

Iridoids. An Updated Review, Part II

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IRIDOIDS. AN UPDATED REVIEW, PART II

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ABSTRACT.—The structures of valeriana and plumeria iridoids, miscellaneous iridoid-like compounds, simple secoiridoids, terpene- and phenolic-conjugated secoiridoids, bis- and tris-secoiridoids, and other miscellaneous secoiridoids published for the first time during 1980–1989 are listed with available physical and spectral data: mp, $[\alpha]_D$, uv, ^1H nmr, ^{13}C nmr. Also included are revisions of structures originally published prior to 1980. The compounds are indexed alphabetically and by molecular weight, and a plant source index is included.

This is the second part of a review (1) that is mainly a compilation of new iridoids and secoiridoids reported in the literature from the El-Naggar and Beal review of 1980 (2) through December 1989. The large number of new structures necessitated division into two parts for publication. The first part (1) included iridoids (except valeriana and plumeria types), iridoid aglycones, and bis-iridoids. This second part includes valeriana and plumeria iridoids, other miscellaneous iridoid-like structures, and a variety of secoiridoid types. This work does not include the separately recognized classes of bis-iridoid-alkaloids or pyridine monoterpene alkaloids. A few semisynthetic compounds were also included.

The main anticipated use of the entire review is for the rapid identification of isolated iridoids by ^1H - and ^{13}C -nmr spectroscopy. It is intended to be a comprehensive list of the designated 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 D_2O or CD_3OD were usually used. Compounds reported in the earlier review (2) have been included only when the structures (including stereochemistry) were revised or when significantly better spectral data (^1H and ^{13}C nmr) were reported.

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 (2). Group 6 contains valeriana iridoids; Group 7 contains plumeria iridoids; Group 8 contains miscellaneous iridoid-like compounds; Group 9 consists of simple secoiridoids; Group 10 contains terpene-conjugated secoiridoids; Group 11 contains phenolic-conjugated secoiridoids; Group 12 consists of bis-secoiridoids; and Group 13 includes a few miscellaneous secoiridoids. The oxidation state of C-10 and C-11 (see Figure 1) guides the arrangement of compounds where possible. The available data were listed in the following order: name; molecular formula; molecular weight; melting point ($^{\circ}\text{C}$); optical rotation (solvent); uv (λ max, nm); ^1H 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}C nmr (solvent) chemical shifts (in ppm, starting with C-1 and listed in order) with assignments; plant source (family); reference(s). Assignments with the same superscript may be interchanged.

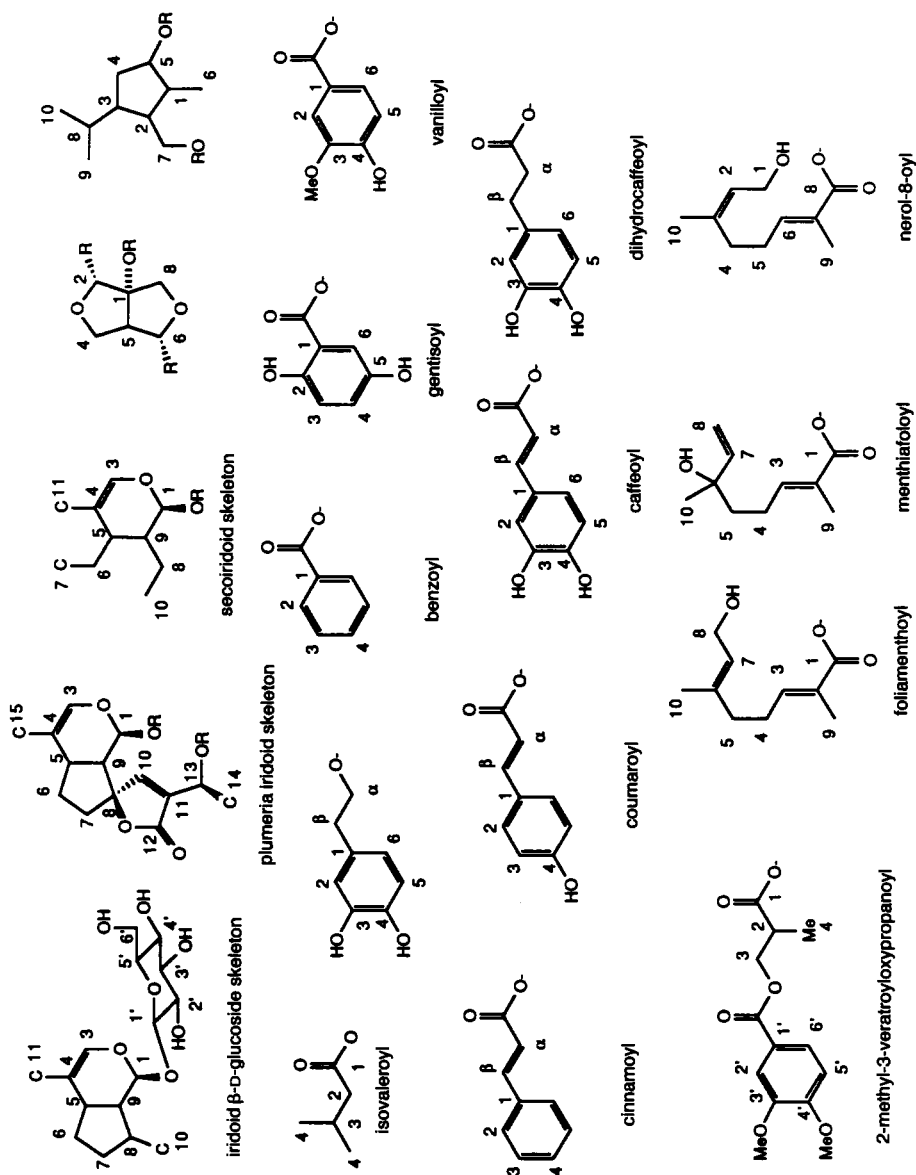


FIGURE 1. Numbering of some common substituents.

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 compound, was isolated.

Numbering of the iridoid and secoiridoid skeletons 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 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 the more complex structures, the separate parts are designated as a, b, etc., then numbered as above. Cinnamoyl, coumaroyl, etc., groups are in the trans configuration unless otherwise indicated.

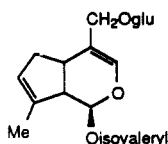
Three indices are included: compounds listed alphabetically (Table 2), compounds listed by molecular formula (Table 3), and plant sources listed alphabetically (Table 4).

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.

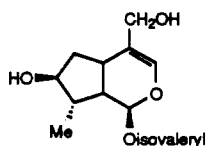
Group 6 (valeriana iridoids)

1 10-DEOXYPENSTEMIDE



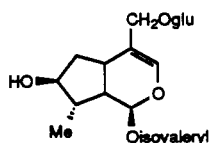
$C_{21}H_{32}O_9$ 428.48 (400 MHz CD_3OD) 5.77 (H-1, d, 7.0), 6.41 (H-3, bs), 3.10 (H-5, m), 2.59–2.65, 2.20–2.31 (H-6, m's), 5.53 (H-7, bs), 2.59–2.65 (H-9, m), 1.76 (H-10, bs), 4.18 (H-11, 11.4), 2.2–2.31 (H-2'), 2.09 (H-3'), 0.97 (H-4', d, 6.6), 4.28 (H-1'', d, 7.8); (CD_3OD) 93.4 (C-1), 140.6 (C-3), 116.3 (C-4), 37.6 (C-5), 38.1 (C-6), 128.6 (C-7), 139.5 (C-8), 50.1 (C-9), 16.0 (C-10), 69.9 (C-11), 173.1 (C-1'), 44.2 (C-2'), 26.7 (C-3'), 22.6 (C-4'), 103.4 (C-1''), 75.1 (C-2''), 78.1 (C-3''), 71.7 (C-4''), 77.9 (C-5''), 62.8 (C-6''). Catalytic hydrogenation of penstemide (3)

2 10-DEOXYPATRINOSIDE AGLYCONE



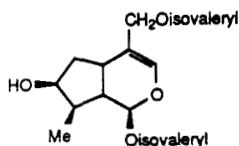
$C_{15}H_{24}O_5$ 284.35 (400 MHz CD_3OD) 6.12 (H-1, d, 3.5), 6.27 (H-3, bs), 2.97 (H-5, m), 3.92 (H-7, q, 5), 2.64 (H-9, dt), 1.04 (H-10, d, 6.4), 4.04 (H-11, 12.2), 2.26 (H-2'), 2.19 (H-3'), 0.98 (H-4', d, 6.6). *Penstemon richardsonii* (Scrophulariaceae) (4)

3 10-DEOXYPATRINOSIDE



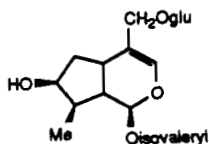
$C_{21}H_{34}O_{10}$ 446.49 (400 MHz CD_3OD) 6.08 (H-1, d, 3.8), 6.31 (H-3, s), 2.95 (H-5, m), 2.17–1.97, 1.87 (H-6, m's), 3.80 (H-7, q, 5.6), 2.17–1.97 (H-8, m), 2.57 (H-9, dt, 9, 9, 4), 1.02 (H-10, d, 7.4), 4.17 (H-11, 11.6), 2.20 (H-2'), 2.17–1.97 (H-3'), 0.95 (H-4', d, 6.6), 4.27 (H-1'', d, 7.8), 3.19 (H-2'', dd, 8.8, 8.0), 3.86 (H-6'', dd, 11.7, 1.9), 3.66 (H-6'', dd, 11.8, 5.2); (CD_3OD) 92.0 (C-1), 139.9 (C-3), 116.7 (C-4), 32.3 (C-5), 38.7 (C-6), 79.6 (C-7), 44.4 (C-8), 42.2 (C-9), 14.5 (C-10), 69.8 (C-11), 173.2 (C-1'), 44.2 (C-2'), 26.7 (C-3'), 22.6 (C-4'), 103.6 (C-1''), 75.1 (C-2''), 77.9 (C-3''), 71.7 (C-4''), 78.1 (C-5''), 62.8 (C-6''). *Penstemon richardsonii* (Scrophulariaceae), hydrogenation of serrulatolide (4,5)

4 NARDOSTACHIN



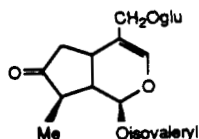
$C_{20}H_{32}O_6$ 368.47 $[\alpha] -80.9^\circ$ ($CHCl_3$) uv 212 (MeOH) (100 MHz $CDCl_3$) 5.94 (H-1, d, 4), 6.31 (H-3, bs), 2.90 (H-5, q, 7.5), 4.12 (H-7, dt, 5.2, 2.2), 1.12 (H-10, d, 6.8), 4.48 (H-11, 12.5), 1.00 (H-4', H-4'', d, 5.7); ($CDCl_3$) 91.6 (C-1), 139.5 (C-3), 114.3 (C-4), 32.0 (C-5), 39.8 (C-6), 74.9 (C-7), 40.5 (C-8), 45.0 (C-9), 12.8 (C-10), 63.8 (C-11), 171.0 (C-1')^a, 43.5 (C-2')^b, 25.8 (C-3'), 22.4 (C-4'), 173.0 (C-1'')^a, 43.6 (C-2'')^b, 25.8 (C-3''), 22.4 (C-4''). *Nardostachys chinensis* (Valerianaceae) (6)

5 7,7-O-DIHYDROEBULOSIDE



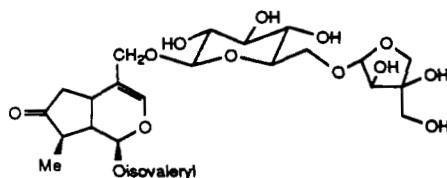
$C_{21}H_{34}O_{10}$ 446.49 $[\alpha] -73.8^\circ$ (?) uv 204 (?) (300 MHz CD_3OD) 5.88 (H-1, d, 4.5), 6.32 (H-3, s), 3.00 (H-5, bq, 8.0), 2.06 (H-6 α , m), 1.83 (H-6 β , m), 4.07 (H-7, m), 1.86 (H-8, m), 2.02 (H-9, m), 1.09 (H-10, d, 6.9), 4.26, 4.07 (H-11, 12.0), 2.3 (H-2', m), 2.0 (H-3', m), 0.97 (H-4', d, 6.6), 4.28 (H-1'', d, 7.8), 3.15–3.4 (H-2''–H-5'', m) 3.86 (H-6'', dd, 11.5, 1.8), 3.66 (H-6'', dd, 11.5, 5.3); (CD_3OD) 93.6 (C-1), 139.5 (C-3), 117.0 (C-4), 33.7 (C-5), 40.6 (C-6), 75.2 (C-7), 42.2 (C-8), 46.6 (C-9), 13.7 (C-10), 69.9 (C-11), 173.5 (C-1'), 44.3 (C-2'), 26.9 (C-3'), 22.9 (C-4'), 103.5 (C-1''), 75.2 (C-2''), 77.9 (C-3''), 71.7 (C-4''), 78.1 (C-5''), 62.9 (C-6''). *Sambucus ebulus* (Caprifoliaceae), *Penstemon confertus* (Scrophulariaceae) (7,8)

6 EBULOSIDE



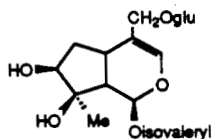
$C_{21}H_{32}O_{10}$ 444.48 $[\alpha] -169.1^\circ$ (MeOH) uv 279, 204 (MeOH) (300 MHz CD_3OD) 6.24 (H-1, bs), 6.41 (H-3, bs), 3.4–3.1 (H-5, m), 2.77 (H-6 α , bd, 19), 2.46 (H-6 β , dd, 19, 8.6), 2.2–2.0 (H-8, m), 2.3 (H-9, m), 1.15 (H-10, d, 6.9), 4.27, 4.18 (H-11, 11.3), 2.25 (H-2', d, 6.5), 2.2–2.0 (H-3', m), 0.97 (H-4', d, 6.6), 4.26 (H-1'', d, 7.5), 3.34–3.14 (H-2''–H-4'', m), 4.07–3.97 (H-5'', m), 3.85 (H-6'', bd, 11.8), 3.65 (H-6'', bd, 11.8); (CD_3OD) 90.5 (C-1), 141.0 (C-3), 113.4 (C-4), 29.4 (C-5), 41.1 (C-6), 220.5 (C-7), 44.5 (C-8), 46.0 (C-9), 13.3 (C-10), 69.4 (C-11), 173.1 (C-1'), 44.1 (C-2'), 26.8 (C-3'), 22.7 (C-4'), 103.3 (C-1''), 75.0 (C-2''), 77.9 (C-3''), 71.6 (C-4''), 78.0 (C-5''), 62.9 (C-6''). *Sambucus ebulus* (Caprifoliaceae) (9)

7 6'-O-APIOSYLEBULOSIDE



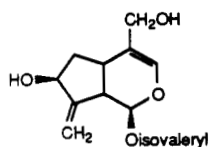
$C_{26}H_{40}O_{14}$ 576.59 $[\alpha] -215.5^\circ (?)$ uv 279, 204 (?) (400 MHz pyridine- d_5) 6.54 (H-1, d, 2.5), 6.61 (H-3, d, 1.3), 3.36 (H-5, br, 7.3), 3.08 (H-6 α , br, -19), 2.56 (H-6 β , dd, -19, 8.6), 2.17 (H-8, m), 2.54 (H-9, ddd, 11.2, 6.8, 2.5), 1.08 (H-10, d, 6.9), 4.27, 4.04 (H-11, -12.8), 2.21 (H-2', d, 8), 2.08 (H-3', m), 0.88, 0.87 (H-4', d's, 6.6), 4.79 (H-1'', d, 7.7), 3.96 (H-2'', m), 4.14 (H-3'', H-4'', m), 4.06 (H-5'', m), 4.72 (H-6'', dd, -11.2, 1.6), 4.17 (H-6'', m), 5.80 (H-1''', d, 2.6), 4.75 (H-2''', d, 2.6), 4.06, 3.96 (H-4''', m's), 4.57, 4.34 (H-5''', -9.5); (D₂O) 92.6 (C-1), 142.1 (C-3), 114.6 (C-4), 30.6 (C-5), 42.8 (C-6), 227.0 (C-7), 46.4 (C-8), 46.7 (C-9), 14.9 (C-10), 71.5 (C-11), 177.6 (C-1'), 45.8 (C-2'), 28.4 (C-3'), 24.5 (C-4'), 103.8 (C-1''), 75.9 (C-2''), 78.6 (C-3''), 72.5 (C-4''), 77.6 (C-5''), 70.5 (C-6''), 111.8 (C-1'''), 79.5 (C-2'''), 82.2 (C-3'''), 76.5 (C-4'''), 66.5 (C-5'''). *Sambucus ebulus* (Caprifoliaceae) (7)

8 8-*epi*-VALEROSIDATE



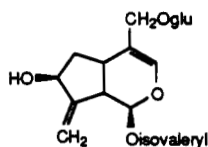
$C_{21}H_{34}O_{11}$ 462.49 mp 60° (400 MHz CD₃OD) 6.24 (H-1, d, 1.8), 6.28 (H-3, bs), 3.01 (H-5, m), 2.01 (H-6 α , m, 9, 3.5), 1.90 (H-6 β , m, 6, 5), 3.63 (H-7, t, 5, 3.5), 2.47 (H-9, dd, 10, 1.8), 1.21 (H-10, s), 4.23, 4.07 (H-11, 11.5), 2.18 (H-2'), 2.06 (H-3', m), 0.95 (H-4', d, 6.6), 4.27 (H-1'', d, 7.8), 3.19 (H-2'', dd, 9, 7.8), 3.83 (H-6'', dd, 12.2, 4.4), 3.66 (H-6'', dd, 12.2, 1.8); (CD₃OD) 91.1 (C-1), 138.7 (C-3), 116.7 (C-4), 28.7 (C-5), 35.9 (C-6), 79.2 (C-7), 79.6 (C-8), 48.4 (C-9), 21.9 (C-10), 69.7 (C-11), 173.2 (C-1'), 44.2 (C-2'), 26.8 (C-3'), 22.64, 22.61 (C-4'), 103.7 (C-1''), 75.1 (C-2''), 78.1 (C-3''), 71.7 (C-4''), 78.0 (C-5''), 62.9 (C-6''). *Penstemon serrulatus* (Scrophulariaceae) (10)

9 SERRULATOLOSIDE AGLYCONE



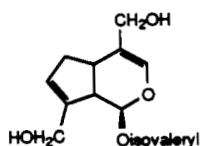
$C_{15}H_{22}O_5$ 282.34 (400 MHz CD₃OD) 5.91 (H-1, d, 5.9), 6.35 (H-3, bs), 3.07 (H-5, m), 2.25, 2.19 (H-6, m's), 4.51 (H-7, br), 2.97 (H-9, br), 5.41, 5.31 (H-10, bs's), 4.07 (H-11, 12.1), 2.26 (H-2'), 2.19 (H-3'), 0.98 (H-4', d, 6.6). *Penstemon richardsonii* (Scrophulariaceae) (4)

10 SERRULATOLOSIDE



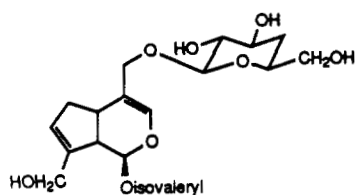
$C_{21}H_{32}O_{10}$ 444.48 mp $71-73^\circ$ (400 MHz CD₃OD) 5.95 (H-1, d, 5.4), 6.40 (H-3, bs), 3.04 (H-5, q, 6.5, 6.5), 2.08 (H-6, m, 13, 6.5, 6), 1.91 (H-6, m, 13, 6.5, 6), 4.44 (H-7, br, 6), 2.94 (H-9, m), 5.36, 5.26 (H-10, d's, <1), 4.19 (H-11, 11.5), 2.25 (H-2'), 2.08 (H-3'), 0.95 (H-4', d, 6.6), 4.28 (H-1'', d, 7.8), 3.19 (H-2'', dd, 8.8, 8.0), 3.86 (H-6'', dd, 11.7, 1.9), 3.66 (H-6'', dd, 11.8, 5.2); (CD₃OD) 92.3 (C-1), 141.2 (C-3), 114.8 (C-4), 33.7 (C-5), 39.5 (C-6), 73.9 (C-7), 153.4 (C-8), 44.6 (C-9), 112.7 (C-10), 69.5 (C-11), 173.2 (C-1'), 44.1 (C-2'), 26.7 (C-3'), 22.6 (C-4'), 103.4 (C-1''), 75.2 (C-2''), 78.2 (C-3''), 71.8 (C-4''), 77.9 (C-5''), 62.9 (C-6''). *Penstemon serrulatus*, *Penstemon richardsonii* (Scrophulariaceae) (4, 11)

