxoside  
**233** 5-Hydroxy-8-*epi*-loganin  
**236** 6 $\beta$ -Hydroxyloganin  
**272** 10-Hydroxyloganin  
**240** Ipolamiide  
**230** Penstemoside  
**241** Shanzhiside methyl ester  
**274** Splendoside  
 $C_{17}H_{26}O_{12}$   
**253** 6 $\beta$ -Hydroxyipolamiide  
**279** 6 $\beta$ -Hydroxysplendoside  
**281** 7 $\alpha$ -Hydroxysplendoside  
**282** 7 $\beta$ -Hydroxysplendoside  
**54** Jaranidoside  
**254** Lamiide  
**277** Nyctanthoside  
 $C_{18}H_{20}O_6$   
**336** Syringopicrogenin A  
 $C_{18}H_{20}O_7$   
**337** Syringopicrogenin B  
 $C_{18}H_{22}O_{11}S$   
**203** Paederoside  
 $C_{18}H_{24}O_{12}$   
**193** 6-*O*-Acetylscandoside  
 $C_{18}H_{26}O_{11}$   
**171** 7-*O*-Acetyl-8-*epi*-loganic acid (MS-6)  
**178** 7-*O*-Acetylloganic acid  
**184** 8-*O*-Acetylmussaenosidic acid (MS-5)  
 $C_{18}H_{26}O_{12}$   
**291**  $\alpha$ -Dihydrogriselinoside  
**292**  $\beta$ -Dihydrogriselinoside  
 $C_{18}H_{28}O_{10}$   
**139** 10-*O*-Acetyl-6 $\beta$ -hydroxymongolioside  
**135** 5-Deoxylamioside  
**136** 6-Deoxylamioside  
 $C_{19}H_{22}O_8$   
**338** Syringopicrogenin C  
 $C_{19}H_{26}O_{11}$   
**260** 10-*O*-Acetylgeniposide  
 $C_{19}H_{26}O_{12}$   
**285** Galioside 10-acetate  
**206** V3  
 $C_{19}H_{26}O_{12}S$   
**263** Methyl paederosidate  
 $C_{19}H_{28}O_{12}$   
**243** 6-*O*-Acetylshanzhiside methyl ester  
**244** 8-*O*-Acetylshanzhiside methyl ester  
**275** Splendoside 10-acetate (10-*O*-Acetyl-splendoside)  
 $C_{19}H_{28}O_{13}$   
**280** 6 $\beta$ -Hydroxysplendoside 10-acetate  
 $C_{20}H_{26}O_8$   
**309** Specionin  
 $C_{20}H_{28}O_{11}$   
**26** 6-*O*-Angeloylantirrinoside  
**27** 6-*O*-Seneciolyantirrinoside  
 $C_{20}H_{30}O_{13}$   
**62** Aucubigenin-1-*O*- $\beta$ -serotinoside  
**14** Mentzelosylepoxydecaloside  
**66** 6-*O*- $\beta$ -D-Xylopyranosylaucubin  
 $C_{21}H_{28}O_{11}$   
**45** Caprarioside (8-*O*-Benzoylharpagide)  
 $C_{21}H_{30}O_{13}$   
**235** Barbatoside  
**245** 6,8-di-*O*-Acetylshanzhiside methyl ester  
**18** Teucardoside  
 $C_{21}H_{30}O_{14}$   
**19** Allobetonicoside  
 $C_{21}H_{32}O_{13}$   
**10** Quinovosyldecaloside  
**68** Sinuatol (6-*O*- $\alpha$ -L-Rhamnopyranosyl-aucubin)  
 $C_{21}H_{32}O_{14}$   
**8** Allosyldecaloside  
**60** Aucubigenin-1-*O*- $\beta$ -cellobioside  
**16** 10-Deoxymelittoside  
**65** 6-*O*-Glucopyranosylaucubin  
**61** 6'-*O*-Glucosylaucubin  
**9** Glucosyldecaloside  
 $C_{21}H_{32}O_{15}$   
**12** Allosylepoxydecaloside  
**13** Glucosylepoxydecaloside  
**81** Melittoside  
**89** Rehmannioside A  
**90** Rehmannioside B  
 $C_{21}H_{32}O_{16}$   
**119** Calycinoside (5-*O*-Glucosyl-macfadienoside)  
 $C_{21}H_{34}O_{14}$   
**34** Rehmannioside C  
 $C_{21}H_{34}O_{15}$   
**126** Verbascoside B  
 $C_{22}H_{26}O_{10}$   
**63** 2'-*O*-Benzoylaucubin  
 $C_{22}H_{26}O_{11}$   
**76** Agnuside (10-*O*-*p*-Hydroxybenzoyl-aucubin)  
**73** 6-*O*-*p*-Hydroxybenzoyl-6-*epi*-aucubin  
 $C_{22}H_{26}O_{12}$   
**84** 6-*O*-*p*-Hydroxybenzoyl-6-*epi*-monomelittoside  
 $C_{22}H_{26}O_{13}$   
**107** Verprosidi  
 $C_{22}H_{28}O_{11}$   
**37** 6-*O*-*p*-Hydroxybenzoylajugol  
 $C_{22}H_{32}O_{14}$   
**293** Asystasioside B  
**299** Asystasioside C  
 $C_{22}H_{32}O_{15}$   
**300** Asystasioside D  
 $C_{22}H_{34}O_{14}$   
**294** Asystasioside A  
**146** Plantarenalosigenin-1-*O*- $\beta$ -gentiobioside  
**148** Stansiosigenin-1-*O*- $\beta$ -gentiobioside  
 $C_{23}H_{26}O_{12}$   
**190** 7-*O*-*p*-Hydroxybenzoylgardoside