11 PENSTEMIDE AGLYCONE



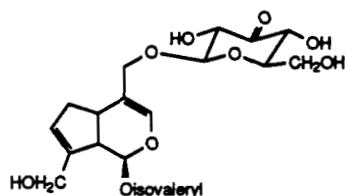
$C_{15}H_{22}O_5$ 282.34 (CD₃OD) 93.1 (C-1), 139.1 (C-3), 119.3 (C-4), 37.3 (C-5), 38.0 (C-6), 129.1 (C-7), 144.2 (C-8), 47.3 (C-9), 61.0 (C-10), 62.4 (C-11), 173.1 (C-1'), 44.1 (C-2'), 26.6 (C-3'), 22.6 (C-4'). Enzymatic hydrolysis of penstemide (10)

12 DEGLUCOSERRULATOSIDE



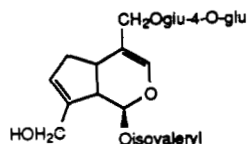
$C_{21}H_{32}O_9$ 428.48 (400 MHz CD_3OD) 4.78 (H-1", d, 1.1), 3.47 (H-2", bd, 3.1), 3.97 (H-3", m), 1.81 (H-4" $_{ax}$, td, 14, 7, 10), 1.45 (H-4" $_{eq}$, dt, 14, 2.5, 2.5), 3.85 (H-5", m), 3.56 (H-6", d, 5.2); (CD_3OD) 93.1 (C-1), 141.0 (C-3), 115.9 (C-4), 38.4 (C-5), 38.2 (C-6), 129.4 (C-7), 144.2 (C-8), 47.2 (C-9), 61.1 (C-10), 69.3 (C-11), 173.1 (C-1'), 44.2 (C-2'), 26.7 (C-3'), 22.6 (C-4'), 98.6 (C-1"), 70.8 (C-2"), 69.4 (C-3"), 30.6 (C-4"), 73.1 (C-5"), 66.0 (C-6"). Enzymatic hydrolysis of serrulatolide (12)

13 SERRULOSIDE



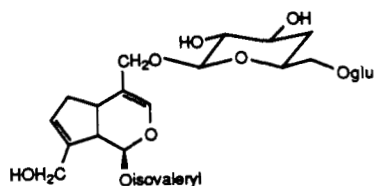
$C_{21}H_{30}O_{10}$ 442.46 mp 60° (400 MHz CD_3OD) 5.77 (H-1, d, 7.5), 6.45 (H-3, bs), 3.15 (H-5, m), 2.70, 2.26 (H-6, m's), 5.82 (H-7, bs), 2.83 (H-9, br, 7.5), 4.13 (H-10, dd, 8, 1.6), 4.20 (H-11, 11.5), 2.26 (H-2'), 2.09 (H-3'), 0.97 (H-4', d, 6.6), 4.39 (H-1", d, 7.9); (CD_3OD) 93.2 (C-1), 141.1 (C-3), 115.8 (C-4), 37.9 (C-5), 37.9 (C-6), 129.4 (C-7), 144.0 (C-8), 47.1 (C-9), 61.1 (C-10), 70.3 (C-11), 173.1 (C-1'), 44.1 (C-2'), 26.7 (C-3'), 22.6 (C-4'), 104.7 (C-1"), 78.6 (C-2"), 179.9 (C-3", fold-in), 73.7 (C-4"), 78.6 (C-5"), 62.6 (C-6"). *Penstemon serrulatus* (Scrophulariaceae) (12)

14 PENSTEBIOSIDE

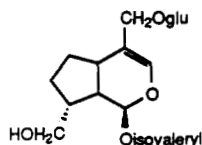


$C_{27}H_{42}O_{15}$ 606.62 mp 84–86° (400 MHz CD_3OD) 5.77 (H-1, d, 7.3), 6.42 (H-3, bs), 3.17 (H-5, m), 2.69, 2.26 (H-6, m's), 5.82 (H-7, bs), 2.81 (H-9, br, 7.5), 4.12 (H-10), 4.20 (H-11, 11.5), 2.26 (H-2'), 2.09 (H-3'), 0.96 (H-4', d, 6.6), 4.31 (H-1", d, 7.9), 4.39 (H-1", d, 7.9); (CD_3OD) 93.2 (C-1), 140.9 (C-3), 116.2 (C-4), 37.9 (C-5), 38.0 (C-6), 129.4 (C-7), 144.1 (C-8), 47.2 (C-9), 61.1 (C-10), 70.0 (C-11), 173.1 (C-1'), 44.1 (C-2'), 26.5 (C-3'), 22.6 (C-4'), 104.6 (C-1"), 74.9 (C-2"), 76.5 (C-3"), 80.9 (C-4"), 76.4 (C-5"), 62.1 (C-6"), 103.3 (C-1"), 74.9 (C-2"), 78.1 (C-3"), 71.4 (C-4"), 77.9 (C-5"), 62.5 (C-6"). *Penstemon richardsonii* (Scrophulariaceae) (13)

15 SERRULATOSIDE

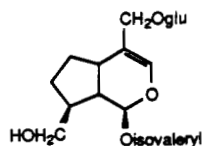


$C_{27}H_{42}O_{14}$ 590.62 mp 92–94° (400 MHz CD_3OD) 5.78 (H-1, d, 7.5), 6.47 (H-3, bs), 3.19 (H-5, m), 2.70, 2.26 (H-6, m's), 5.83 (H-7, bs), 2.80 (H-9, br, 7.5), 4.13 (H-10, 11.8), 4.20 (H-11, 11.8), 2.26 (H-2'), 2.09 (H-3'), 0.97 (H-4', d, 6.6), 4.78 (H-1", d, 1.3), 4.38 (H-1", d, 7.7); (CD_3OD) 93.2 (C-1), 141.1 (C-3), 115.7 (C-4), 38.3 (C-5), 38.4 (C-6), 129.3 (C-7), 144.2 (C-8), 47.1 (C-9), 61.1 (C-10), 69.4 (C-11), 173.1 (C-1'), 44.1 (C-2'), 26.6 (C-3'), 22.6 (C-4'), 98.6 (C-1"), 70.7 (C-2"), 69.2 (C-3"), 30.9 (C-4"), 72.0 (C-5"), 72.9 (C-6"), 104.8 (C-1"), 75.1 (C-2"), 78.0 (C-3"), 71.7 (C-4"), 78.0 (C-5"), 62.8 (C-6"). *Penstemon serrulatus* (Scrophulariaceae) (12)

16 8-*epi*-DIHYDROPENSTEMIDE

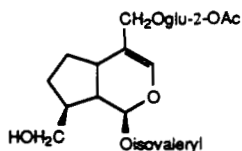
$C_{21}H_{34}O_{10}$ 446.49 (400 MHz CD_3OD) 6.26 (H-1, d, 4), 6.36 (H-3, bs), 2.87 (H-5, m), 1.83 (H-6, m), 1.83, 1.39 (H-7, m's), 2.38 (H-8, H-9, m), 3.67 (H-10, dd, 10.5, 7.2), 3.43 (H-10, dd, 10.5, 6.7), 4.16 (H-11, d, 11.5), 2.21 (H-2'), 2.07 (H-3'), 0.96 (H-4', d), 4.28 (H-1'', d, 7.8), 3.18 (H-2'', dd, 9, 7.8), 3.86 (H-6'', dd, 11.7, 5.3), 3.67 (H-6'', dd, 11.7, 1.9); (CD_3OD) 91.2 (C-1), 140.4 (C-3), 115.5 (C-4), 35.9 (C-5), 29.9 (C-6), 28.6 (C-7), 44.6 (C-8), 42.7 (C-9), 64.3 (C-10), 69.6 (C-11), 173.2 (C-1'), 44.2 (C-2'), 26.7 (C-3'), 22.6 (C-4'), 103.6 (C-1''), 75.1 (C-2''), 77.8 (C-3''), 71.7 (C-4''), 78.1 (C-5''), 62.8 (C-6''). Catalytic hydrogenation of penstemide (14)

17 DIHYDROPENSTEMIDE



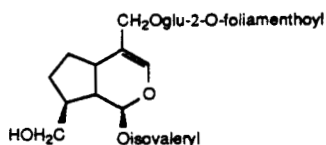
$C_{21}H_{34}O_{10}$ 446.49 mp 62° (400 MHz CD_3OD) 5.96 (H-1, d, 4.6), 6.37 (H-3, bs), 2.82 (H-5, m), 1.70, 1.39 (H-6, m's), 2.02–1.90, 1.82 (H-7, m's), 2.02–1.90 (H-8, H-9, m), 3.52 (H-10, d, 6.0), 4.16 (H-11, d, 11.5), 2.22 (H-2'), 2.07 (H-3'), 0.96 (H-4', d), 4.28 (H-1'', d, 7.7), 3.18 (H-2'', dd, 9.1, 7.8), 3.86 (H-6'', dd, 11.7, 1.8), 3.65 (H-6'', dd, 11.7, 5.4); (CD_3OD) 93.2 (C-1), 140.6 (C-3), 115.2 (C-4), 36.9 (C-5), 30.9 (C-6), 28.1 (C-7), 43.9 (C-8), 45.0 (C-9), 66.5 (C-10), 69.6 (C-11), 173.5 (C-1'), 44.2 (C-2'), 26.8 (C-3'), 22.6 (C-4'), 103.5 (C-1''), 75.2 (C-2''), 77.9 (C-3''), 71.8 (C-4''), 78.2 (C-5''), 62.9 (C-6''). *Penstemon confertus* (Scrophulariaceae) (14)

18 2'-O-ACETYLDIHYDROPENSTEMIDE



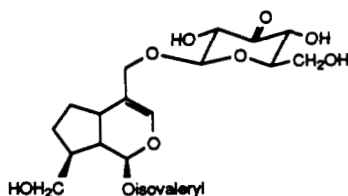
$C_{23}H_{36}O_{11}$ 488.53 uv 212 (MeOH) (250 MHz CD_3OD) 5.99 (H-1, d, 4.5), 6.32 (H-3, bs), 2.70 (H-5, m), 1.82, 1.69 (H-6, m's), 1.9–2.2, 1.40 (H-7, m's), 1.9–2.2 (H-8, H-9, m), 3.53 (H-10, d, 6), 4.21, 4.04 (H-11, d's, 12), 2.23 (H-2'), 1.9–2.2 (H-3', m), 0.96 (H-4', d), 4.46 (H-1'', d, 8), 4.70 (H-2'', dd, 9, 8), 3.53 (H-3'', t, 9), 3.35 (H-4''), 3.28 (H-5''), 3.88 (H-6'', dd, 12, 2.2), 3.68 (H-6'', dd, 12, 5.5), 2.1 (OAc); (CD_3OD) 92.9 (C-1), 140.7 (C-3), 114.5 (C-4), 36.8 (C-5), 30.6 (C-6), 28.0 (C-7), 44.2 (C-8), 45.0 (C-9), 66.6 (C-10), 69.6 (C-11), 173.4 (C-1'), 44.2 (C-2'), 26.8 (C-3'), 22.6 (C-4'), 21.7 (O=CMe), 171.7 (O=CMe), 102.2 (C-1''), 75.4 (C-2''), 76.3 (C-3''), 71.9 (C-4''), 78.1 (C-5''), 62.8 (C-6''). *Viburnum lentana* (Caprifoliaceae) (15)

19 2'-O-FOLIAMENTHOYLDIHYDROPENSTEMIDE



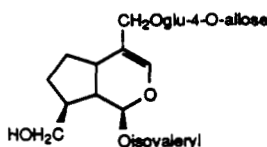
$C_{31}H_{48}O_{12}$ 612.71 (400 MHz CD_3OD) 5.93 (H-1, d, 4.4), 6.30 (H-3, bs), 2.61 (H-5, m), 1.56, 1.30 (H-6, m's), 1.77–1.74 (H-7), 1.96 (H-8, H-9, m), 3.50 (H-10, d, 6), 4.11 (H-11, d, 11.6), 2.23 (H-2'), 2.07 (H-3'), 0.96 (H-4', d, 6.6), 4.51 (H-1'', d, 8.1), 4.79 (H-2'', dd, 9.6, 8.1), 3.58 (H-3'', dd, 9.5, 8.6), 3.36 (H-4'', dd, 9.7, 8.2), 3.89 (H-6'', dd, 11.9, 2), 3.68 (H-6'', dd, 11.9, 5.5), 6.82 (H-3''', qt, 7.4, 1.5), 2.36 (H-4''', q, 7.4), 2.16 (H-5''', t, 7.4), 5.40 (H-7''', qt, 7, 1.3), 4.09 (H-8''', d, 6.6), 1.86 (H-9''', bs), 1.69 (H-10''', bs); (CD_3OD) 93.0 (C-1), 140.5 (C-3), 114.8 (C-4), 36.7 (C-5), 30.7 (C-6), 28.2 (C-7), 43.7 (C-8), 44.9 (C-9), 66.4 (C-10), 69.8 (C-11), 173.4 (C-1'), 44.2 (C-2'), 26.8 (C-3'), 22.7 (C-4'), 101.6 (C-1''), 76.1 (C-2''), 75.4 (C-3''), 71.8 (C-4''), 78.0 (C-5''), 62.7 (C-6''), 168.5 (C-1'''), 129.0 (C-2'''), 143.5 (C-3'''), 28.1 (C-4'''), 39.2 (C-5'''), 138.4 (C-6'''), 125.6 (C-7'''), 59.4 (C-8'''), 12.7 (C-9'''), 16.2 (C-10'''). *Penstemon confertus* (Scrophulariaceae) (16)

20 DIHYDROSERRULOSIDE



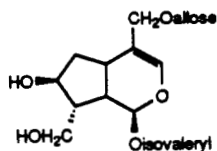
$C_{27}H_{32}O_{10}$ 444.48 (400 MHz CD_3OD) 5.97 (H-1, d, 4.7), 6.38 (H-3, bs), 2.81 (H-5, m), 1.70, 1.38 (H-6, m's), 1.93, 1.81 (H-7, m's), 1.98–2.02 (H-8, H-9, m), 3.53 (H-10, d, 6), 4.22 (H-11, d, 11.6), 2.22 (H-2'), 2.07 (H-3'), 0.96 (H-4', d, 6.6), 4.38 (H-1'', d, 7.9), 4.12 (H-2'', dd, 7.9, 1.7), 4.21 (H-4'', dd, 10, 1.7), 3.94 (H-6'', dd, 12.1, 2.2), 3.78 (H-6'', dd, 12.1, 5.0); (CD_3OD) 93.1 (C-1), 141.0 (C-3), 114.9 (C-4), 36.9 (C-5), 30.8 (C-6), 28.1 (C-7), 43.9 (C-8), 45.0 (C-9), 66.5 (C-10), 70.1 (C-11), 173.5 (C-1'), 44.2 (C-2'), 26.8 (C-3'), 22.6 (C-4'), 104.9 (C-1''), 78.4 (C-2''), 179.8 (C-3'', fold-in), 73.7 (C-4''), 78.4 (C-5''), 62.7 (C-6''). *Penstemon confertus* (Scrophulariaceae) (8)

21 CONFERTOSIDE



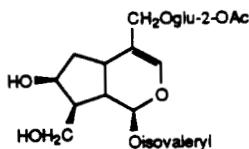
$C_{27}H_{44}O_{15}$ 608.64 mp 100–101° [α] –57° (MeOH) (400 MHz CD_3OD) 5.96 (H-1, d, 4.7), 6.37 (H-3, bs), 2.81 (H-5, m), 1.39, 1.68 (H-6, m's), 1.81, 1.93 (H-7, m's), 1.98–2.02 (H-8, H-9, m), 3.52 (H-10, d, 6.2), 4.15 (H-11, d, 11.5), 2.22 (H-2'), 2.07 (H-3'), 0.96 (H-4', d, 6.6), 4.31 (H-1'', d, 7.8), 3.25 (H-2'', dd, 9.2, 7.8), 3.88 (H-6'', dd, 12.1, 2.6), 3.76 (H-6'', dd, 12.1, 5.9), 4.71 (H-1''', d, 8), 3.35 (H-2''', dd, 8, 3), 4.05 (H-3''', t, 3), 3.64 (H-4''', dd, 10.4, 3.2, in D_2O), 3.85 (H-6''', dd, 11.8, 1.8), 3.64 (H-6''', dd, 11.8, 5.9); (CD_3OD) 93.2 (C-1), 140.6 (C-3), 115.3 (C-4), 36.9 (C-5), 30.9 (C-6), 28.1 (C-7), 44.0 (C-8), 45.0 (C-9), 66.5 (C-10), 69.8 (C-11), 173.5 (C-1'), 44.2 (C-2'), 26.7 (C-3'), 22.6 (C-4'), 103.4 (C-1''), 74.5 (C-2''), 76.5 (C-3''), 81.6 (C-4''), 76.6 (C-5''), 62.3 (C-6''), 102.6 (C-1'''), 72.2 (C-2'''), 73.0 (C-3'''), 68.8 (C-4'''), 75.8 (C-5'''), 62.9 (C-6''). *Penstemon confertus* (Scrophulariaceae) (8)

22 PATRINALLOSIDE



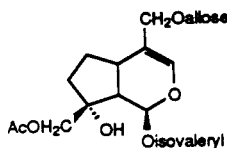
$C_{21}H_{34}O_{11}$ 462.49 mp 63° [α] –69° (MeOH) (400 MHz CD_3OD) 5.90 (H-1, d, 5.3), 6.36 (H-3, s), 3.01 (H-5, m), 2.09–2.03, 1.83 (H-6, m's), 4.32 (H-7, m), 1.95 (H-8, m), 2.18 (H-9, dr, 8.6, 5.3), 3.81 (H-10, dd, 11.0, 7.4), 4.15 (H-11, 11.6), 2.23 (H-2'), 2.09–2.03 (H-3'), 0.96 (H-4', d, 6.6), 4.63 (H-1'', d, 8.0), 4.04 (H-3'', t, 3.0), 3.47 (H-4'', dd, 9.4, 3.0), 3.84 (H-6'', dd, 11.0, 1.7), 3.72 (H-6'', dd, 10.9, 5.6); (CD_3OD) 93.6 (C-1), 139.9 (C-3), 116.6 (C-4), 34.0 (C-5), 40.9 (C-6), 73.4 (C-7), – (C-8), 42.7 (C-9), 62.3 (C-10), 69.6 (C-11), 173.3 (C-1'), 44.1 (C-2'), 26.7 (C-3'), 22.6 (C-4'), 101.0 (C-1''), 72.4 (C-2''), 73.0 (C-3''), 69.0 (C-4''), 75.4 (C-5''), 63.2 (C-6''). *Penstemon hirsutus* (Scrophulariaceae) (17)

23 2'-O-ACETYL PATRINOSIDE



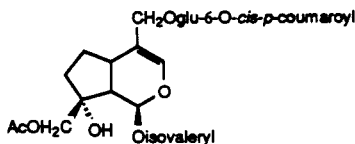
$C_{23}H_{36}O_{12}$ 504.53 uv 212 (MeOH) (250 MHz CD_3OD) 5.93 (H-1, d, 5), 6.31 (H-3, bs), 2.89 (H-5, m), 1.80, 1.97 (H-6, m's), 4.31 (H-7, m), 1.90–2.10 (H-8, m), 2.18 (H-9, m), 3.83 (H-10, dd, 10, 6), 3.71 (H-10, dd, 10, 7.5), 4.22, 4.05 (H-11, d's, 11), 2.24 (H-2'), 1.9–2.1 (H-3', m), 0.96 (H-4', d), 4.46 (H-1'', d), 4.71 (H-2'', dd, 11), 3.52 (H-3'', t, 9), 3.35 (H-4''), 3.27 (H-5''), 3.88 (H-6'', dd, 12, 2), 3.67 (H-6'', dd, 12, 4.5), 2.10 (OAc); (CD_3OD) 93.5 (C-1), 140.1 (C-3), 116.2 (C-4), 34.0 (C-5), 41.0 (C-6), 73.5 (C-7), 49.0 (C-8), 41.0 (C-9), 62.3 (C-10), 69.8 (C-11), 173.5 (C-1'), 44.3 (C-2'), 26.9 (C-3'), 22.7 (C-4'), 101.3 (C-1''), 75.5 (C-2''), 76.3 (C-3''), 71.9 (C-4''), 78.2 (C-5''), 62.8 (C-6''), 172.0 (O=CMe), 21.2 (O=CMe). *Viburnum lantana* (Caprifoliaceae) (15)

24 FURCATOSIDE C



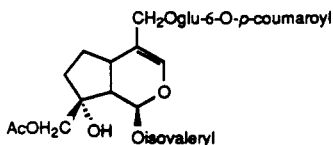
$C_{23}H_{36}O_{12}$ 504.53 $[\alpha] -58.1^\circ$ (MeOH) uv 204 (MeOH) (100 MHz Me_2CO-d_6/D_2O) 6.14 (H-1, d, 6), 6.42 (H-3, bs), 2.04 (OAc), 0.94 (H-4', d, 6), 4.64 (H-1'', d, 8); (CD_3OD) 92.3 (C-1), 141.6 (C-3), 116.2 (C-4), 37.0 (C-5), 30.5 (C-6), 38.7 (C-7), 81.6 (C-8), 47.5 (C-9), 72.4 (C-10)^a, 70.5 (C-11)^a, 173.4 (O=CMe)^b, 21.5 (O=CMe), 173.9 (C-1')^b, 45.1 (C-2'), 27.6 (C-3'), 23.4 (C-4'), 101.9 (C-1''), 73.8 (C-2''), 73.1 (C-3''), 69.7 (C-4''), 76.2 (C-5''), 64.0 (C-6''). *Viburnum furcatum* (Caprifoliaceae) (18)

25 FURCATOSIDE B



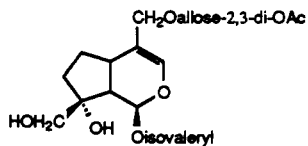
$C_{32}H_{42}O_{14}$ 650.68 $[\alpha] -26.6^\circ$ (MeOH) uv 312, 300, 227, 204 (MeOH) (60 MHz Me_2CO-d_6) 6.28 (H-1, d, 6), 6.62 (H-3, bs), 2.88 (OH, bs), 2.02 (OAc), 0.95 (H-4', d, 6), 5.06 (H-1'', d, 8), 3.3-4.7 (H-2''-H-6''), 6.00/7.13 (H α , H β , d's, 14), 8.02 (H-2''', d, 8), 7.06 (H-3''', d, 8). *Viburnum furcatum* (Caprifoliaceae) (18)

26 FURCATOSIDE A



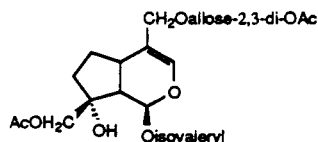
$C_{32}H_{42}O_{14}$ 650.68 $[\alpha] -103.1^\circ$ (MeOH) uv 314, 300, 228, 213 (MeOH) (100 MHz Me_2CO-d_6) 6.17 (H-1, d, 6), 6.46 (H-3, bs), 2.00 (OAc), 0.93 (H-4', d, 6), 5.10 (H-1'', d, 8), 3.3-4.8 (H-2''-H-6''), 6.42/7.80 (H α , H β , d's, 16), 7.62 (H-2''', d, 8), 6.98 (H-3''', d, 8); (CD_3OD) 91.6 (C-1), 140.5 (C-3), 115.4 (C-4), 36.4 (C-5), 30.7 (C-6), 38.1 (C-7), 80.7 (C-8), 45.7 (C-9), 69.9 (C-10)^a, 68.7 (C-11)^a, 167.8 (O=CMe)^b, 172.7 (C-1')^b, 44.5 (C-2'), 26.8 (C-3'), 22.7 (C-4'), 99.2 (C-1''), 73.6 (C-2''), 76.4 (C-3''), 71.7 (C-4''), 75.7 (C-5''), 63.7 (C-6''), 172.7 (O=C)^b, 146.9 (C α), 115.4 (C β), 127.1 (C-1'''), 131.3 (C-2'''), 117.0 (C-3'''), 161.5 (C-4'''). *Viburnum furcatum* (Caprifoliaceae) (18)

27 VIBURNALLOSIDE



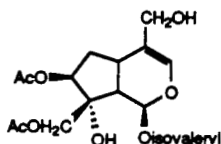
$C_{25}H_{38}O_{13}$ 546.57 $[\alpha] -86^\circ$ (MeOH) (90 MHz D_2O) 6.16 (H-1, d, 3.5), 6.42 (H-3, bs), 2.76 (H-5, m), 3.54 (H-10, bs), 4.25 (H-11, bs), 0.93 (H-4', d, 6), 4.98 (H-1'', d, 8.5), 4.74 (H-2'', dd, 8.5, 3), 5.57 (H-3'', bt), 2.20, 2.04 (OAc); (D_2O) 91.4 (C-1), 140.7 (C-3), 114.6 (C-4), 34.0 (C-5), 28.2 (C-6), 36.3 (C-7), 82.3 (C-8), 45.3 (C-9), 69.9 (C-10), 68.5 (C-11), 173.2 (C-1'), 43.9 (C-2'), 26.3 (C-3'), 22.4 (C-4'), 98.1 (C-1''), 71.2 (C-2''), 72.4 (C-3''), 65.8 (C-4''), 75.3 (C-5''), 61.6 (C-6''), 175.0 (O=CMe), 21.0 (O=CMe). *Viburnum betulifolium* (Caprifoliaceae) (19)

28 2',3'-O-DIACETYLFURCATOSIDE C (10-O-Acetylviburnalloside)



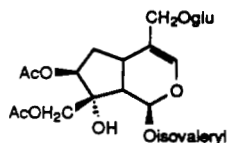
$C_{27}H_{40}O_{14}$ 588.60 $[\alpha] -60.8^\circ$ (MeOH) uv 209 (MeOH) (100 MHz $CDCl_3$) 6.18 (H-1, d, 4), 6.40 (H-3, bs), 4.83 (H-10, s), 4.16 (H-11, s), 0.95 (H-4', d, 6), 4.20–4.36 (H-1'', H-2'', m), 5.60 (H-3'', m), 3.88 (H-4'', H-6'', m), 2.03, 2.16, 2.20 (OAc); ($CDCl_3$) 89.8 (C-1), 140.1 (C-3), 113.3 (C-4), 35.1 (C-5), 28.4 (C-6), 37.5 (C-7), 80.3 (C-8), 45.8 (C-9), 70.0 (C-10), 68.9 (C-11), 169.6 (C-1')*, 43.4 (C-2'), 25.7 (C-3'), 22.3 (C-4'), 97.4 (C-1''), 70.8 (C-2''), 71.3 (C-3''), 66.6 (C-4''), 74.0 (C-5''), 62.4 (C-6''), 171.0, 171.3, 171.5 (O=CMe)*, 20.8 (O=CMe). *Viburnum japonicum* (Caprifoliaceae) (20)

29 SUSPENSOLIDE A AGLYCONE



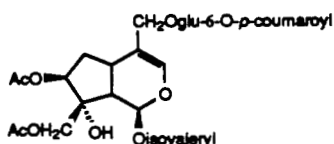
$C_{19}H_{28}O_9$ 400.42 $[\alpha] -56^\circ$ (MeOH) (100 MHz $CDCl_3$) 6.31 (H-1, d, 4), 6.41 (H-3, bs), 5.07 (H-7, t, 5), 2.46 (H-9, dd, 9, 4), 4.24 (H-10, s), 4.07, 3.98 (H-11, d's, 12), 2.09, 2.05 (OAc), 0.98 (H-4', d, 7); (Me_2CO-d_6) 89.5 (C-1), 138.5 (C-3), 117.4 (C-4), 30.9 (C-5), 34.6 (C-6), 80.5 (C-7), 81.0 (C-8), 44.8 (C-9), 62.2 (C-10), 67.0 (C-11), 170.7 (C-1')*, 43.3 (C-2'), 25.6 (C-3'), 22.3 (C-4'), 171.2, 171.5 (O=CMe)*, 21.0, 20.7 (O=CMe). *Viburnum suspensum* (Caprifoliaceae) (21,22)

30 SUSPENSOLIDE A



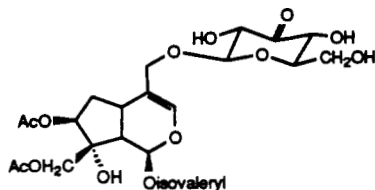
$C_{25}H_{38}O_{14}$ 562.57 $[\alpha] -42.9^\circ$ (MeOH) uv 204 (MeOH) (100 MHz Me_2CO-d_6) 6.16 (H-1, d, 6), 6.44 (H-3, bs), 5.06 (H-7, t, 4), 2.40 (H-9, dd, 10, 6), 1.98 (OAc), 0.95 (H-4', d, 6); (CD_3OD) 91.4 (C-1), 140.8 (C-3), 115.9 (C-4), 33.6 (C-5), 36.2 (C-6), 81.2 (C-7), 82.2 (C-8), 45.3 (C-9), 68.2 (C-10), 69.8 (C-11), 21.1, 20.8 (O=CMe), 173.0, 172.7, 171.9 (C-1', O=CMe), 44.3 (C-2'), 26.8 (C-3'), 22.7 (C-4'), 103.5 (C-1''), 75.2 (C-2''), 78.2 (C-3''), 71.8 (C-4''), 78.0 (C-5''), 62.9 (C-6''). *Viburnum suspensum* (Caprifoliaceae) (21,22)

31 SUSPENSOLIDE B



$C_{34}H_{44}O_{16}$ 708.71 mp 132–134° (100 MHz Me_2CO-d_6) 6.16 (H-1, d, 4), 6.36 (H-3, bs), 4.99 (H-7, t-like, 4), 2.36 (H-9, dd, 10, 4), 1.92, 1.88 (OAc), 0.96 (H-4', d, 6), 4.42 (H-1'', d, 8), 6.32/7.62 (H α , H β , d's, 16), 7.52 (H-2'', d, 8), 6.88 (H-3'', d, 8), 8.92 (ArOH); (CD_3OD) 91.2 (C-1), 140.4 (C-3), 115.9 (C-4), 32.7 (C-5), 36.0 (C-6), 81.1 (C-7), 81.9 (C-8), 45.7 (C-9), 67.9 (C-10), 69.7 (C-11), 173.0, 172.5, 171.6, 168.2 (O=C, C-1', O=CMe), 20.9, 20.7 (O=CMe), 44.2 (C-2'), 26.8 (C-3'), 22.71, 22.67 (C-4'), 101.4 (C-1''), 75.2 (C-2''), 78.1 (C-3''), 71.8 (C-4''), 76.2 (C-5''), 62.7 (C-6''), 115.3 (C α), 147.0 (C β), 127.2 (C-1'''), 131.3 (C-2'''), 116.9 (C-3'''), 161.3 (C-4'''). *Viburnum suspensum* (Caprifoliaceae) (22)

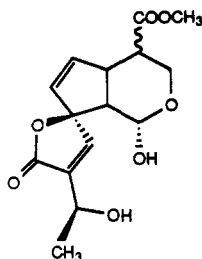
32 SUSPENSOLIDE C



$C_{25}H_{36}O_{14}$ 560.55 $[\alpha] -50^\circ$ (MeOH) uv 205 (MeOH) (100 MHz Me_2CO-d_6) 6.12 (H-1, d, 6), 6.40 (H-3, bs), 5.00 (H-7, t-like, 4), 2.38 (H-9, dd, 10, 6), 1.98 (OAc), 0.92 (H-4', d, 6), 4.44 (H-1'', d, 8); (CD_3OD) 92.2 (C-1), 141.8 (C-3), 116.3 (C-4), 34.5 (C-5), 37.0 (C-6), 81.9 (C-7), 83.0 (C-8), 46.7 (C-9), 68.9 (C-10), 71.0 (C-11), 21.9, 21.6 (O=CMe), 173.7, 173.4, 172.5 (O=CMe, C-1'), 45.1 (C-2'), 27.6 (C-3'), 23.5 (C-4'), 105.6 (C-1''), 79.1 (C-2''), 207.9 (C-3''), 74.6 (C-4''), 79.1 (C-5''), 63.5 (C-6''). *Viburnum suspensum* (Caprifoliaceae) (22)

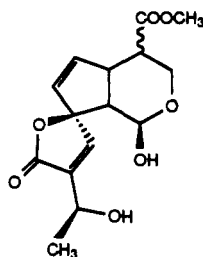
Group 7 (plumeria iridoids)

33 ALLAMCIDIN A



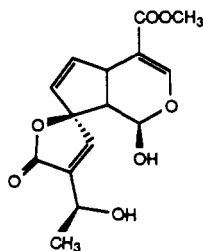
$C_{15}H_{18}O_7$ 310.30 $[\alpha] +35.0^\circ$ ($CHCl_3$) uv 213 (MeOH) (? MHz $CDCl_3$) 5.80 (H-1, d, 9), 3.80 (H-3, m), 2.80 (H-4, m), 3.32 (H-5, m), 6.17 (H-6, dd, 6, 2), 5.54 (H-7, dd, 6, 1), 2.44 (H-9, dd, 11, 9), 7.03 (H-10, d, 2), 5.58 (H-13, dq, 6, 2), 1.49 (H-14, d, 6), 3.74 (COOMe), 2.10, 2.08 (OAc); (pyridine- d_5) 93.6 (C-1), 62.0 (C-3), 44.8 (C-4)^a, 44.6 (C-5)^a, 131.4 (C-6), 139.5 (C-7), 97.2 (C-8), 49.8 (C-9), 149.1 (C-10), 135.1 (C-11), 171.6 (C-12)^b, 65.5 (C-13), 19.4 (C-14), 170.4 (C-15)^b, 52.2 (OMe), 20.8, 20.7 (O=CMe), 169.8, 169.2 (O=CMe). *Allamanda nerifolia* (Apocynaceae) (23)

34 ALLAMCIDIN B



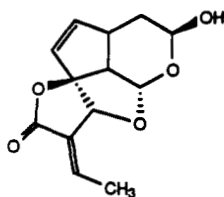
$C_{15}H_{18}O_7$ 310.30 mp 161–163° $[\alpha] +38.0^\circ$ ($CHCl_3$) uv 213 (MeOH) (? MHz $CDCl_3$) 6.42 (H-1, d, 3), 3.94 (H-3, dd, 13, 4), 3.49 (H-3, dd, 13, 1), 2.82 (H-4, m), 3.56 (H-5, m), 6.38 (H-6, dd, 6, 2), 5.61 (H-7, dd, 6, 1), 2.48 (H-9, dd, 11, 3), 7.01 (H-10, d, 2), 5.64 (H-13, dq, 6, 2), 1.48 (H-14, d, 6), 3.73 (COOMe), 2.09 (OAc); (pyridine- d_5) 89.6 (C-1), 57.2 (C-3), 44.4 (C-4), 38.3 (C-5), 131.5 (C-6), 139.5 (C-7), 97.5 (C-8), 48.3 (C-9), 149.3 (C-10), 135.1 (C-11), 171.6 (C-12)^a, 65.5 (C-13), 19.6 (C-14), 170.3 (C-15)^a, 52.2 (OMe), 20.8, 20.5 (O=CMe), 169.8, 169.2 (O=CMe). *Allamanda nerifolia* (Apocynaceae) (23)

35 PLUMIERIDINE (Deglucosyl plumeride)



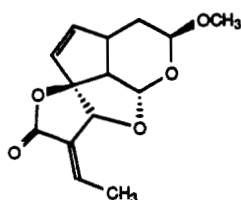
$C_{15}H_{16}O_7$ 308.29 mp 161–163° $[\alpha] -57.4^\circ$ (EtOAc) uv 245, 215 (EtOH) 5.33 (H-1, d, 4), 7.47 (H-3, d, 2), 3.94 (H-5, bq, 8), 6.38 (H-6, td, 6, 2), 5.33 (H-7, d, 6), 3.10 (H-9, q, 8, 4), 7.29 (H-10, d, 1), 4.82 (H-13, bq, 7, 1), 1.47 (H-14, d, 7), 3.53 (OMe). Hydrolysis of plumeride (24)

36 ALLAMCIN



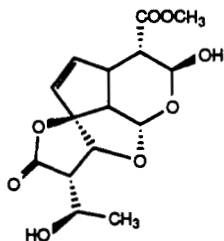
$C_{13}H_{14}O_5$ 250.25 mp 198–210° (dec) $[\alpha] +65.6^\circ$ (pyridine) uv 214 (MeOH) (? MHz DMSO- d_6) 5.54 (H-1, d, 5), 4.94 (H-3, dd, 8, 5), 1.98 (H-4, m), 1.55 (m), 3.28 (H-5, m), 6.04 (H-6, dd, 6, 2), 5.82 (H-7, dd, 6, 2), 2.90 (H-9, dd, 8, 5), 5.03 (H-10, bs), 6.94 (H-13, dq, 7, 2), 1.97 (H-14, d, 7); (DMSO- d_6) 98.5 (C-1), 89.6 (C-3), 30.0 (C-4), 38.4 (C-5), 129.1 (C-6), 142.0 (C-7), 103.3 (C-8), 51.2 (C-9), 78.7 (C-10), 128.3 (C-11), 167.9 (C-12), 143.2 (C-13), 15.5 (C-14). *Allamanda neriifolia* (Apocynaceae) (23)

37 3-O-METHYLALLAMCIN



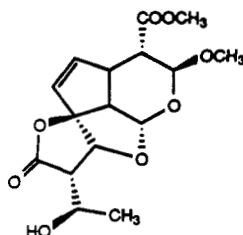
$C_{14}H_{16}O_5$ 264.28 mp 138–140° $[\alpha] +48.4^\circ$ (MeOH) uv 215 (MeOH) (? MHz pyridine- d_5) 5.71 (H-1, d, 4), 4.77 (H-3, dd, 8, 6), 2.30–1.50 (H-4, m), 3.17 (H-5, m), 5.98 (H-6, dd, 5, 2), 5.88 (H-7, dd, 5, 2), 2.98 (H-9, dd, 9, 4), 5.29 (H-10, bs), 7.07 (H-13, dq, 7, 2), 1.88 (H-14, d, 7), 3.37 (OMe); (pyridine- d_5) 98.3 (C-1)^a, 99.0 (C-3)^a, 28.8 (C-4), 39.1 (C-5), 130.2 (C-6), 142.2 (C-7), 103.6 (C-8), 53.3 (C-9), 80.2 (C-10), 129.3 (C-11), 168.6 (C-12), 143.7 (C-13), 15.7 (C-14), 55.0 (OMe). *Allamanda neriifolia* (Apocynaceae) (23)

38 ALLAMANCIN



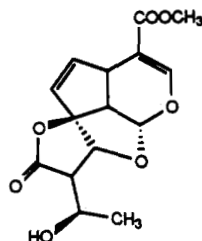
$C_{15}H_{18}O_8$ 326.30 $[\alpha] +74.5^\circ$ (CHCl₃) (? MHz CDCl₃) 5.67 (H-1, d, 4), 5.40 (H-3, d, 8), 2.78 (H-4, dd, 8, 5), 3.58 (H-5, m), 5.93 (H-6, H-7, m), 3.07 (H-9, dd, 8, 4), 4.83 (H-10, d, 2), 2.73 (H-11, t, 2), 4.45 (H-13, m), 1.38 (H-14, d, 6), 3.79 (COOMe); (pyridine- d_5) 98.7 (C-1), 91.6 (C-3), 47.0 (C-4)^a, 43.0 (C-5)^a, 132.4 (C-6), 138.2 (C-7), 105.0 (C-8), 53.7 (C-9), 83.4 (C-10), 56.1 (C-11), 177.4 (C-12), 66.1 (C-13), 22.3 (C-14), 172.8 (C-15), 52.1 (OMe). *Allamanda neriifolia* (Apocynaceae) (23)

39 3-O-METHYLALLAMANCIN



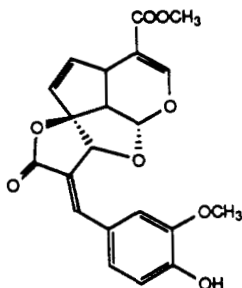
$C_{16}H_{20}O_8$ 340.33 $[\alpha] + 112.3^\circ$ (CHCl₃) (? MHz CDCl₃) 5.54 (H-1, d, 4), 4.99 (H-3, d, 8), 2.74 (H-4, dd, 8, 4), 3.52 (H-5, m), 5.90 (H-6, H-7, m), 3.04 (H-9, dd, 8, 4), 4.83 (H-10, d, 2), 2.77 (H-11, d, 2), 4.48 (H-13, m), 1.39 (H-14, d, 6), 3.79 (COOMe), 3.43 (OMe); (pyridine-*d*₅) 98.6 (C-1), 99.1 (C-3), 45.2 (C-4)^a, 42.6 (C-5)^a, 132.6 (C-6), 137.9 (C-7), 104.8 (C-8), 53.6 (C-9), 83.7 (C-10), 56.1 (C-11), 177.3 (C-12), 66.2 (C-13), 22.3 (C-14), 172.1 (C-15), 52.2 (COOMe), 55.5 (OMe). *Allamanda nerifolia* (Apocynaceae) (23)