- $C_{23}H_{28}O_9$   
**1** Undulatin (4'-*O-p*-Coumaroyl-7,8-dihydro-8-dehydroxymethylbartsioside)
- $C_{23}H_{28}O_{11}$   
**152** 7-*O*-Benzoyltecomoside
- $C_{23}H_{28}O_{12}$   
**172** 7-*O-p*-Hydroxybenzoyl-8-*epi*-loganic acid  
**186** 6'-*O-p*-Hydroxybenzoylmussaenosidic acid  
**153** 7-*O-p*-Hydroxybenzoyltecomoside  
**85** 6-*O-p*-Methoxybenzoyl-6-*epi*-monomelitroside  
**185** Negundoside (2'-*O-p*-hydroxybenzoylmussaenosidic acid)  
**180** Swertiaside (7-*epi*-(*m*-Hydroxybenzoyl)loganic acid)
- $C_{23}H_{28}O_{13}$   
**108** 6-*O*-Isovanilloylcatalpol
- $C_{23}H_{30}O_{11}$   
**295** Urceolatoside D
- $C_{23}H_{30}O_{12}$   
**57** Nishindaside  
**38** 6-*O*-Vanilloylajugol
- $C_{23}H_{34}O_{13}$   
**257** Jioglutoside B
- $C_{23}H_{36}O_{16}$   
**242** Shanzhisin methyl ester gentiobioside
- $C_{24}H_{28}O_{10}$   
**77** Isoscrophularioside (10-*O*-Cinnamoylaucubin, Lyranthosalin)
- $C_{24}H_{28}O_{11}$   
**23** Decumbeside A  
**22** Decumbeside B  
**78** *cis*-Eurostoside (10-*O-cis-p*-Coumaroylaucubin)  
**79** *trans*-Eurostoside (10-*O-trans-p*-Coumaroylaucubin)  
**117** Globularicisin (10-*O-cis*-Cinnamoylcatalpol)  
**118** Globularin
- $C_{24}H_{28}O_{12}$   
**24** 6'-*O-p*-Coumaroylprocumbide  
**110** Specioside (6-*O-p*-Coumaroylcatalpol)
- $C_{24}H_{30}O_{11}$   
**46** 8-*O-cis*-Cinnamoylharpagide  
**40** 6-*O-p*-Coumaroylajugol
- $C_{24}H_{30}O_{12}$   
**246** 6-*O*-Benzoylshanzhiside methyl ester  
**247** 8-*O*-Benzozylshanzhiside methyl ester  
**48** 6'-*O-p*-Coumaroylharpagide  
**47** 8-*O-p*-Coumaroylharpagide  
**216** 4'-*O-m*-Hydroxybanozyloganin  
**217** 6'-*O-m*-Hydroxybenzozyloganin  
**297** Syringopicroside B
- $C_{24}H_{30}O_{13}$   
**109** 6-*O*-Veratroylcatalposide
- $C_{25}H_{28}O_{11}$   
**25** 6'-*O*-Cinnamoylantirrinoside
- $C_{25}H_{28}O_{12}$   
**204** V 1
- $C_{25}H_{28}O_{13}$   
**197** Andromedoside
- $C_{25}H_{30}O_{10}$   
**150** Campenoside
- $C_{25}H_{30}O_{11}$   
**162** Campside  
**173** 7-*O*-Cinnamoyl-8-*epi*-loganic acid  
**187** 2'-*O*-Cinnamoylmussaenosidic acid  
**154** 7-*O*-Cinnamoyltecomoside (5-Hydroxycampenoside)  
**74** 6-*O-p*-Methoxycinnamoylaucubin
- $C_{25}H_{30}O_{12}$   
**176** 4'-*O-cis-p*-Coumaroylloganic acid  
**177** 4'-*O-trans-p*-Coumaroylloganic acid  
**155** 7-*O-p*-Coumaroyltecomoside  
**111** 6-*O-p*-Methoxycinnamoylcatalposide  
**164** Pondraneoside (5-Hydroxycampside)
- $C_{25}H_{30}O_{13}$   
**165** Cachineside III  
**112** 6-*O-cis*-Feruloylcatalpol  
**113** 6-*O-trans*-Feruloylcatalpol
- $C_{25}H_{32}O_{12}$   
**30** 6-Desoxy-8-*O*-isoferuloylharpagide  
**213** 7-*epi*-(*m*-Methoxybenzoyl)loganin  
**41** 6-*O-cis*-Feruloylajugol  
**42** 6-*O-trans*-Feruloylajugol
- $C_{25}H_{32}O_{13}$   
**298** Syringopicroside C
- $C_{25}H_{36}O_{11}$   
**75** Amareloside (6-*O*-Foliamenthoyl-6-*epi*-aucubin)
- $C_{25}H_{36}O_{12}$   
**28** Kickxioside  
**116** Nemoroside (6-*O*-Foliamenthoylcatalpol)  
**29** 6-*O*-Nerol-8-oylantirrinoside
- $C_{25}H_{38}O_{11}$   
**43** Nemorososide (6-*O*-Foliamenthoylajugol)
- $C_{26}H_{30}O_{13}$   
**266** 6-*O-p*-Coumaroylscandoside methyl ester (Oldenlandoside I)
- $C_{26}H_{30}O_{14}$   
**264** 10-Caffeoyldeacetyldaphylloside
- $C_{26}H_{32}O_{12}$   
**218** 2'-*O-cis*-Coumaroylloganin  
**219** 2'-*O-trans*-Coumaroylloganin  
**220** 4'-*O-cis-p*-Coumaroylloganin  
**221** 4'-*O-trans-p*-Coumaroylloganin  
**227** 7-*O-p*-Coumaroylloganin  
**156** 7-*O-p*-Methoxycinnamoyltecomoside
- $C_{26}H_{32}O_{13}$   
**248** 6-*O*-Benzoyl-6'-*O*-acetylshanzhiside methyl ester  
**222** 2'-*O-cis*-Caffeoylloganin  
**223** 2'-*O-trans*-Caffeoylloganin  
**237** 6-*O-trans-p*-Coumaroyl-6 $\beta$ -hydroxyloganin  
**50** Decumbeside C