40 ISOALLAMANDICIN



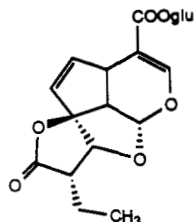
$C_{15}H_{16}O_7$ 308.29 mp 170–173° $[\alpha] + 187.5^\circ$ (MeOH) (? MHz CDCl₃) 5.58 (H-1, d, 6), 7.42 (H-3, s), 3.97 (H-5, dt, 9, 2), 6.12 (H-6, dd, 5, 2), 5.66 (H-7, dd, 5, 2), 3.43 (H-9, dd, 9, 6), 4.58 (H-10, d, 6), 2.78 (H-11, dd, 9, 6), 4.27 (H-13, m), 1.39 (H-14, d, 6), 3.78 (COOMe); (pyridine-*d*₅) 102.0 (C-1), 152.8 (C-3), 108.1 (C-4), 38.1 (C-5), 126.2 (C-6), 141.4 (C-7), 105.9 (C-8), 53.5 (C-9), 84.0 (C-10), 51.6 (C-11), 175.9 (C-12), 64.4 (C-13), 22.2 (C-14), 166.7 (C-15), 51.3 (OMe). *Allamanda nerifolia* (Apocynaceae) (23)

41 ORUWACIN



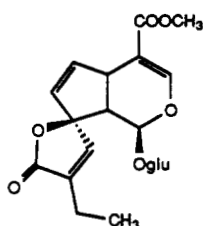
$C_{21}H_{18}O_8$ 398.37 mp 223° $[\alpha] + 193^\circ$ (CHCl₃) uv 205, 241, 317, 348 (EtOH) (100 MHz CDCl₃) 5.63 (H-1, d, 6), 7.45 (H-3, s), 4.06 (H-5, ddd, 9, 2, 2), 5.61 (H-6, dd, 6, 2)^a, 6.02 (H-7, dd, 6, 2)^a, 3.55 (H-9, dd, 9, 6), 5.21 (H-10, bs), 7.75 (H-13, bs), 6.97 (H-2', d, 2, 5), 3.78 (OMe), 3.92 (ArOMe), 6.1 (-OH, brs); (CDCl₃) 104.4 (C-1), 147.2 (C-3), 112.7 (C-4), 38.7 (C-5), 115.2 (C-6), 141.0 (C-7), 102.4 (C-8), 51.7 (C-9), 82.3 (C-10), 144.8 (C-11), 169.9 (C-12), 120.3 (C-13), 126.4 (C-1'), 126.5 (C-2'), 152.9 (C-3'), 149.2 (C-4'), 127.0 (C-5'), 126.0 (C-6'), 54.3 (OMe), 166.6 (C=O), 56.1 (ArOMe). *Morinda lucida* (Rubiaceae) (25)

42 PLUMENOSIDE (β-Dihydroplumericinic acid glucosyl ester)

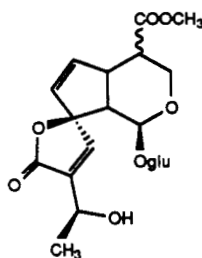


$C_{20}H_{24}O_{11}$ 440.40 $[\alpha] + 117.3^\circ$ (MeOH) uv 238 (MeOH) (400 MHz pyridine-*d*₅) 5.71 (H-1, d, 6), 7.73 (H-3, s), 3.93 (H-5, rd, 10, 2), 6.14 (H-6, dd, 5, 2), 5.70 (H-7, dd, 5, 2), 3.48 (H-9, dd, 10, 6), 4.52 (H-10, s), 2.92 (H-11, t, 8), 1.79, 1.64 (H-13, m's), 0.99 (H-14, t, 7), 6.47 (H-1', d, 8), 4.23 (H-2', dd, 9, 8), 4.33 (H-3', t, 9), 4.36 (H-4', t, 9), 4.10 (H-5', m), 4.50 (H-6', dd, 12, 2), 4.40 (H-6', dd, 12, 5); (pyridine-*d*₅) 101.8 (C-1), 154.0 (C-3), 108.4 (C-4), 38.2 (C-5), 141.4 (C-6), 126.9 (C-7), 106.3 (C-8), 53.7 (C-9), 87.0 (C-10), 49.0 (C-11), 176.7 (C-12), 22.8 (C-13), 11.8 (C-14), 165.5 (C=O), 95.9 (C-1'), 74.2 (C-2'), 78.6 (C-3'), 71.1 (C-4'), 79.4 (C-5'), 62.2 (C-6'). *Plumeria acutifolia* (Apocynaceae) (26)

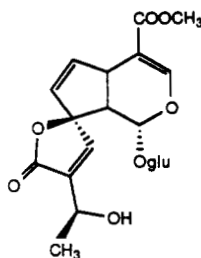
43 13-DEOXYPLUMIERIDE



$C_{21}H_{26}O_{11}$ 454.43 mp 129–131° $[\alpha] -113.6^\circ$ (MeOH) uv 238, 213 (MeOH) (400 MHz pyridine- d_5) 5.64 (H-1, d, 5), 7.65 (H-3, d, 1), 3.98 (H-5, bd, 7), 6.46 (H-6, dd, 5, 2), 5.45 (H-7, dd, 5, 2), 3.07 (H-9, dd, 7, 5), 7.41 (H-10, t, 1), 2.21 (H-13, m), 1.10 (H-14, t, 7), 3.64 (OMe), 5.34 (H-1', d, 8), 3.99 (H-2', dd, 9, 8), 4.23 (H-3', t, 9), 4.27 (H-4', t, 9), 3.90 (H-5', m), 4.43 (H-6', dd, 12, 2), 4.33 (H-6', dd, 12, 5); (pyridine- d_5) 93.8 (C-1), 151.9 (C-3), 109.7 (C-4), 39.8 (C-5), 140.5 (C-6), 130.6 (C-7), 96.3 (C-8), 50.0 (C-9), 148.3 (C-10), 135.0 (C-11), 172.4 (C-12), 18.9 (C-13), 11.8 (C-14), 166.7 (C=O), 51.2 (OMe), 100.6 (C-1'), 74.7 (C-2'), 78.2 (C-3')^a, 71.3 (C-4'), 78.8 (C-5')^a, 62.3 (C-6'). *Plumeria acutifolia* (Apocynaceae) (26)

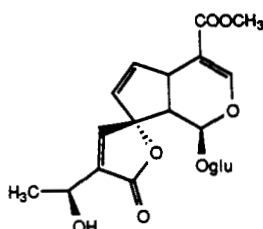
44 ALLAMCIDIN B β -D-GLUCOSE

$C_{21}H_{28}O_{12}$ 472.45 mp 135–138° $[\alpha] +49.4^\circ$ (MeOH) uv 212 (MeOH) (? MHz pyridine- d_5) 5.83 (H-1, d, 3), 4.58 (H-3, dd, 13, 4), 3.47 (dd, 13, 1), 2.69 (H-4, m), 6.42 (H-6, dd, 6, 2), 5.63 (H-7, dd, 6, 1), 2.80 (H-9, dd, 10, 3), 7.74 (H-10, d, 2), 5.05 (H-13, dq, 6, 2), 1.67 (H-14, d, 6), 3.83 (COOMe), 5.02 (H-1', d, 8); (pyridine- d_5) 98.1 (C-1), 56.0 (C-3), 44.3 (C-4), 38.3 (C-5), 131.7 (C-6), 141.3 (C-7), 97.5 (C-8), 50.0 (C-9), 148.3 (C-10), 140.0 (C-11), 171.8 (C-12)^a, 62.9 (C-13), 23.3 (C-14), 170.9 (C-15)^a, 51.9 (OMe), 104.7 (C-1'), 75.0 (C-2'), 78.8 (C-3'), 71.0 (C-4'), 78.6 (C-5'), 62.4 (C-6'). *Allamanda neriifolia* (Apocynaceae) (23)

45 1 α -PLUMIERIDE

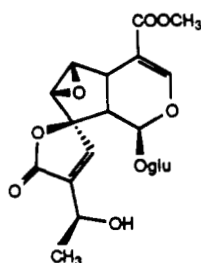
$C_{21}H_{26}O_{12}$ 470.43 $[\alpha] -46.4^\circ$ (MeOH) uv 205 (MeOH) (400 MHz pyridine- d_5) 5.68 (H-1, d, 4), 7.60 (H-3, d, 1), 3.97 (H-5, ddd, 8, 3, 2), 6.47 (H-6, dd, 6, 3), 5.49 (H-7, dd, 6, 2), 3.17 (H-9, dd, 8, 4), 7.81 (H-10, d, 1), 4.96 (H-13, q, 6), 1.63 (H-14, d, 6), 3.62 (OMe), 5.25 (H-1', d, 8), 4.06 (H-2', dd, 9, 8), 4.21 (H-3', t, 9), 4.32 (H-4', t, 9), 3.85 (H-5', m), 4.36 (H-6', bs); (pyridine- d_5) 93.7 (C-1), 151.7 (C-3), 109.9 (C-4), 39.5 (C-5), 140.1 (C-6), 129.7 (C-7), 96.3 (C-8), 49.9 (C-9), 148.7 (C-10), 139.0 (C-11), 171.2 (C-12), 62.8 (C-13), 22.9 (C-14), 166.6 (C=O), 51.1 (OMe), 100.7 (C-1'), 74.6 (C-2'), 78.2 (C-3')^a, 70.9 (C-4'), 78.7 (C-5')^a, 62.2 (C-6'). *Plumeria acutifolia* (Apocynaceae) (26)

46 8-ISOPLUMIERIDE



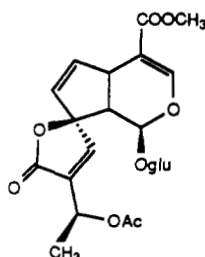
$C_{21}H_{26}O_{12}$ 470.43 mp 168–173° $[\alpha] -164.8^\circ$ (MeOH) uv 230, 210 (MeOH) (400 MHz pyridine- d_5) 58.4 (H-1, d, 1), 7.66 (H-3, d, 1), 3.80 (H-5, ddd, 8, 3, 1), 6.68 (H-6, dd, 5, 3), 5.58 (H-7, dd, 5, 1), 3.25 (H-9, dd, 8, 1), 7.50 (H-10, d, 1), 4.97 (H-13, dq, 7, 1), 1.67 (H-14, d, 7), 3.57 (OMe), 5.21 (H-1', d, 8), 4.00 (H-2', dd, 9, 8), 4.19 (H-3', t, 9), 4.24 (H-4', t, 9), 3.84 (H-5', m), 4.40 (H-6', dd, 12, 2), 4.27 (H-6', dd, 12, 5); (pyridine- d_5) 92.6 (C-1), 151.7 (C-3), 108.3 (C-4), 38.3 (C-5), 141.3 (C-6), 128.6 (C-7), 94.9 (C-8), 46.2 (C-9), 149.3 (C-10), 140.9 (C-11), 171.5 (C-12), 62.9 (C-13), 22.6 (C-14), 166.8 (C=O), 51.0 (OMe), 101.1 (C-1'), 74.7 (C-2'), 78.3 (C-3'), 71.3 (C-4'), 78.4 (C-5'), 62.7 (C-6'). *Plumeria acutifolia* (Apocynaceae) (26)

47 PLUMIEPOXIDE



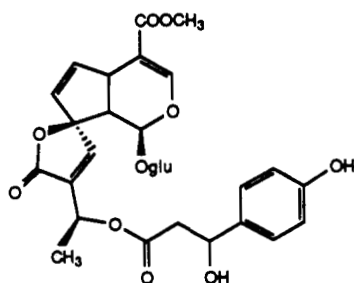
$C_{21}H_{26}O_{13}$ 486.43 mp 224–225° $[\alpha] -129.5^\circ$ (MeOH) uv 222 (MeOH) (? MHz pyridine- d_5) 5.87 (H-1, bs), 7.71 (H-3, d, 1), 3.47 (H-6, d, 2), 4.24 (H-7, d, 2), 3.22 (H-9, dd, 9, 1), 7.48 (H-10, d, 2), 4.95 (H-13, dq, 6, 2), 1.59 (H-14, d, 6), 3.60 (COOMe), 5.18 (H-1', d, 8); (pyridine- d_5) 93.0 (C-1), 153.5 (C-3), 106.7 (C-4), 32.3 (C-5), 57.1 (C-6)*, 58.7 (C-7)*, 91.3 (C-8), 43.1 (C-9), 146.0 (C-10), 141.9 (C-11), 170.7 (C-12), 62.8 (C-13), 22.9 (C-14), 166.3 (C-15), 51.3 (OMe), 100.8 (C-1'), 74.4 (C-2'), 78.5 (C-3'), 70.7 (C-4'), 78.2 (C-5'), 61.8 (C-6'). *Allamanda neriifolia* (Apocynaceae) (23)

48 13-O-ACETYLPLUMIERIDE



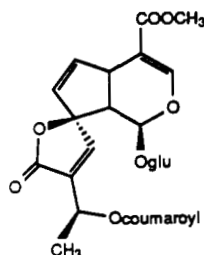
$C_{23}H_{28}O_{13}$ 512.47 $[\alpha] -37.8^\circ$ (MeOH) uv 235, 210 (MeOH) (? MHz pyridine- d_5) 5.57 (H-1, d, 6), 7.61 (H-3, d, 2), 6.43 (H-6, dd, 5, 2), 5.37 (H-7, dd, 5, 2), 2.99 (H-9, t, 6), 7.91 (H-10, d, 2), 5.88 (H-13, dq, 7, 2), 1.50 (H-14, d, 7), 3.64 (OMe), 2.06 (OAc), 5.37 (H-1', d, 8); (pyridine- d_5) 93.6 (C-1), 152.2 (C-3), 109.3 (C-4), 40.4 (C-5), 128.3 (C-6), 141.9 (C-7), 96.7 (C-8), 50.3 (C-9), 150.6 (C-10), 133.3 (C-11), 170.2 (C-12), 65.2 (C-13), 19.1 (C-14), 166.7 (C-15), 51.3 (OMe), 21.0 (O=CMe), 170.2 (O=CMe), 100.3 (C-1'), 74.7 (C-2'), 78.8 (C-3'), 71.3 (C-4'), 78.0 (C-5'), 62.3 (C-6'). *Allamanda neriifolia* (Apocynaceae) (23)

49 ALLANEROSIDE



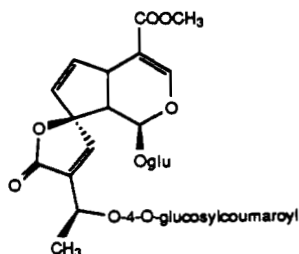
$C_{30}H_{34}O_{15}$ 634.60 [α] -67.5° (MeOH) uv 275.4, 222.4, 200 (MeOH) (? MHz CD_3OD) 5.25 (H-1, d, 5), 7.51 (H-3, d, 1.6), 3.62 (H-5, m), 6.46 (H-6, dd, 5.6, 2.5), 5.46 (H-7, dd, 5.5, 2.2), 2.92 (H-9, dd, 7.5, 4.9), 7.42 (H-10, d, 1.2), 5.60 (H-13, dq, 6, 1.5), 1.42 (H-14, d, 6.5), 3.75 (COOMe), 2.88 (H- α , dd, 15.5, 8.7), 2.69 (H- α , dd, 15.5, 5.4), 4.99 (H- β , dd, 8.7, 5.4), 7.20 (H-2", d, 8.6), 6.75 (H-3", d, 8.6), 3.2–4.0 (sugar protons); (CD_3OD) 93.9 (C-1), 152.6 (C-3), 110.8 (C-4), 40.5 (C-5), 129.5 (C-6), 141.8 (C-7), 98.1 (C-8), 50.6 (C-9), 152.0 (C-10), 134.4 (C-11), 171.9 (C-12), 66.3 (C-13), 19.5 (C-14), 168.4 (C=O), 52.0 (COOMe), 99.7 (C-1'), 74.6 (C-2'), 77.7 (C-3'), 71.4 (C-4'), 78.4 (C-5'), 62.7 (C-6'), 171.9 (C=O), 44.9 (C- α), 71.5 (C- β), 135.4 (C-1"), 116.2 (C-2"), 128.3 (C-3"), 158.1 (C-4"). *Allamanda nerifolia* (Apocynaceae) (27)

50 PLUMIERIDE COUMARATE (13-O-Coumaroylplumieride)

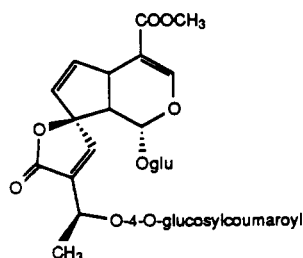


$C_{30}H_{32}O_{14}$ 616.57 [α] -60.0° (MeOH) uv 230, 302, 318 (EtOH) (90 MHz $DMSO-d_6$) 5.16 (H-1, d, 5), 7.65–7.4 (H-3), 3.9–3.5 (H-5), 6.35 (H-6, dd, 5, 2.5), ~5.55 (H-7), 2.80 (H-9, dd, 7, 5), 7.65–7.4 (H-10), ~5.55 (H-13), 4.53 (H-1', d, 7), 3.33–3.0 (H-2'–H-5'), 3.9–3.5 (H-6'), 1.42 (H-14, d, 6.5, cis), 1.46 (H-14, d, 6.5, trans), 3.68 (OMe), 5.74 (H- α , d, 13, cis), 6.33 (H- α , d, 16, trans), 6.70 (H- β , cis), 7.65–7.4 (H- β , trans), 7.65–7.4 (H-2"), 6.73 (H-3", d, 8.5). *Allamanda cathartica* (Apocynaceae) (28)

51 PROTOPLUMERICIN A (Plumieride coumarate glucoside)

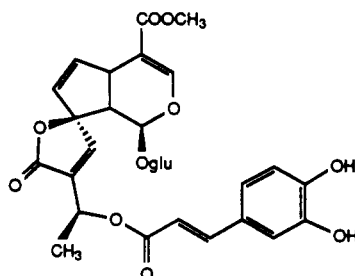


$C_{36}H_{42}O_{19}$ 778.72 [α] -89.9° (MeOH) uv 305, 296, 290, 222, 210 (MeOH) (? MHz pyridine- d_5) 5.63 (H-1, d, 6), 7.66 (H-3, d, 2), 6.48 (H-6, dd, 5, 2), 5.43 (H-7, dd, 5, 2), 3.03 (H-9, dd, 7, 6), 8.03 (H-10, d, 2), 3.61 (COOMe), 6.09 (H-13, dq, 6, 2), 1.62 (H-14, d, 7), 5.29 (H-1', d, 6), 4.60–3.80 (sugars), 6.69 (H- α , d, 16), 7.96 (H- β , d, 16), 7.60 (H-2", d, 7), 7.33 (H-3", d, 7); (pyridine- d_5) 93.7 (C-1), 152.1 (C-3), 109.3 (C-4), 40.3 (C-5), 141.7 (C-6), 150.8 (C-7), 96.7 (C-8), 50.2 (C-9), 128.4 (C-10), 133.6 (C-11), 170.2 (C-12), 65.1 (C-13), 19.3 (C-14), 166.6 (C-15), 51.2 (COOMe), 166.2 (COOMe), 100.5 (C-1'), 101.6 (C-1"), 74.8 (C-2', C-2"), 78.2 (C-3'), 78.4 (C-3"), 71.7 (C-4', C-4"), 78.9 (C-5', C-5"), 62.2 (C-6', C-6"), 116.2 (C- α), 145.3 (C- β), 128.4 (C-1"), 130.3 (C-2"), 117.0 (C-3"), 160.2 (C-4"). *Allamanda nerifolia* (Apocynaceae) (28, 29)

52 1 α -PROTOPLUMERICIN A

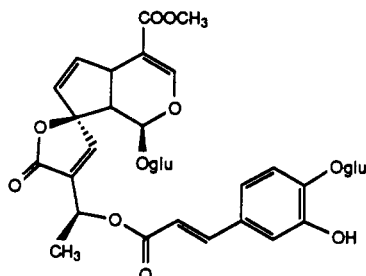
$C_{36}H_{42}O_{19}$ 778.72 $[\alpha] -44.1^\circ$ (MeOH) uv 305, 295, 220, 205 (MeOH) (400 MHz pyridine- d_5) 5.66 (H-1, d, 5), 7.60 (H-3, d, 1), 3.97 (H-5, td, 8, 2), 6.48 (H-6, dd, 5, 2), 5.47 (H-7, dd, 5, 2), 3.05 (H-9, dd, 7, 5), 7.88 (H-10, d, 1), 6.08 (H-13, dq, 7, 1), 1.66 (H-14, d, 7), 3.63 (OMe), 5.33 (H-1', d, 8), 5.62 (H-1'', d, 8), 6.67 (H- α , d, 16), 7.94 (H- β , d, 16), 7.61 (H-2'', d, 8), 7.29 (H-3'', d, 8); (pyridine- d_5) 93.6 (C-1), 152.0 (C-3), 109.6 (C-4), 40.0 (C-5), 141.3 (C-6), 128.6 (C-7), 96.6 (C-8), 50.4 (C-9), 151.3 (C-10), 133.6 (C-11), 170.3 (C-12), 65.0 (C-13), 19.2 (C-14), 166.6 (COOMe)^a, 51.2 (OMe), 100.6, 101.7 (C-1', C-1''), 74.8, 74.7 (C-2', C-2''), 78.4 (C-3', C-3''), 71.2 (C-4', C-4''), 78.9 (C-5', C-5''), 62.3 (C-6', C-6''), 166.4 (C=O)^a, 116.3 (C- α), 145.3 (C- β), 128.9 (C-1''), 130.4 (C-2''), 117.1 (C-3''), 160.2 (C-4''). *Plumeria acutifolia* (Apocynaceae) (26)

53 13-O-CAFFEYOYLPLUMERICIDE



$C_{30}H_{32}O_{15}$ 632.57 $[\alpha] -60.0^\circ$ (MeOH) uv 323, 300, 220, 205 (MeOH) (400 MHz pyridine- d_5) 5.62 (H-1, d, 6), 7.63 (H-3, d, 1), 3.99 (H-5, td, 7, 2), 6.43 (H-6, dd, 5, 2), 5.38 (H-7, dd, 5, 2), 3.04 (H-9, dd, 7, 6), 7.97 (H-10, s), 6.07 (H-13, q, 6), 1.61 (H-14, d, 6), 3.63 (OMe), 5.39 (H-1', d, 8), 4.05 (H-2', dd, 9, 8), 4.26 (H-3', t, 9), 4.31 (H-4', t, 9), 4.52 (H-6', dd, 12, 2), 4.39 (H-6'', dd, 12, 5), 6.68 (H- α , d, 16), 8.02 (H- β , d, 16), 7.61 (H-2'', d, 1), 7.19 (H-5'', d, 8), 7.17 (H-6'', dd, 8, 1); (pyridine- d_5) 93.8 (C-1), 152.1 (C-3), 109.5 (C-4), 40.3 (C-5), 141.6 (C-6), 128.5 (C-7), 96.7 (C-8), 50.3 (C-9), 150.7 (C-10), 133.9 (C-11), 170.2 (C-12), 64.9 (C-13), 19.5 (C-14), 166.6 (COOMe)^a, 51.2 (COOMe), 100.6 (C-1'), 74.8 (C-2'), 78.2 (C-3')^b, 71.5 (C-4'), 79.0 (C-5')^b, 62.5 (C-6'), 166.5 (C=O)^a, 116.6 (C- α)^c, 146.7 (C- β), 126.8 (C-1''), 114.4 (C-2''), 150.6 (C-3''), 147.6 (C-4''), 116.0 (C-5'')^c, 122.2 (C-6''). *Plumeria acutifolia* (Apocynaceae) (26)

54 PROTOPLUMERICIN B

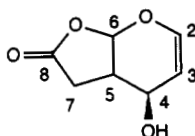


$C_{36}H_{42}O_{20}$ 794.72 $[\alpha] -61.2^\circ$ (MeOH) uv 320, 288, 230, 206 (MeOH) (? MHz pyridine- d_5) 5.60 (H-1, d, 6), 7.60 (H-3, d, 2), 6.43 (H-6, dd, 6, 2), 5.40 (H-7, dd, 6, 2), 3.04 (H-9, dd, 9, 6), 7.97 (H-10, d, 1), 6.06 (H-13, dq, 6, 1), 1.62 (H-14, d, 6), 3.64 (OMe), 5.36 (H-1', d, 8), 5.55 (H-1'', d, 8), 6.68 (H- α , d, 16), 7.94 (H- β , d, 16), 7.54 (H-2'', d, 2), 7.47 (H-5'', d, 8), 7.07 (H-6'', dd, 8, 2); (pyridine- d_5) 93.7 (C-1), 152.1 (C-3), 109.4 (C-4), 40.3 (C-5), 128.4 (C-6), 141.6 (C-7), 96.7 (C-8), 50.3 (C-9), 148.8 (C-10), 133.6 (C-11), 170.2 (C-12), 65.1 (C-13), 19.4 (C-14), 166.6 (COOMe)^a, 51.2 (COOMe), 166.2 (C=O)^a, 100.5, 103.4 (C-1', C-1''), 74.7 (C-2', C-2''), 79.0 (C-3',

C-3^m), 71.0, 71.3 (C-4', C-4^m), 78.2, 78.3 (C-5', C-5^m), 62.1, 62.4 (C-6', C-6^m), 116.6 (C- α), 145.8 (C- β), 130.2 (C-1ⁿ), 116.6 (C-2ⁿ), 149.4 (C-3ⁿ), 149.4 (C-4ⁿ), 118.1 (C-5ⁿ), 121.1 (C-6ⁿ). *Allamanda nerifolia* (Apocynaceae) (23)

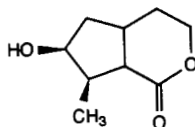
Group 8 (miscellaneous iridoid-like compounds)

55 OXYSPORONE



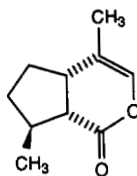
C₇H₈O₄ 156.14 uv 284, 215 (?) (100 MHz D₂O) 6.37 (H-2, d, 6), 5.06 (H-3, ddd, 6, 5.5, 1.0), 4.16 (H-4, dd, 5.5, 2.0), 5.82 (H-6, d, 4.5), 2-3 (4H); (?) 143.5 (C-2), 100.1 (C-3), 60.0 (C-4), 29.5 (C-5), 96.0 (C-6), 41.8 (C-7), 175.3 (C-8). The fungus *Fusarium oxysporum* (30)

56 BOONEIN



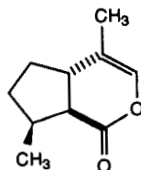
C₉H₁₄O₃ 170.21 mp 95-96° [α] +28.6° (CHCl₃) (100 MHz CDCl₃) 4.1-4.5 (H-3, H-7, m), 2.00 (H-5, bd, 6), 1.20 (H-10, d, 7); (CDCl₃) 175.0 (C-1), 66.9 (C-3), 29.4 (C-4), 33.3 (C-5), 40.7 (C-6), 74.4 (C-7), 43.8 (C-8), 46.8 (C-9), 13.3 (C-10). *Alstonia boonei* (Apocynaceae) (31)

57 4 α ,7 α ,7 α -NEPETALACTONE

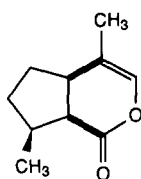


C₁₀H₁₄O₂ 166.22 [α] +3.7° (CHCl₃) (100 MHz CDCl₃) 6.15 (H-3, m), 1.19 (H-10, d, 6), 1.64 (H-11, m); (CDCl₃) 170.5 (C-1), 133.4 (C-3), 115.1 (C-4), 40.7 (C-5), 30.9 (C-6), 33.0 (C-7), 39.7 (C-8), 49.3 (C-9), 20.3 (C-10), 15.4 (C-11). *Nepeta cataria* (Labiatae) (32)

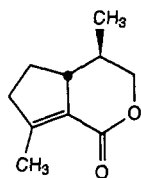
58 4 α ,7 α ,7 α -NEPETALACTONE



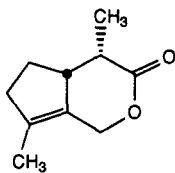
C₁₀H₁₄O₂ 166.22 mp 37-39° [α] -24.4° (CHCl₃) (100 MHz CDCl₃) 6.23 (H-3, m), 1.11 (H-10, d, 6), 1.71 (H-11, m); (CDCl₃) 169.9 (C-1), 135.7 (C-3), 120.4 (C-4), 37.3 (C-5), 26.1 (C-6), 30.0 (C-7), 32.1 (C-8), 49.0 (C-9), 17.6 (C-10), 14.3 (C-11). *Nepeta cataria* (Labiatae) (32)

59 4a β ,7 α ,7a β -NEPETALACTONE

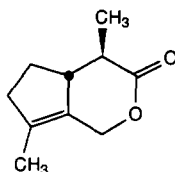
$C_{10}H_{14}O_2$ 166.22 bp 60° (0.1 mm) $[\alpha] +81.0^\circ$ (CHCl₃) (100 MHz CDCl₃) 6.18 (H-3, m), 0.99 (H-10, d, 7), 1.70 (H-11, m); (CDCl₃) 169.8 (C-1), 134.0 (C-3), 115.4 (C-4), 39.4 (C-5), 30.4 (C-6), 32.7 (C-7), 38.3 (C-8), 46.2 (C-9), 17.2 (C-10), 14.7 (C-11). *Nepeta cataria* (Labiatae) (32)

60 ISONEONEPETALACTONE

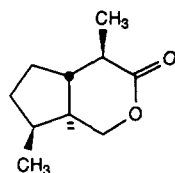
$C_{10}H_{14}O_2$ 166.22 $[\alpha] -66.2^\circ$ (CHCl₃) (100 MHz CDCl₃) 4.24 (H-3, dd, 11, 11), 3.89 (H-3, dd, 11, 5), 2.20 (H-10, t, 1), 0.94 (H-11, d, 7). *Actinidia polygama* (Actinidiaceae) (33)

61 DEHYDROIRIDOMYRMECIN

$C_{10}H_{14}O_2$ 166.22 $[\alpha] -105.6^\circ$ (CHCl₃) (100 MHz CDCl₃) 4.91 (H-1, bs), 1.73 (H-10, t, 1), 1.14 (H-11, d, 7). *Actinidia polygama* (Actinidiaceae) (34)

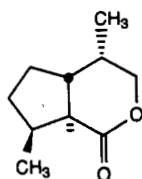
62 ISOEDEHYDROIRIDOMYRMECIN

$C_{10}H_{14}O_2$ 166.22 $[\alpha] -79.2^\circ$ (CHCl₃) (100 MHz CDCl₃) 4.96 (H-1, bs), 1.68 (H-10, t, 1), 1.27 (H-11, d, 7). *Actinidia polygama* (Actinidiaceae) (34)

63 ISOEPIIRIDOMYRMECIN

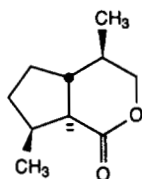
$C_{10}H_{16}O_2$ 168.24 $[\alpha] +6.17^\circ$ (CHCl₃) (100 MHz CDCl₃) 4.48 (H-1, dd, 11, 8), 4.21 (H-1, dd, 11, 5), 0.86 (H-10, d, 7), 1.31 (H-11, d, 7). *Actinidia polygama* (Actinidiaceae) (33)

64 DIHYDROEPINEPETALACTONE



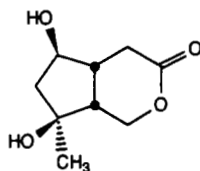
$C_{10}H_{16}O_2$ 168.24 $[\alpha] +31.3^\circ$ ($CHCl_3$) (100 MHz $CDCl_3$) 4.35 (H-3, dd, 11, 4), 4.02 (H-3, dd, 11, 3), 1.03 (H-10, d, 7), 1.00 (H-11, d, 7). *Actinidia polygama* (Actinidiaceae) (33)

65 ISODIHYDROEPINEPETALACTONE



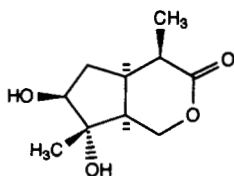
$C_{10}H_{16}O_2$ 168.24 $[\alpha] +90.3^\circ$ ($CHCl_3$) (100 MHz $CDCl_3$) 4.35 (H-3, dd, 11, 4), 3.81 (H-3, dd, 11, 3), 1.01 (H-10, H-11, d, 7, 6H). *Actinidia polygama* (Actinidiaceae) (33)

66 JIOGLUTOLIDE



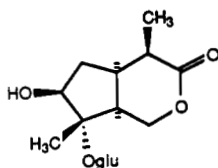
$C_9H_{14}O_4$ 186.21 mp 141–142° $[\alpha] -8.4^\circ$ (MeOH) (500 MHz CD_3OD) 4.29 (H-1, dd, 11.9, 5.5), 4.22 (H-1, dd, 11.9, 6.8), 2.71 (H-4, dd, 14.5, 7.2), 2.47 (H-4, dd, 14.5, 6.2), 2.66 (H-5, m), 3.82 (H-6, ddd, 5.4, 5.3, 4.0), 1.89 (H-7, dd, 13.3, 5.4), 1.85 (H-7, dd, 13.3, 5.3), 2.55 (H-9, m), 1.26 (H-10, s); (CD_3OD) 68.1 (C-1), 175.8 (C-3), 33.1 (C-4), 45.1 (C-5), 78.7 (C-6), 48.4 (C-7), 80.3 (C-8), 49.1 (C-9), 24.2 (C-10). *Rebmannia glutinosa* (Scrophulariaceae) (34)

67 VILLOSOL



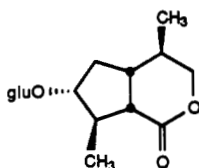
$C_{10}H_{16}O_4$ 200.23 mp 228–230° $[\alpha] +93.37^\circ$ (H_2O) (90 MHz ?) 4.60 (H-1, dd, 12.6, 1), 4.44 (H-1, dd, 12.6, 5.4), 3.0 (H-4, m), 2.9 (H-5, m), 1.7 (H-6, m), 3.8 (H-7, t, 5.4), 2.52 (H-9, ddd, 10.4, 5.4, 1), 1.36 (H-10, s), 1.10 (H-11, d, 7); (?) 69.0 (C-1), 183.6 (C-3), 47.5 (C-4), 39.4 (C-5)^a, 35.7 (C-6), 81.0 (C-7), 84.4 (C-8), 40.2 (C-9)^a, 24.1 (C-10), 14.7 (C-11). *Patrinia villosa* (Valerianaceae) (35)

68 VILLOSOLOSIDE



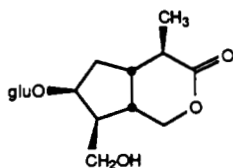
$C_{16}H_{26}O_9$ 362.38 mp 143–145° $[\alpha] +170.73^\circ$ (MeOH) (90 MHz ?) 4.68 (H-1, q), 4.25 (H-1, q), 2.9 (H-4, H-5, m), 1.6 (H-6, m), 4.00 (H-7, t, 5), 2.50 (H-9, m), 1.34 (H-10, s), 1.08 (H-11, d, 7), 3.80 (H-1', d, 9), 3.40 (H-2'–H-6', m, 6H); (?) 69.3 (C-1), 187.7 (C-3), 48.3 (C-4), 39.3 (C-5)*, 34.2 (C-6), 78.9 (C-7), 90.6 (C-8), 39.1 (C-9)*, 19.7 (C-10), 14.2 (C-11), 100.3 (C-1'), 76.2 (C-2'), 78.5 (C-3'), 72.8 (C-4'), 78.9 (C-5'), 63.8 (C-6'). *Patrinia villosa* (Valerianaceae) (35)

69 NEPETASIDE



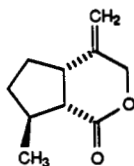
$C_{16}H_{26}O_8$ 346.38 mp 204–205° $[\alpha] -52.5^\circ$ (MeOH) (200 MHz CD_3OD) 4.20 (H-3, dd, 10.9, 3.4), 3.95 (H-3, dd, 10.9, 10), 1.20 (H-10, d, 6.6), 1.00 (H-11, d, 6.6), 4.30 (H-1', d, 7.6); (?) 177.2 (C-1), 74.3 (C-3), 36.1 (C-4), 41.1 (C-5), 37.0 (C-6), 84.8 (C-7), 48.7 (C-8), 44.5 (C-9), 18.5 (C-10), 15.8 (C-11), 102.7 (C-1'), 75.1 (C-2'), 78.0 (C-3'), 71.4 (C-4'), 78.1 (C-5'), 62.9 (C-6'). *Nepeta cataria* (Labiatae) (36)

70 GIBBOSIDE



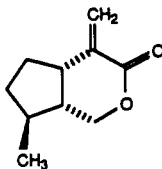
$C_{16}H_{26}O_9$ 362.38 $[\alpha] -22.1^\circ$ (MeOH) (200 MHz CD_3OD) 4.37 (H-7, t, 3.7, 3.7), 1.14 (H-11, d, 6.4); (CD_3OD) 71.0 (C-1), 179.2 (C-3), 39.9 (C-4), 41.2 (C-5), 42.3 (C-6), 84.7 (C-7), 51.4 (C-8), 40.5 (C-9), 61.6 (C-10), 14.4 (C-11), 105.1 (C-1'), 75.4 (C-2'), 77.9 (C-3'), 71.1 (C-4'), 78.2 (C-5'), 62.7 (C-6'). *Patrinia gibbosa* (Valerianaceae) (37)

71 DOLICHOLACTONE



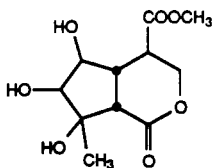
$C_{10}H_{14}O_2$ 166.22 $[\alpha] +31.7^\circ$ (C_6H_6) (? MHz CCl_4) 4.5 (H-3, s), 3.0 (H-5, m), 1.17 (H-10, d, 6.5), 4.95, 5.05 (H-11, m's). *Teucrium marum* (Labiatae) (38)

72 ALLODOLICHOLACTONE



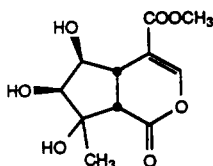
$C_{10}H_{14}O_2$ 166.22 $[\alpha] + 122.0^\circ$ (C_6H_6) uv 238 (MeOH) (? MHz CCl_4) 4.1 (H-1, m), 1.12 (H-10, d, 6.5), 5.90, 5.38 (H-11, t's, 1.5). *Teucrium marum* (Labiatae) (38)

73 LATIFONIN



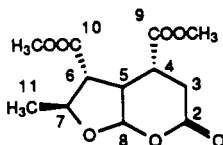
$C_{11}H_{16}O_7$ 260.24 mp 157–159° $[\alpha] + 7.2^\circ$ (MeOH) uv 210 (MeOH) (60 MHz CD_3OD) 4.45 (H-3, m), 4.27 (H-6, q, 4), 3.56 (H-7, d, 4), 1.48 (H-10, s), 3.72 (COOMe). *Posoqueria latifolia* (Rubiaceae) (39)

74 POSOQUENIN



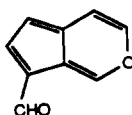
$C_{11}H_{14}O_7$ 258.23 mp 150–151° $[\alpha] - 7.4^\circ$ (MeOH) uv 248 (MeOH) (60 MHz CD_3OD) 7.31 (H-3, s), 3.02 (H-5, d, 4)^a, 3.99 (H-6, d, 6), 3.83 (H-7, d, 6), 3.31 (H-9, d, 4)^a, 1.54 (H-10, s), 3.65 (COOMe). *Posoqueria latifolia* (Rubiaceae) (39)

75 STRYSPINOLACTONE



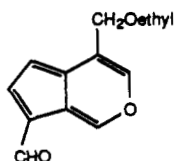
$C_{12}H_{16}O_7$ 272.26 mp 108–110° (220 MHz $CDCl_3$) 2.70 (H-3, dd, 17, 7), 2.60 (H-3, dd, 17, 8), 3.10 (H-4, dddd, 8, 7, 7, 3), 2.80 (H-5, ddd, 7, 1.5, 1), 2.75 (H-6, ddd, 3, 1, 0.5), 4.40 (H-7, dq, 6, 0.5), 5.86 (H-8, d, 1.5), 1.28 (H-11, d, 6), 3.78, 3.70 (COOMe); ($CDCl_3$) 170.7 (C-2)^a, 35.4 (C-3), 45.7 (C-4), 30.3 (C-5), 49.5 (C-6), 67.1 (C-7), 96.9 (C-8), 169.6 (C-9)^a, 169.2 (C-10)^a, 21.3 (C-11), 52.8, 52.0 (OMe). *Strychnos spinosa* (Loganiaceae) (40)

76 NORVIBURTINAL



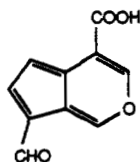
$C_9H_6O_2$ 146.15 uv 424, 293, 242, 228 (MeOH) (220 MHz $CDCl_3$) 9.19 (H-1, s), 7.85 (H-3, d, 3.5), 6.55 (H-4, d, 3.5), 7.30 (H-6, d, 6), 7.77 (H-7, d, 6), 9.89 (H-10, s). *Kigelia pinnata* (Bignoniaceae) (41)