- 49** Decumbeside D  
 $C_{26}H_{32}O_{14}$   
**255** Durantoside 4  
**188** Tarennine (6-*O*-Feruloylshanzhiside)  
 $C_{26}H_{32}O_{15}$   
**278** Arbortrioside B (6-*O*-Caf-  
 feoylnyctanthoside)  
 $C_{26}H_{34}O_{15}$   
**250** 6-*O*-Syringylshanzhiside methyl ester  
 $C_{26}H_{36}O_{13}$   
**339** Urceolatoside B  
 $C_{26}H_{38}O_{11}$   
**167** Lamourouxide I  
 $C_{26}H_{38}O_{12}$   
**159** 8-*O*-Foliamenthoyleuphoside  
 $C_{26}H_{40}O_{18}$   
**67** Sinuatoside (6-*O*-Sinuatosylaucubin)  
 $C_{27}H_{28}O_{13}$   
**205** V 2  
 $C_{27}H_{30}O_{11}$   
**192** 10-*O*-(5-Phenyl-2,4-pentadienyl)  
 geniposidic acid  
 $C_{27}H_{32}O_{11}$   
**174** 7-*O*-(5-Phenyl-2,4-Pentadienyl)-8-  
*epi*-loganic acid  
 $C_{27}H_{32}O_{13}$   
**267** 6-*O*-*p*-Methoxycinnamoylscandoside  
 methyl ester  
 $C_{27}H_{32}O_{14}$   
**268** 6-*O*-*p*-Feruloylscandoside methyl  
 ester (Oldenlandoside II)  
 $C_{27}H_{34}O_{13}$   
**238** Arbortrioside A  
**224** 2'-*O*-*cis*-Feruloylloganin  
**225** 2'-*O*-*trans*-Feruloylloganin  
 $C_{27}H_{42}O_{20}$   
**83** Rehmannioside D (Sophorosylmono-  
 melittoside)  
 $C_{27}H_{44}O_{15}$   
**64** 6-*O*-Glucosyl-2'-*O*-benzoylaucubin  
 $C_{28}H_{36}O_{16}$   
**251** 6-*O*-Syringyl-8-*O*-acetylshanzhiside  
 methyl ester  
 $C_{29}H_{40}O_{16}$   
**39** 6-*O*-(4"-*O*- $\alpha$ -L-Rhamnopyranosyl-  
 vanilloyl)ajugol  
 $C_{30}H_{32}O_{14}$   
**182** Senburiside II [7-*epi*-(*di*-*m*-Hydroxy-  
 benzoyl)loganic acid]  
 $C_{30}H_{38}O_{14}$   
**70** Nigroside 1 [6-*O*-(3"-*O*-Cinnamoyl- $\alpha$ -  
 L-rhamnopyranosyl)aucubin]  
**69** Nigroside 2 [6-*O*-(2"-*O*-Cinnamoyl- $\alpha$ -  
 L-rhamnopyranosyl)aucubin]  
 $C_{30}H_{38}O_{15}$   
**71** 3"-*O*-*p*-Coumaroylsinuato [6-*O*-(3"-  
*O*-*p*-Coumaroyl- $\alpha$ -L-rhamnopy-  
 ranosyl)aucubin]  
 $C_{30}H_{38}O_{16}$   
**82** 10-*O*-*trans*-Cinnamoylmelittoside  
**92** 6-*O*-(3"-*O*-*p*-Coumaroyl- $\alpha$ -L-rhamno-  
 pyranosyl)catalpol  
**91** Saccatoside [6-*O*-(2"-*O*-*p*-Coumaroyl-  
 $\alpha$ -L-rhamnopyranosyl)catalpol]  
 $C_{30}H_{38}O_{17}$   
**94** 6-*O*-(2"-*O*-Caffeoylrhamnopyranosyl)  
 catalpol  