77 11-ETHOXYVIBURTINAL



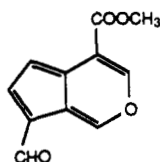
$C_{12}H_{12}O_3$ 204.23 mp 95–98° uv 427, 283, 244, 228 (EtOH) (? MHz $CDCl_3$) 9.20 (H-1, s), 7.87 (H-3, s), 6.60 (H-6, dd), 7.83 (H-7, d), 9.93 (H-10, s), 4.68 (H-11, s), 3.64 (OCH_2Me , q), 1.28 (OCH_2Me , t). *Centranthus ruber* (Labiatae) (42)

78 CERBERINIC ACID



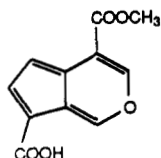
$C_{10}H_6O_4$ 190.16 uv 433, 310, 293, 250 (MeOH) (? MHz $CDCl_3$) 8.48 (H-1, s), 9.20 (H-3, s), 7.20 (H-6, d, 4), 8.00 (H-7, d, 4), 9.78 (H-10, s). *Cerbera manghas* (Apocynaceae) (43)

79 CERBINAL



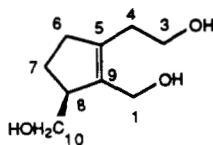
$C_{11}H_8O_4$ 204.18 mp 188–189° uv 428, 326, 288, 277, 249 (MeOH) (90 MHz $CDCl_3$) 8.51 (H-1, s), 7.94 (H-3, d, 3.2), 7.13 (H-6, dd, 3.2, 1.0), 9.14 (H-7, d, 1), 9.94 (H-10, s), 4.00 ($COOMe$); ($CDCl_3$) 148.1 (C-1), 149.7 (C-3), 115 (C-4), 125.1 (C-5), 113.4 (C-6), 147.8 (C-7), 130.2 (C-8), 124.4 (C-9), 184.9 (C-10), 164.6 (C-11), 52.4 (OMe). *Cerbera manghas* (Apocynaceae), *Gardenia jasminoides* (Rubiaceae) (43,44)

80 CERBERIC ACID



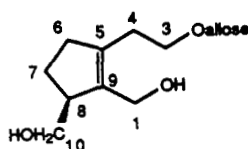
$C_{11}H_8O_5$ 220.18 mp 213–223° (dec) uv 425, 330, 282, 272, 260, 238 (MeOH) (? MHz $CDCl_3$) 8.42 (H-1, s), 9.23 (H-3, s), 7.22 (H-6, d, 4), 8.24 (H-7, d, 4), 3.84 ($COOMe$). *Cerbera manghas* (Apocynaceae) (43)

81 CERBERIDOL



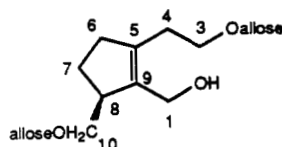
$C_{15}H_{24}O_5$ 172.22 $[\alpha] + 11.0^\circ$ (MeOH) (400 MHz pyridine- d_5) 4.64, 4.44 (H-1, d's, 12), 3.89 (H-3, t, 7), 2.54–2.68 (H-4, m), 2.50 (H-6, m), 2.38 (H-6, ddd, 15, 7, 6), 2.01, 1.79 (H-7, m's), 3.22 (H-8, m), 3.99 (H-10, d, 6); (pyridine- d_5) 57.5 (C-1), 60.4 (C-3), 33.0 (C-4), 138.8 (C-5)^a, 35.2 (C-6), 26.3 (C-7), 51.5 (C-8), 139.6 (C-9)^a, 65.6 (C-10). *Cerbera manghas* (Apocynaceae) (45)

82 3-O-ALLOSYL CERBERIDOL



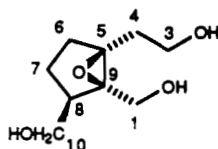
$C_{15}H_{26}O_8$ 334.37 $[\alpha] -18.1^\circ$ (MeOH) (400 MHz pyridine- d_5) 4.55, 4.42 (H-1, d's, 13), 3.92 (H-3, t, 6), 2.50–2.62 (H-4, m), 2.42, 2.28 (H-6, m's), 1.97, 1.76 (H-7, m's), 3.21 (H-8, m), 3.92 (H-10, d, 5), 5.30 (H-1', d, 8), 3.92 (H-2', dd, 8, 3), 4.67 (H-3', t, 3), 4.17 (H-4', dd, 10, 3), 4.45 (H-6', dd, 11, 2), 4.32 (H-6', dd, 11, 5); (pyridine- d_5) 57.4 (C-1), 67.8 (C-3), 29.7 (C-4), 137.8 (C-5)^a, 35.1 (C-6), 26.3 (C-7), 51.0 (C-8), 139.5 (C-9)^a, 65.4 (C-10), 101.9 (C-1'), 72.4 (C-2'), 72.9 (C-3'), 69.0 (C-4'), 75.9 (C-5'), 63.0 (C-6'). *Cerbera manghas* (Apocynaceae) (45)

83 3,10-BIS-O-ALLOSYL CERBERIDOL



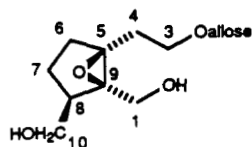
$C_{21}H_{36}O_{13}$ 496.51 $[\alpha] -25.7^\circ$ (MeOH) (400 MHz pyridine- d_5) 4.47 (H-1, bs), 2.64 (H-4, dt, 14, 7), 2.20–2.30 (H-4, H-6, m), 2.45 (H-6, m), 1.92, 1.67 (H-7, m's), 3.35 (H-8, m), 5.28 (H-1', d, 8), 3.91 (H-2', dd, 8, 3), 4.66 (H-3', t, 3), 5.24 (H-1'', d, 8), 3.93 (H-2'', dd, 8, 3), 4.67 (H-3'', t, 3); (pyridine- d_5) 57.1 (C-1), 67.9 (C-3), 29.6 (C-4), 137.7 (C-5)^a, 34.8 (C-6), 26.5 (C-7), 47.7 (C-8), 139.6 (C-9)^a, 73.4 (C-10), 102.1 (C-1'), 102.3 (C-1''), 72.4 (C-2'), 72.8 (C-2''), 72.8 (C-3'), 72.9 (C-3''), 69.0 (C-4'), 75.9 (C-5'), 62.9 (C-6'), 62.9 (C-6''). *Cerbera manghas* (Apocynaceae) (45)

84 EPOXY CERBERIDOL



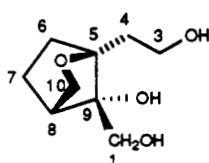
$C_9H_{16}O_4$ 188.22 $[\alpha] -0.40^\circ$ (MeOH) (400 MHz pyridine- d_5) 4.53, 4.18 (H-1, d's, 13), 4.00–4.04 (H-3, m), 2.10–2.30 (H-4, m), 2.10–2.30 (H-6, m), 1.98 (H-6, dd, 13, 8), 1.80 (H-7, m), 1.67 (H-7, dd, 13, 9), 2.91 (H-8, m), 4.16, 4.05 (H-10, dd's, 11, 5); (pyridine- d_5) 61.8 (C-1), 58.8 (C-3), 34.1 (C-4), 69.5 (C-5)^a, 30.1 (C-6), 23.8 (C-7), 44.4 (C-8), 72.2 (C-9)^a, 63.5 (C-10). *Cerbera manghas* (Apocynaceae) (45)

85 3-O-ALLOSYLEPOXY CERBERIDOL



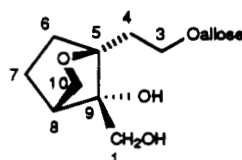
$C_{15}H_{26}O_9$ 350.37 $[\alpha] -33.5^\circ$ (MeOH) (400 MHz pyridine- d_5) 4.47, 4.06 (H-1, d's, 12), 2.19 (H-4, bt, 7), 2.12 (H-6, dt, 13, 9), 1.92 (H-6, dd, 13, 8), 1.60–1.75 (H-7, m), 2.89 (H-8, q, 7), 4.00–4.10 (H-10, m), 5.26 (H-1', d, 8), 3.91 (H-2', dd, 8, 3), 4.67 (H-3', t, 3), 4.16 (H-4', dd, 10, 3); (pyridine- d_5) 61.6 (C-1), 66.5 (C-3), 31.3 (C-4), 69.3 (C-5)^a, 30.1 (C-6), 23.3 (C-7), 44.6 (C-8), 72.4 (C-9)^a, 63.0 (C-10), 102.0 (C-1'), 72.3 (C-2'), 72.9 (C-3'), 69.0 (C-4'), 75.9 (C-5'), 63.0 (C-6'). *Cerbera manghas* (Apocynaceae) (45)

86 CYCLOCERBERIDOL



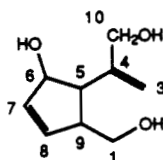
$C_9H_{16}O_4$ 188.22 $[\alpha] -16.9^\circ$ (MeOH) (400 MHz pyridine- d_5) 4.36, 4.32 (H-1, d's, 12), 4.02–4.15 (H-3, m), 2.32–2.39 (H-4, m), 2.17 (H-4, dt, 14, 6), 2.32–2.39 (H-6, m), 1.51 (H-6, ddd, 12, 10, 4), 2.47 (H-7, td, 12, 3), 1.84 (H-7, ddd, 12, 9, 4), 2.50 (H-8, bs), 4.11 (H-10, dt, 7, 3), 3.64 (H-10, d, 7); (pyridine- d_5) 62.5 (C-1), 59.0 (C-3), 33.8 (C-4), 85.9 (C-5), 27.2 (C-6), 33.7 (C-7), 43.5 (C-8), 83.5 (C-9), 71.7 (C-10). *Cerbera manghas* (Apocynaceae) (45)

87 3-O-ALLOSYLCYCLOCERBERIDOL

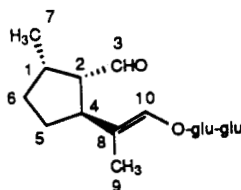


$C_{15}H_{26}O_9$ 350.37 $[\alpha] -26.6^\circ$ (MeOH) (400 MHz pyridine- d_5) 4.27 (H-1, s), 2.27–2.38 (H-4, m), 2.21 (H-4, ddd, 14, 7, 6), 2.27–2.38 (H-6, m), 1.45 (H-6, m), 2.27–2.38 (H-7, m), 1.79 (H-7, m), 2.44 (H-8, bs), 4.05 (H-10, dt, 7, 3), 3.58 (H-10, d, 7), 5.29 (H-1', d, 8), 3.91 (H-2', dd, 8, 3), 4.68 (H-3', t, 3), 4.19 (H-4', dd, 10, 3), 4.44 (H-6', dd, 11, 2), 4.31 (H-6', dd, 11, 4); (pyridine- d_5) 62.3 (C-1), 66.4 (C-3), 30.8 (C-4), 85.1 (C-5), 27.1 (C-6), 33.9 (C-7), 43.4 (C-8), 83.8 (C-9), 71.4 (C-10), 101.8 (C-1'), 72.4 (C-2'), 72.8 (C-3'), 68.9 (C-4'), 75.8 (C-5'), 62.9 (C-6'). *Cerbera manghas* (Apocynaceae) (45)

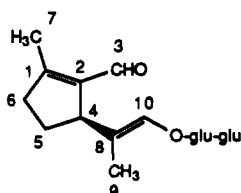
88 MENTZETRIOL



$C_9H_{14}O_3$ 170.21 $[\alpha] -345^\circ$ (270 MHz, ?) 3.46 (H-1, 11), 3.38 (11), 5.27 (H-3, bs), 5.15 (bs), 2.69 (H-5, t, 7.5), 5.12 (H-6, dd, 8, 1.5), 5.92 (H-7, H-8, m), 3.02 (H-9, m), 4.07 (H-10, m); (?) 65.8 (C-1), 111.1 (C-3), 154.4 (C-4), 48.7 (C-5), 78.5 (C-6), 135.6 (C-7), 135.0 (C-8), 53.1 (C-9), 63.0 (C-10). *Mentzelia* spp. (Loasaceae) (46)

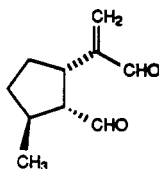
89 IRIDODIALO- β -D-GENTIOBIOSIDE

$C_{22}H_{36}O_{12}$ 492.52 mp 192° $[\alpha] -6.5^\circ$ (MeOH) (100 MHz D_2O) 9.60 (H-3, d, 3), 0.98 (H-7, d, 7), 1.54 (H-9, s), 6.20 (H-10, s); (D_2O) 38.4 (C-1), 59.2 (C-2), 212.6 (C-3), 43.6 (C-4), 35.7 (C-5), 30.9 (C-6), 17.1 (C-7), 119.6 (C-8), 10.8 (C-9), 139.4 (C-10), 104.6 (C-1'), 73.9 (C-2'), 70.4 (C-3'), 71.9 (C-4'), 76.7 (C-5'), 69.2 (C-6'), 103.1 (C-1''), 73.5 (C-2''), 76.6 (C-3''), 70.4 (C-4''), 76.7 (C-5''), 67.4 (C-6''). *Actinidia polygama* (Actinidiaceae) (47)

90 DEHYDROIRIDODIALO- β -D-GENTIOBIOSIDE

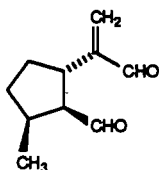
$C_{22}H_{34}O_{12}$ 490.28 mp 126–127° $[\alpha] -23.4^\circ$ (MeOH) uv 250 (EtOH) (100 MHz D_2O) 9.80 (H-3, s), 2.20 (H-7, s), 1.40 (H-9, s), 6.18 (H-10, s); (D_2O) 173.3 (C-1), 138.2 (C-2), 192.9 (C-3), 48.0 (C-4), 40.7 (C-5)^a, 29.1 (C-6), 15.5 (C-7), 120.2 (C-8), 11.9 (C-9), 139.3 (C-10), 104.6 (C-1'), 74.0 (C-2'), 70.5 (C-3'), 71.9 (C-4'), 76.7 (C-5'), 69.4 (C-6'), 103.2 (C-1''), 73.5 (C-2''), 76.5 (C-3''), 70.5 (C-4''), 76.7 (C-5''), 67.4 (C-6''). *Actinidia polygama* (Actinidiaceae) (47)

91 DOLICHODIAL



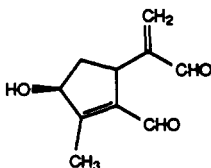
$C_{10}H_{14}O_2$ 166.22 $[\alpha] -72.0^\circ$ (C_6H_6) uv 223 (H_2O) (60 MHz $CDCl_3$) 9.38 (H-1, d, 2.5), 9.51 (H-3, s), 3.3 (H-5, m), 1.08 (H-10, d, 6.5), 6.28 (H-11, d, 1.4), 6.12 (H-11, s). *Teucrium marum* (Labiatae) (38)

92 ISODOLICHODIAL



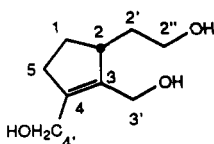
$C_{10}H_{14}O_2$ 166.22 $[\alpha] +3.5^\circ$ (C_6H_6) uv 223 (H_2O) (60 MHz $CDCl_3$) 9.76 (H-1, d, 2.6), 9.52 (H-3, s), 3.4 (H-8, m), 1.07 (H-10, d, 6.5), 6.3, 6.0 (H-11, s). *Teucrium marum* (Labiatae) (38)

93 8,9-DIDEHYDRO-7-HYDROXYDOLICHODIAL



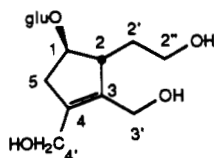
$C_{10}H_{12}O_3$ 180.20 mp 59–62° $[\alpha] -108.2^\circ$ (EtOH) uv 252, 223 (EtOH) (? MHz $CDCl_3$) 10.00 (H-1, s), 9.54 (H-3, s), 4.04 (H-5, m), 2.03–2.11 (H-6, m), 4.89 (H-7, m), 2.26 (H-10, m), 6.01, 5.94 (H-11, s), 2.42 (C-7 hydroxyl proton); ($CDCl_3$) 193.9 (C-1), 188.3 (C-3), 137.4 (C-4), 39.7 (C-5), 39.4 (C-6), 79.4 (C-7), 164.2 (C-8), 150.6 (C-9), 11.5 (C-10), 133.5 (C-11). *Centranthus ruber* (Labiatae) (42)

94 1-DEOXYEUCOMMIOL



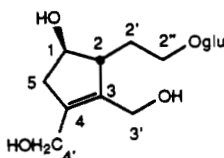
$C_9H_{16}O_3$ 172.22 $[\alpha] -15.4^\circ$ (MeOH) (400 MHz CD_3OD) 2.05 (H-1, m), 1.53 (H-1, m), 2.90 (H-2, bm), 1.96 (H-2', m), 1.40 (H-2', m), 3.61 (H-2'', m), 4.25 (H-3', d, 12.5), 4.08 (H-3', d, 12.5), 4.17 (H-4', q), 2.44 (H-5); (Me_2CO-d_6) 30.0 (C-1), 45.5 (C-2), 34.7 (C-2'), 62.0 (C-2''), 140.2 (C-3), 57.9 (C-3'), 142.0 (C-4), 59.8 (C-4'), 38.1 (C-5). *Eucommia ulmoides* (Eucommiaceae) (48)

95 EUCOMMIOSE II



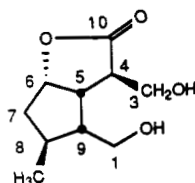
$C_{15}H_{26}O_9$ 350.37 $[\alpha] -38.6$ (H₂O) uv 208 (EtOH) (80 MHz D_2O) 4.40 (H-1, m), 3.00 (H-2, bd), 2.88 (H-5, bdd, 18.0), 2.50 (H-5, bd, 18.0), 4.55 (H-1'', d, 7.5), 2.3-1.2 (H-2', m, 2H), 4.24 (H-3', H-4', bs, 4H), 3.72 (H-2'', t, 7.0); (D_2O) 83.5 (C-1), 51.0 (C-2), 137.0 (C-3), 139.2 (C-4), 40.1 (C-5), 102.3 (C-1''), 73.9 (C-2''), 76.8 (C-3''), 70.4 (C-4''), 76.8 (C-5''), 61.6 (C-6''), 33.0 (C-2'), 56.2 (C-3'), 57.8 (C-4'), 60.7 (C-2''). *Aucuba japonica* (Cornaceae) (49)

96 EUCOMMIOSE I



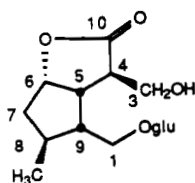
$C_{15}H_{26}O_9$ 350.37 oil uv 208 (?) (90 MHz D_2O) 4.24 (H-1, bs), 2.82 (H-2, m), 2.90 (H-5, bdd, 18.0), 2.32 (H-5, bd, 18.0), 2.2-1.2 (H-2', cm, 2H), 4.24 (H-3', H-4', bs, 4H), 4.50 (H-1'', d, 7.5), 3.9-3.6 (H-2''); (D_2O) 75.2 (C-1), 53.0 (C-2), 137.3 (C-3), 138.9 (C-4), 42.2 (C-5), 30.7 (C-2'), 56.3 (C-3'), 57.9 (C-4'), 69.5 (C-2''), 103.1 (C-1''), 74.0 (C-2''), 76.7 (C-3''), 70.5 (C-4''), 76.7 (C-5''), 61.6 (C-6''). *Eucommia ulmoides* (Eucommiaceae) (50)

97 GELSEMIOL



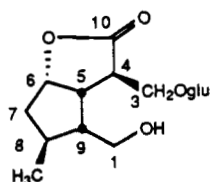
$C_{10}H_{16}O_4$ 200.23 mp 91-93° $[\alpha] +13^\circ$ (MeOH) (400 MHz D_2O) 3.84 (H-1, dd, 11.5, 4.5), 3.59 (H-1, dd, 11.5, 9.5), 3.94 (H-3, dd, 11.5, 4.5), 3.82 (H-3, dd, 11.5, 4), 2.95 (H-4, brq, ~4.5), 3.11 (H-5, dt, 8.0, 5.5), 5.09 (H-6, dd, 8, 6), 2.12 (H-7 α , dd, 14.5, 6), 1.55 (H-7 β , ddd, 14.5, 12, 6.5), 1.75 (H-8, dtq, 12, 6, 6), 1.86 (H-9, dddd, 12, 9, 8, 4.5), 1.00 (H-10, d, 6.1); (?) 62.6 (C-1), 61.2 (C-3), 51.1 (C-4), 44.7 (C-5), 86.4 (C-6), 41.9 (C-7), 33.5 (C-8), 44.7 (C-9), 17.4 (C-10), 183.1 (C-11). *Gelsemium sempervirens* (Loganiaceae) (51)

98 GELSEMIOL 1-GLUCOSIDE



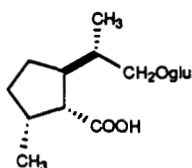
$C_{16}H_{26}O_9$ 362.38 (270 MHz D_2O) 4.24 (H-1, dd, 10, 4), 3.02 (H-4, brq, 6.5), 5.16 (H-6, t, 7), 1.08 (H-10, d, 6.2), 4.48 (H-1', d, 8); (D_2O) 70.5 (C-1), 61.0 (C-3), 51.0 (C-4), 44.8 (C-5), 86.5 (C-6), 41.6 (C-7), 33.3 (C-8), 42.9 (C-9), 17.2 (C-10), 182.6 (C-11), 103.4 (C-1'), 73.7 (C-2'), 76.3 (C-3'), 70.4 (C-4'), 76.7 (C-5'), 61.5 (C-6'). *Gelsemium sempervirens* (Loganiaceae) (51)

99 GELSEMIOL 3-GLUCOSIDE



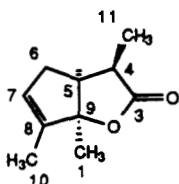
$C_{16}H_{26}O_9$ 362.38 (270 MHz D_2O) 4.20 (H-3, dd, 10.2, 3.9), 3.14 (H-4, brt, 6.7), 5.19 (H-6, t, 7), 1.07 (H-10, d, 6), 4.50 (H-1', d, 8); (D_2O) 62.2 (C-1), 69.6 (C-3), 49.0 (C-4), 44.8 (C-5), 86.5 (C-6), 41.6 (C-7), 33.3 (C-8), 44.4 (C-9), 17.2 (C-10), 182.6 (C-11), 103.2 (C-1'), 73.9 (C-2'), 76.7 (C-3'), 70.4 (C-4'), 76.7 (C-5'), 61.5 (C-6'). *Gelsemium sempervirens* (Loganiaceae) (51)

100 NEPETARIASIDE



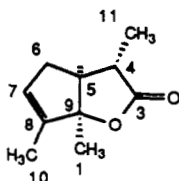
$C_{16}H_{28}O_8$ 348.39 mp 139–141° (dec) $[\alpha] -14.0^\circ$ (MeOH) (100 MHz CD_3OD) 4.22 (H-3, d, 8.0), 0.92 (H-10, d, 7.0), 0.97 (H-11, d, 7.0); (CD_3OD) 179.3 (C-1), 75.2 (C-3), 38.6 (C-4), 45.7 (C-5), 29.4 (C-6), 35.2 (C-7), 38.6 (C-8), 53.2 (C-9), 16.7 (C-10), 14.7 (C-11), 104.4 (C-1'), 75.1 (C-2'), 77.8 (C-3'), 71.6 (C-4'), 77.9 (C-5'), 62.7 (C-6'). *Nepeta cataria* (Labiatae) (52)

101 ACTINIDIALACTONE



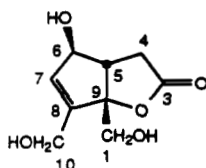
$C_{10}H_{14}O_2$ 166.22 $[\alpha] -18.3^\circ$ ($CHCl_3$) (100 MHz $CDCl_3$) 1.47 (H-1, s), 5.56 (H-7, bs), 1.75 (H-10, t, 1), 1.23 (H-11, d, 7). *Actinidia polygama* (Actinidiaceae) (33)

102 ISOACTINIDIALACTONE



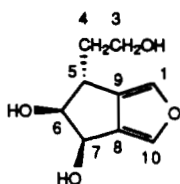
$C_{10}H_{14}O_2$ 166.22 $[\alpha] -13.9^\circ$ ($CHCl_3$) (100 MHz $CDCl_3$) 1.46 (H-1, s), 5.41 (H-7, bs), 1.73 (H-10, t, 1), 1.29 (H-11, d, 7). *Actinidia polygama* (Actinidiaceae) (33)

103 REHMA GLUTIN C



$C_9H_{12}O_3$ 200.19 $[\alpha] -51.4^\circ$ (MeOH) (triacetate 500 MHz $CDCl_3$) 4.25, 4.47 (H-1, d's, 11.9), 2.65 (H-4 α , dd, 18.6, 5.2), 3.05 (H-4 β , dd, 18.6, 11.3), 2.86 (H-5, ddd, 11.3, 5.2, 1.8), 5.35 (H-6, bs), 6.07 (H-7, dd, 4.0, 1.5), 4.76, 4.80 (H-10, 13.4, 1.5); (Me_2CO-d_6) 59.0 (C-1), 177.0 (C-3), 35.4 (C-4), 50.5 (C-5), 81.0 (C-6), 134.7 (C-7), 147.4 (C-8), 99.6 (C-9), 65.8 (C-10). *Rehmannia glutinosa* (Scrophulariaceae) (53)

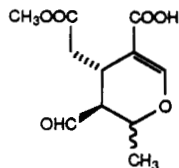
104 JIOFURAN



$C_9H_{12}O_4$ 184.19 $[\alpha] -30.4^\circ$ (MeOH) (200 MHz CD_3OD) 7.23 (H-1, s)^a, 3.80 (H-3, m, 2H), 1.76, 2.02 (H-5, m's), 2.97 (H-5, m), 3.90 (H-6, dd, 7.6, 4.8), 4.76 (H-7, d, 4.8), 7.40 (H-10, s)^a; (CD_3OD) 135.6 (C-1), 62.1 (C-3), 36.5 (C-4), 41.4 (C-5), 68.1 (C-6), 85.6 (C-7), 131.1 (C-8), 132.3 (C-9), 137.4 (C-10). *Rehmannia glutinosa* (Scrophulariaceae) (34)

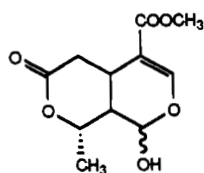
Group 9 (simple secoiridoids)

105 METHYL SYRAMURALDEHYDATE



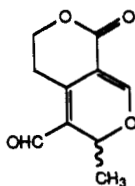
$C_{11}H_{14}O_6$ 242.23 $[\alpha] -87.4$ (EtOH) uv 238 (EtOH) (90 MHz, ?) 9.65 (H-1, d, 1.5), 7.64 (H-3, s), 3.39 (H-5, dd, 11, 4), 2.98 (H-6, dd, 16, 4), 2.30 (H-6, dd, 16, 11), 4.21 (H-8, qd, 7, 2), 2.67 (H-9, m), 1.60 (H-10, d, 7), 3.76 (OMe), 8.4 (COOH, br); (?) 199.1 (C-1), 156.8 (C-3), 106.7 (C-4), 28.2 (C-5), 38.5 (C-6), 175.7 (C-7), 69.7 (C-8), 51.2 (C-9), 17.8 (C-10), 167.1 (C-11), 51.4 (OMe). *Syringa amurensis* (Oleaceae) (54)

106 KINGISIDE AGLYCONE (isolated in 3:7 α/β ratio)



$C_{11}H_{14}O_6$ 242.23 $[\alpha] +137^\circ$ (MeOH) uv 242 (EtOH) (100 MHz $CDCl_3$) 5.36 (H-1 α , d, 9), 5.88 (H-1 β , d, 2), 7.52 (H-3, d, 1), 4.92 (H-8, dq, 7, 2), 2.12 (H-9, m), 1.58 (H-10, d, 7), 3.84 (COOMe); ($CDCl_3$) 91.1 (C-1), 151.9 (C-3), 109.2 (C-4), 25.1 (C-5), 32.9 (C-6), 172.2 (C-7)^a, 75.2 (C-8), 35.6 (C-9), 17.7 (C-10), 167.1 (C-11)^a, 51.3 (OMe). *Strychnos spinosa* (Loganiaceae) (55)

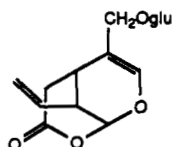
107 GENTIOGENAL (Gentiopical)



$C_{10}H_{10}O_4$ 194.19 X-ray data available mp 138–142^o $[\alpha] 0^\circ$ (MeOH) uv 370, 309, 288, 269, 225 (MeOH), 353, 269 ($CHCl_3$) (90 MHz $CDCl_3$) 9.88 (H-1, s), 7.95 (H-3, s), 3.11–3.09 (H-6, t, 4.9), 4.44–4.43 (H-7, t, 4.9), 5.64 (H-8, q, 6.5), 1.39 (H-10, d, 6.5); ($CDCl_3$) 185.7 (C-1), 163.3 (C-3), 103.9 (C-4), 142.7 (C-5), 22.6 (C-6), 65.1 (C-7), 73.1 (C-8), 120.2 (C-9), 19.8 (C-10), 163.9 (C-11); (CD_3OD) 188.2 (C-1), 164.3 (C-3), 105.7 (C-4),

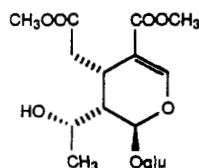
144.7 (C-5), 23.7 (C-6), 66.9 (C-7), 74.4 (C-8), 121.7 (C-9), 19.9 (C-10), 166.3 (C-11). Enzymatic hydrolysis of gentiopicroside, prepared from gentiopicrotin (56,57)

108 ISOSWEROSE



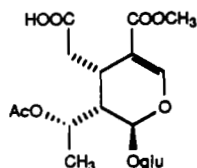
$C_{16}H_{22}O_9$ 358.34 $[\alpha] +52.8^\circ$ (MeOH) uv 204 (MeOH) (300 MHz CD_3OD) 5.86 (H-1, t, 1.6), 6.48 (H-3, s), 2.7 (H-5, H-6, m), 6.0 (H-8, ddd, 17.3, 11, 6.1), 2.8 (H-9, m), 5.4 (H-10 trans, ddd, 17.3, 1.5, 1.1), 5.39 (H-10 cis, ddd, 11, 1.5, 1.1), 4.13, 4.32 (H-11, -11.8), 4.27 (H-1', d, 7.7), 3.1-3.4 (H-2'-H-5', m), 3.88 (H-6', -11.7); (CD_3OD) 98.5 (C-1), 139.3 (C-3), 117.4 (C-4), 29.4 (C-5), 33.0 (C-6), 171.4 (C-7), 134.3 (C-8), 38.9 (C-9), 119.7 (C-10), 69.8 (C-11), 103.6 (C-1'), 75.1 (C-2'), 78.0 (C-3'), 71.7 (C-4'), 78.1 (C-5'), 62.9 (C-6'). *Sambucus ebulus* (Caprifoliaceae) (58)

109 ALPIGENOSIDE



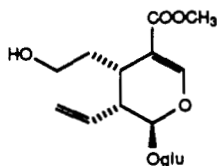
$C_{18}H_{28}O_{12}$ 436.41 uv 235 (MeOH) (270 MHz CD_3OD) 7.35 (H-3, s), 2.60 (H-6, 16), 1.50 (H-10, d, 7), 3.65, 3.60 (OMe); (pentaacetate 270 MHz $CDCl_3$) 5.60 (H-1, d), 3.30 (H-5, m), 3.78 (H-8, m), 2.16 (H-9, m). *Lonicera alpigena* (Caprifoliaceae) (59)

110 DIDERROSIDE



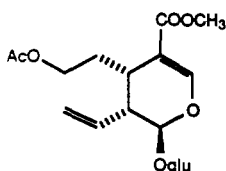
$C_{19}H_{28}O_{13}$ 464.42 $[\alpha] -34.6^\circ$ (MeOH) uv 234 (MeOH) (300 MHz D_2O) 5.8 (H-1, d, 8), 7.55 (H-3, s), 3.3-4.08 (H-5, m), 2.33 (H-6, d, 7), 5.25 (H-8, m), 2.2 (H-9, m), 1.4 (H-10, d, 7), 3.71 (OMe), 2.07 (OAc), 4.8 (H-1', d, 8), 3.3-4.08 (H-2'-H-6', m); (D_2O) 97.2 (C-1), 154.2 (C-3), 110.4 (C-4), 29.6 (C-5), 36.4 (C-6), 70.5 (C-8), 43.6 (C-9), 19.1 (C-10), 169.6 (C-11), 52.6 (OMe), 21.8 (O=CMe), 174.0 (O=CMe), 99.7 (C-1'), 73.7 (C-2'), 76.7 (C-3'), 70.8 (C-4'), 77.2 (C-5'), 61.9 (C-6'). *Nauclea diderrichii* (Rubiaceae) (60)

111 SECOLOGANOL



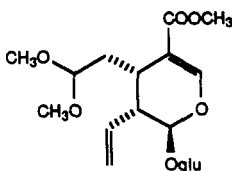
$C_{17}H_{26}O_{10}$ 390.39 uv 235 (MeOH) (300 MHz CD_3OD) 5.52 (H-1, d, 6.5), 7.43 (H-3, s), 2.85 (H-5, bdd, 13, 6), 1.88 (H-6, dt, 16, 6), 1.69 (H-6, ddd, 16, 13, 6), 3.55 (H-7, m), 5.77 (H-8, ddd, 17, 10, 8.5), 2.63 (H-9, ddd, 8.5, 6.5, 6), 5.28 (H-10, dd, 17, 1.5), 5.23 (H-10, dd, 10, 1.5), 3.68 (OMe), 4.62 (H-1', d, 8), 3.89-3.20 (H-2'-H-6'); (CD_3OD) 97.8 (C-1), 153.5 (C-3), 111.8 (C-4), 30.9 (C-5), 33.6 (C-6), 61.3 (C-7), 135.8 (C-8), 45.4 (C-9), 119.5 (C-10), 169.5 (C-11), 51.7 (OMe), 100.3 (C-1'), 74.7 (C-2'), 78.0 (C-3'), 71.6 (C-4'), 78.4 (C-5'), 62.8 (C-6'). *Gentiana verna* (Gentianaceae) (61)

112 7-O-ACETYLSECOLOGANOL



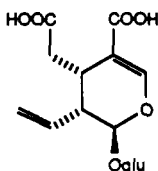
$C_{19}H_{28}O_{11}$ 432.42 uv 235 (MeOH) (300 MHz CD_3OD) 5.52 (H-1, d, 6.5), 7.44 (H-3, s), 2.85 (H-5, bdd, 12.5, 6), 1.93 (H-6, dt, 16, 6), 1.81 (H-6, ddd, 16, 12.5, 6), 4.08 (H-7, m), 5.77 (H-8, ddd, 17, 10, 8.5), 2.66 (H-9, ddd, 8.5, 6.5, 6), 5.30 (H-10, dd, 17, 1.5), 5.25 (H-10, dd, 10, 1.5), 3.68 (OMe), 2.01 (OAc), 4.69 (H-1', d, 8), 3.90–3.19 (H-2'–H-6'); (CD_3OD) 97.8 (C-1), 153.6 (C-3), 111.5 (C-4), 30.0 (C-5), 31.4 (C-6), 64.2 (C-7), 135.6 (C-8), 45.4 (C-9), 119.5 (C-10), 169.2 (C-11), 51.7 (OMe), 100.2 (C-1'), 74.7 (C-2'), 78.1 (C-3'), 71.6 (C-4'), 78.4 (C-5'), 62.8 (C-6'), 20.8 (O=CMe), 172.9 (O=CMe). *Gentiana verna* (Gentianaceae) (61)

113 SECOLOGANIN DIMETHYL ACETAL



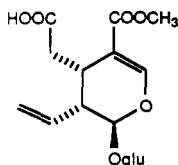
$C_{19}H_{30}O_{11}$ 434.44 $[\alpha] -108.1^\circ$ (MeOH) (90 MHz pyridine- d_5) 5.65 (H-1, d, 4.8), 7.46 (H-3, s), 3.07 (7-OMe), 3.38 (11-OMe); (pyridine- d_5) 97.3 (C-1), 152.4 (C-3), 110.9 (C-4), 28.8 (C-5), 32.6 (C-6), 100.6 (C-7), 135.1 (C-8), 44.5 (C-9), 119.1 (C-10), 167.4 (C-11), 51.0, 52.0, 53.0 (OMe), 103.4 (C-1'), 74.6 (C-2'), 78.4 (C-3'), 71.5 (C-4'), 78.8 (C-5'), 62.6 (C-6'). *Lonicera japonica* (Caprifoliaceae) (62)

114 SECOLOGANOSIDE



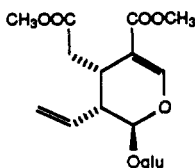
$C_{16}H_{22}O_{11}$ 390.34 $[\alpha] -103.5^\circ$ (H_2O) uv 230 (MeOH) (300 MHz D_2O) 5.46 (H-1, d, 4.5), 7.28 (H-3, d, 1.6), 3.17 (H-5, m), 2.27 (H-6 α , dd, 16.0, 9.5), 2.75 (H-6 β , dd, 16.0, 4.9), 5.69 (H-8, ddd, 17.0, 10.0, 9.6), 2.79 (H-9, ddd, 9.6, 4.9, 4.5), 5.27 (H-10 cis, dd, 10.0, 1.4), 5.30 (H-10 trans, dd, 17.0, 1.4), 4.80 (H-1', d, 8.0), 3.29–3.53 (H-2'–H-5', m), 3.91 (H-6', dd, 12.4, 2.0), 3.72 (H-6', dd, 12.4, 5.7); (D_2O) 99.4 (C-1), 152.3 (C-3), 114.8 (C-4), 31.0 (C-5), 38.3 (C-6), 181.4 (C-7), 135.3 (C-8), 46.2 (C-9), 123.1 (C-10), 175.3 (C-11), 100.0 (C-1'), 75.2 (C-2'), 78.1 (C-3'), 72.2 (C-4'), 78.8 (C-5'), 63.3 (C-6'). *Lonicera periclymenum* (Caprifoliaceae) (63)

115 SECOXYLOGANIN



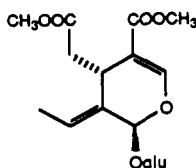
$C_{17}H_{24}O_{11}$ 404.37 $[\alpha] -111.7^\circ$ (MeOH) uv 233 (MeOH) (300 MHz D_2O) 5.55 (H-1, d, 4.4), 7.54 (H-3, bs), 3.24 (H-5, m), 2.63 (H-6, dd, 16.0, 4.0), 2.36 (H-6, dd, 16.0, 7.5), 5.71 (H-8, ddd, 16.6, 9.5, 9.5), 2.79 (H-9, m), 5.36 (H-10, d, 16.6), 5.31 (H-10, d, 9.5), 4.85 (H-1', d, 7.7), 3.56–3.32 (H-2'–H-5'), 3.95 (H-6', d, 12.4), 3.75 (H-6'), 3.75 (OMe); (CD_3OD) 97.7 (C-1), 153.6 (C-3), 110.8 (C-4), 29.3 (C-5), 36.9 (C-6), 176.6 (C-7), 134.7 (C-8), 45.4 (C-9), 120.5 (C-10), 169.2 (C-11), 51.8 (OMe), 99.9 (C-1'), 74.7 (C-2'), 77.9 (C-3'), 71.6 (C-4'), 78.4 (C-5'), 62.8 (C-6'). *Lonicera periclymenum* (Caprifoliaceae) (63)

116 SECOLOGANOSIDE DIMETHYL ESTER



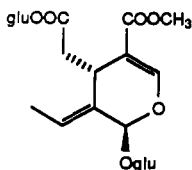
$C_{18}H_{26}O_{11}$ 418.40 mp 140.5° $[\alpha] -99^\circ$ (CHCl₃) uv 230 (EtOH) (300 MHz CD₃OD) 5.48 (H-1, d, 5.4), 7.47 (H-3, d, 1.7), 3.22 (H-5, m), 2.37 (H-6 α , dd, 16.2, 8.4), 2.85 (H-6 β , dd, 16.2, 5.6), 5.63 (H-8, ddd, 18.0, 10.2, 9.2), 2.76 (H-9, ddd, 9.2, 5.4, 4.8), 5.24 (H-10, dd, 18.0, 1.8), 5.22 (H-10, dd, 10.2, 1.8), 3.70, 3.65 (COOMe), 4.66 (H-1', d, 7.8), 3.4-3.28 (H-2'-H-5', m), 3.89 (H-6', dd, 12.0, 1.8), 3.67 (H-6, dd, 12.0, 5.0); (CD₃OD) 97.8 (C-1), 153.8 (C-3), 110.0 (C-4), 29.3 (C-5), 35.5 (C-6), 174.9 (C-7), 134.5 (C-8), 45.5 (C-9), 120.5 (C-10), 168.9 (C-11), 52.2, 51.9 (OMe), 100.1 (C-1'), 74.7 (C-2'), 78.2 (C-3'), 71.6 (C-4'), 78.4 (C-5'), 62.8 (C-6'). Methylation of secologanic acid or secologanin. (63,64)