**95** 6-*O*-(3"-*O*-Caffeoylrhamnopyranosyl)  
 catalpol  
 $C_{30}H_{38}O_{18}$   
**115** Speedoside  
 $C_{30}H_{40}O_{15}$   
**226** 6'-*O*-[2(*R*)-Methyl-3-veratroxyloxy-  
 propanoyl]loganin  
 $C_{31}H_{34}O_{13}$   
**249** 6,6'-*O*-Dibenzoylshanzhiside methyl  
 ester  
 $C_{31}H_{40}O_{16}$   
**93** Verbascoside A  
 $C_{31}H_{40}O_{17}$   
**96** 6-*O*-(2"-*O*-Isoferuloylrhamnopyranosyl)  
 catapol  
**97** 6-*O*-(3"-*O*-Isoferuloylrhamnopyranosyl)  
 catapol  
 $C_{31}H_{40}O_{18}$   
**114** Welloside  
 $C_{31}H_{42}O_{18}$   
**340** Radiatoside C  
 $C_{31}H_{42}O_{19}$   
**341** Radiatoside B  
 $C_{31}H_{44}O_{18}$   
**342** Argyliside  
 $C_{31}H_{44}O_{19}$   
**343** Radiatoside  
 $C_{32}H_{40}O_{17}$   
**261** 6"-*O*-*p*-Coumaroylgenipin gentiobioside  
 $C_{32}H_{42}O_{18}$   
**179** Periclymenosidic acid  
 $C_{33}H_{42}O_{14}$   
**344** Urceolatoside A  
 $C_{33}H_{42}O_{15}$   
**345** Urceolatoside C  
 $C_{33}H_{42}O_{16}$   
**72** 6-*O*-(2"-*O*-Acetyl, 3-*O*-*p*-methoxy-  
*trans*-cinnamoyl)rhamnopyranosyl-  
 aucubin  
 $C_{33}H_{42}O_{17}$   
**98** Pulverulentoside I  
 $C_{33}H_{42}O_{18}$   
**99** Pulverulentoside II  
 $C_{33}H_{44}O_{18}$   
**228** Periclymenoside  
 $C_{34}H_{38}O_{16}$   
**181** Senburiside I  
 $C_{34}H_{44}O_{22}$   
**346** 10-Dehydrogardenoside dimer  
 $C_{35}H_{42}O_{20}$   
**296** Depressoside  
 $C_{35}H_{44}O_{18}$   
**104** Scropolioside A  
 $C_{36}H_{52}O_{14}$   
**160** 2',8-*O*-Difoliamenthoyleuphoside

$C_{39}H_{44}O_{19}$   
**101** Premnoside B  
 $C_{39}H_{44}O_{20}$   
**100** Premnoside A  
 $C_{40}H_{46}O_{19}$   
**103** Premnoside D

$C_{40}H_{46}O_{20}$   
**102** Premnoside C  
 $C_{41}H_{46}O_{17}$   
**105** Scropolioside B  
 $C_{42}H_{48}O_{18}$   
**106** 6-O-(2,3,4-O-Acetyl-cinnamoyl-*p*-methoxycinnamoyl)rhamnosylcatalpol

TABLE 4. Plant Index

For cases in which plant family identification were not given or in which two family names were found for a single species, a recent authoritative dictionary (249) was used.

Acanthaceae	<i>Lamiaeum</i> 16
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