117 OLEOSIDE DIMETHYL ESTER



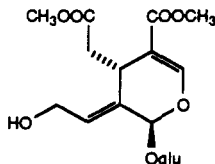
$C_{18}H_{26}O_{11}$ 418.40 $[\alpha] -121.0^\circ$ (MeOH) uv 233 (EtOH) (200 MHz DMSO-*d*₆) 5.54 (H-1, bs), 7.24 (H-3, s), 2.28 (H-6, dd, 14, 4), 2.12 (H-6, dd, 14, 10), 5.82 (H-8, brq, 8), 1.26 (H-10, brd, 8), 3.48, 3.38 (OMe); (CD₃OD) 95.1 (C-1), 155.0 (C-3), 109.2 (C-4), 31.6 (C-5), 40.9 (C-6), 173.4 (C-7), 124.7 (C-8), 130.4 (C-9), 13.3 (C-10), 168.5 (C-11), 53.1, 52.1 (OMe), 100.8 (C-1'), 74.6 (C-2'), 78.2 (C-3'), 71.3 (C-4'), 77.8 (C-5'), 62.6 (C-6'). *Olea europaea* (Oleaceae) (65,66,98)

118 METHYL GLUCOOLEOSIDE

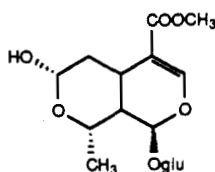


$C_{23}H_{34}O_{16}$ 566.51 $[\alpha] -164.71^\circ$ (MeOH) uv 238 (MeOH) (200 MHz CD₃OD) 5.95 (H-1, bs), 7.54 (H-3, s), 4.02 (H-5, dd, 9.0, 3.9), 2.80 (H-6, dd, 15.4, 3.9), 2.59 (H-6, dd, 15.4, 9.0), 6.12 (H-8, dq, 7.1, 1.0), 1.77 (H-10, dd, 7.1, 1.2), 3.72 (COOMe), 4.82 (H-1', d, 8.0), 3.90 (H-6', dd, 12.5, 1.7)*, 5.44 (H-1'', d, 7.6), 3.82 (H-6'', dd, 12.5, 1.7)*; (CD₃OD) 95.5 (C-1), 155.4 (C-3), 109.2 (C-4), 31.4 (C-5), 40.6 (C-6), 171.9 (C-7), 125.5 (C-8), 130.3 (C-9), 13.8 (C-10), 168.8 (C-11), 52.0 (OMe), 101.0 (C-1'), 74.8 (C-2'), 78.4 (C-3'), 71.5 (C-4'), 78.0 (C-5'), 62.8 (C-6'), 95.9 (C-1''), 73.9 (C-2''), 78.7 (C-3''), 71.1 (C-4''), 78.0 (C-5''), 62.2 (C-6''). *Ligustrum japonicum* (Oleaceae) (67)

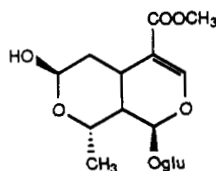
119 10-HYDROXYOLEOSIDE DIMETHYL ESTER



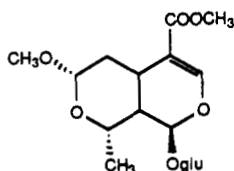
$C_{18}H_{26}O_{12}$ 434.40 $[\alpha] -149.8^\circ$ uv 236 (MeOH) (100 MHz CDCl₃) 5.72 (H-1, bs), 7.45 (H-3, s), 6.00 (H-8, br, 6.0), 4.72 (H-10, bd, 6.0), 3.75, 3.65 (OMe), 2.08, 2.06, 2.03, 2.02 (OAc). Prepared from 10-acetoxyleoside (68)

120 7 α -MORRONISIDE (isolated as 7 α /7 β mixture)

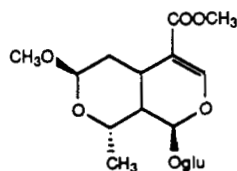
$C_{17}H_{26}O_{11}$ 406.39 [α] -94.2° (MeOH) uv 238 (MeOH) (300 MHz CD_3OD) 5.82 (H-1, d, 9.8), 7.51 (H-3, bs), 2.81 (H-5, dt, 13, 4.4), 2.01 (H-6, ddd, 13, 4.4, 2.3), 1.18 (H-6, td, 13, 10), 4.8 (H-7, dd, 10, 2.3), 3.94 (H-8, qd, 6.8, 2.3), 1.77 (H-9, ddd, 10, 4.4, 2.3), 1.40 (H-10, d, 7), 4.78 (H-1', d, 7.8), 3.5–3.2 (H-2'–H-5', m), 3.87 (H-6', m); (CD_3OD) 97.2 (C-1), 154.6 (C-3), 111.0 (C-4), 34.7 (C-5), 37.4 (C-6), 96.1 (C-7), 75.1 (C-8), 40.0 (C-9), 20.0 (C-10), 168.8 (C-11), 100.2 (C-1'), 74.2 (C-2'), 78.0 (C-3'), 71.7 (C-4'), 78.5 (C-5'), 62.9 (C-6'). *Sambucus ebulus* (Caprifoliaceae) (58)

121 7 β -MORRONISIDE (isolated as 7 α /7 β mixture)

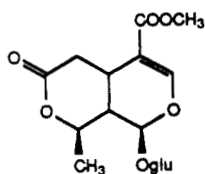
$C_{17}H_{26}O_{11}$ 406.39 [α] -94.2° (MeOH) uv 238 (MeOH) (300 MHz CD_3OD) 5.85 (H-1, d, 10.5), 7.51 (H-3, bs), 3.13 (H-5, dt, 13, 4.6), 1.9 (H-6, bdd, 13, 4.6), 1.5 (H-6, td, 13, 3.5), 5.23 (H-7, bd, 3.5), 4.54 (H-8, qd, 7, 2.3), 1.82 (H-9, m), 1.32 (H-10, d, 7), 4.78 (H-1', d, 7.8), 3.5–3.2 (H-2'–H-5', m), 3.87 (H-6', m); (CD_3OD) 95.8 (C-1), 154.6 (C-3), 111.8 (C-4), 27.6 (C-5), 34.7 (C-6), 92.5 (C-7), 66.0 (C-8), 40.7 (C-9), 20.0 (C-10), 168.8 (C-11), 100.2 (C-1'), 74.2 (C-2'), 78.0 (C-3'), 71.7 (C-4'), 78.5 (C-5'), 62.9 (C-6'). *Sambucus ebulus* (Caprifoliaceae) (58)

122 (7*R*)-O-METHYLMORRONISIDE

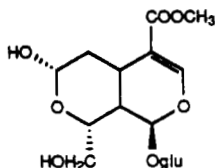
$C_{18}H_{28}O_{11}$ 420.41 tetraacetate mp 144–145° uv 236 (MeOH) (tetraacetate 200 MHz $CDCl_3$) 5.67 (H-1, d, 9), 7.42 (H-3, s), 2.78 (H-5, dt, 12, 4, 4), 4.41 (H-7, dd, 10, 2.5), 1.68 (H-9, m), 1.34 (H-10, d, 7), 3.71 (COOMe), 3.49 (OMe); (tetraacetate $CDCl_3$) 95.1 (C-1), 152.0 (C-3), 110.7 (C-4), 29.9 (C-5), 33.8 (C-6), 102.4 (C-7), 71.6 (C-8), 38.9 (C-9), 18.4 (C-10), 166.1 (C-11), 50.9 (COOMe), 55.5 (OMe), 96.7 (C-1'), 70.7 (C-2'), 72.0 (C-3'), 68.6 (C-4'), 72.5 (C-5'), 61.6 (C-6'). Methylation of (7*R*)-morroniside (69)

123 (7*S*)-O-METHYLMORRONISIDE

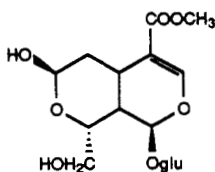
$C_{18}H_{28}O_{11}$ 420.41 tetraacetate mp 103–104° (tetraacetate 200 MHz $CDCl_3$) 5.70 (H-1, d, 9), 7.43 (H-3, s), 3.05 (H-5, dt, 12, 4, 4), 1.45 (H-6_{ax}, m), 1.92 (H-6_{eq}, m), 4.73 (H-7, d, 2.7), 4.20 (H-8, m), 1.72 (H-9, m), 1.27 (H-10, d, 7), 3.71 (COOMe), 3.34 (OMe); (tetraacetate $CDCl_3$) 94.7 (C-1), 152.1 (C-3), 111.7 (C-4), 26.1 (C-5), 32.6 (C-6), 97.7 (C-7), 64.1 (C-8), 39.4 (C-9), 18.6 (C-10), 166.5 (C-11), 51.0 (COOMe), 54.3 (OMe), 96.7 (C-1'), 71.0 (C-2'), 72.0 (C-3'), 68.6 (C-4'), 72.6 (C-5'), 61.7 (C-6'). Methylation of (7*S*)-morroniside (69)

124 8-*epi*-KINGISIDE

$C_{17}H_{24}O_{11}$ 404.37 $[\alpha] -45.87^\circ$ (MeOH) uv 232 (MeOH) (200 MHz CD_3OD) 5.49 (H-1, d, 7.6), 7.58 (H-3, d, 1.0), 3.08 (H-5, dddd, 11.4, 7.3, 4.4, 1.0), 2.50 (H-6ax, dd, 16.5, 11.4), 2.86 (H-6eq, dd, 16.5, 4.4), 4.49 (H-8, bp, 6.8), 2.14 (H-9, bq, 7.3), 1.51 (H-10, d, 6.4), 3.73 (COOMe), 4.70 (H-1', d, 7.8), 3.92 (H-6', dd, 12.0, 2.0), 3.63 (H-6', dd, 12.0, 6.1); (CD_3OD) 96.3 (C-1), 154.4 (C-3), 109.6 (C-4), 28.1 (C-5), 34.6 (C-6), 174.7 (C-7), 75.8 (C-8), 41.9 (C-9), 21.7 (C-10), 168.3 (C-11), 52.0 (OMe), 100.7 (C-1'), 74.7 (C-2'), 78.5 (C-3'), 71.7 (C-4'), 77.9 (C-5'), 62.9 (C-6'). *Ligustrum japonicum* (Oleaceae) (67)

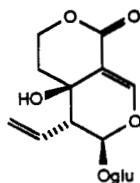
125 (7*R*)-10-HYDROXYMORRONISIDE (isolated as 7*R*/7*S* mixture in 2:1 ratio)

$C_{17}H_{26}O_{12}$ 422.39 $[\alpha] -97.8^\circ$ (MeOH) uv 238 (MeOH) (200 MHz CD_3OD) 5.78 (H-1, d, 9.5), 7.50 (H-3, s), 2.85 (H-5, dt, 12.5, 5.0), 1.23 (H-6ax, m), 2.10 (H-6eq, ddd, 13.5, 4.0, 2.0), 1.93 (H-9, m), 3.70 (OMe); (hexaacetate $CDCl_3$) 94.5 (C-1), 152.4 (C-3), 109.7 (C-4), 30.4 (C-5), 33.5 (C-6), 94.0 (C-7), 75.8 (C-8), 36.5 (C-9), 64.6 (C-10), 166.3 (C-11), 97.4 (C-1'), 71.0 (C-2'), 72.2 (C-3'), 68.8 (C-4'), 72.6 (C-5'), 61.8 (C-6'), 51.5 (OMe). *Galium mollugo* (Rubiaceae) (70)

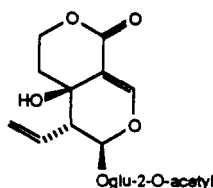
126 (7*S*)-10-HYDROXYMORRONISIDE (isolated as 7*S*/7*R* mixture in 1:2 ratio)

$C_{17}H_{26}O_{12}$ 422.39 $[\alpha] -97.8^\circ$ (MeOH) uv 238 (MeOH) (200 MHz CD_3OD) 5.84 (H-1, d, 9.5), 7.50 (H-3, s), 1.54 (H-6ax, dt, 13.5, 3.5), 1.93 (H-6eq, m), 5.28 (H-7, d, 3.5), 4.45 (H-8, m), 1.93 (H-9, m), 3.70 (OMe); (hexaacetate $CDCl_3$) 94.0 (C-1), 152.4 (C-3), 110.4 (C-4), 26.3 (C-5), 31.8 (C-6), 90.9 (C-7), 69.4 (C-8), 36.6 (C-9), 64.8 (C-10), 166.4 (C-11), 97.2 (C-1'), 71.0 (C-2'), 72.2 (C-3'), 68.4 (C-4'), 72.5 (C-5'), 61.5 (C-6'), 51.4 (OMe). *Galium mollugo* (Rubiaceae) (70)

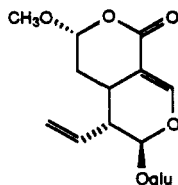
127 SWERTIAMARIN



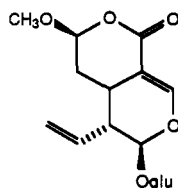
$C_{16}H_{22}O_{11}$ 390.34 (CD_3OD) 99.2 (C-1), 154.7 (C-3), 109.0 (C-4), 64.4 (C-5), 33.7 (C-6), 66.0 (C-7), 133.8 (C-8), 51.9 (C-9), 121.2 (C-10), 168.0 (C-11), 100.2 (C-1'), 74.5 (C-2'), 77.9 (C-3'), 71.5 (C-4'), 78.5 (C-5'), 62.6 (C-6'). *Suertia japonica* (Gentianaceae) (71)

128 2'-O-ACETYSWERTIAMARIN

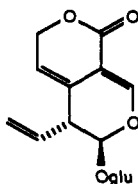
$C_{18}H_{24}O_{11}$ 416.38 mp 104–105° $[\alpha] -92^\circ$ (MeOH) uv 234 (MeOH) (400 MHz CD_3OD) 5.65 (H-1, d, 1.5), 7.55 (H-3, s), 1.85 (H-6, ddd, 14.2, 12.7, 5.1), 1.75 (H-6, ddd, 14.2, 3.2, 1.5), 4.74 (H-7, ddd, 12.7, 10.9, 3.2), 4.33 (H-7, ddd, 10.9, 5.1, 1.5), 5.41 (H-8, ddd, 17.2, 7.8, 7.6), 2.90 (H-9, ddd, 7.6, 1.5, 1.5), 5.36 (H-10, dd, 17.2, 4.2), 5.29 (H-10, ddd, 7.8, 4.2, 1.5), 4.81 (H-1', d, 8.1), 4.68 (H-2', dd, 9.5, 8.1), 3.60 (H-3', dd, 9.5, 8.6), 3.43–3.32 (H-4', H-5', m), 3.69 (H-6', dd, 12.0, 5.9), 2.06 (OAc); (CD_3OD) 99.6 (C-1), 153.2 (C-3), 110.4 (C-4), 64.2 (C-5), 33.4 (C-6), 66.1 (C-7), 133.3 (C-8), 52.2 (C-9), 121.4 (C-10), 167.8 (C-11), 98.8 (C-1'), 75.3 (C-2'), 75.1 (C-3'), 71.4 (C-4'), 78.7 (C-5'), 62.5 (C-6'), 173.2 (O=CMe), 21.0 (O=CMe). *Suertia mileensis* (Gentianaceae) (72)

129 7 α -METHOXYSWEROSE

$C_{17}H_{24}O_{10}$ 388.37 $[\alpha] -91^\circ$ (MeOH) uv 241 (MeOH) (400 MHz CD_3OD) 5.56 (H-1, d, 5.6), 7.48 (H-3, d, 1.2), 2.97 (H-5, m), 2.12 (H-6, ddd, 13.2, 8.0, 4.5), 1.58 (H-6, ddd, 7.2, 6.0), 4.55 (H-7, dd, 7.2, 4.5), 5.79 (H-8, ddd, 19.2, 10.2, 8.6), 2.73 (H-9, dt, 5.6, 5.6), 5.36 (H-10, dd, 10.2, 1.2), 5.31 (H-10, dd, 19.2, 1.8), 3.66 (OMe), 4.74 (H-1', d), 3.26 (H-2', dd), 3.34 (H-3', t), 3.43 (H-4', t), 3.68 (H-5', ddd), 3.97 (H-6', dd), 3.74 (H-6', dd); (CD_3OD) 97.7 (C-1), 153.1 (C-3), 111.8 (C-4), 29.1 (C-5), 33.3 (C-6), 104.3 (C-7), 135.4 (C-8), 45.1 (C-9), 119.8 (C-10), 169.2 (C-11), 100.0 (C-1'), 74.1 (C-2'), 78.1 (C-3')^d, 71.4 (C-4'), 77.9 (C-5')^d, 62.6 (C-6'), 51.7 (OMe). *Cruckshanksia verticillata* (Rubiaceae) (73)

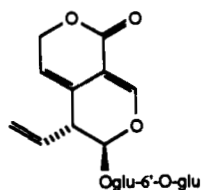
130 7-*epi*-VOGELOSIDE

$C_{17}H_{24}O_{10}$ 388.37 mp 111–112° $[\alpha] -125^\circ$ (MeOH) (90 MHz pyridine- d_5) 7.75 (H-3, d, 2.2), 3.10 (OMe); (pyridine- d_5) 98.1 (C-1), 153.0 (C-3), 104.9 (C-4), 22.4 (C-5), 29.5 (C-6), 101.8 (C-7)^d, 132.7 (C-8), 42.9 (C-9), 120.4 (C-10), 164.5 (C-11), 101.0 (C-1')^d, 74.6 (C-2'), 78.5 (C-3'), 71.4 (C-4'), 78.9 (C-5'), 62.6 (C-6'), 56.5 (OMe). *Lonicera japonica* (Caprifoliaceae) (62)

131 GENTIOPICROSIDE

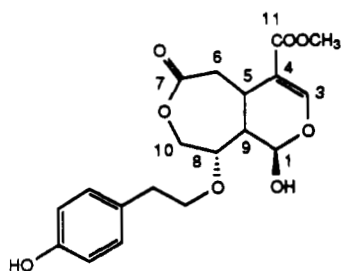
$C_{16}H_{20}O_9$ 356.33 uv 270, 255, 245 (MeOH) (400 MHz CD_3OD) 5.65 (H-1, d, 3.0), 7.44 (H-3, d, 1.5), 5.61 (H-6, m), 5.07, 4.97 (H-7, m's), 5.74 (H-8, ddd, 17.5, 10.5, 7), 3.15 (H-9, ddd, 7.3, 1.5), 5.23 (H-10, ddd, 17.1, 5.1, 5), 5.20 (H-10, ddd, 10.5, 1.5, 1.5), 4.60 (H-1', d, 8), 3.20 (H-2', dd, 9, 8), 3.40–3.30 (H-3', H-4'), 3.45 (H-5', m), 3.85 (H-6', dd, 12, 2), 3.65 (H-6', dd, 12, 6); (CD_3OD) 98.6 (C-1), 150.7 (C-3), 105.0 (C-4), 127.0 (C-5), 117.2 (C-6), 70.9 (C-7), 135.0 (C-8), 46.6 (C-9), 118.5 (C-10), 166.4 (C-11), 100.2 (C-1'), 74.6 (C-2'), 78.0 (C-3'), 71.6 (C-4'), 78.5 (C-5'), 62.8 (C-6'). *Gentiana asclepiadea* (Gentianaceae) (74)

132 6'-O- β -D-GLUCOSYLGENTIOPIICOSIDE



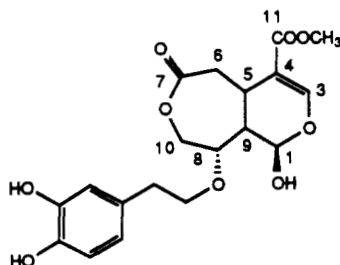
$C_{22}H_{30}O_{14}$ 518.47 uv 270, 255 (MeOH) (400 MHz CD_3OD) 5.63 (H-1, d, 3.5), 7.44 (H-3, d, 1.0), 5.61 (H-6, m), 5.07 (H-7, m), 4.98 (H-7, m), 5.76 (H-8, ddd, 17.5, 10.5, 7.0), 3.15 (H-9, m), 5.24 (H-10, ddd, 17.5, 1.5, 1.5), 5.21 (H-10, ddd, 10.5, 1.5, 1.5), 4.37 (H-1', d, 8.0), 3.20 (H-2', dd, 9.0, 8.0), 3.40–3.30 (H-3', H-4'), 3.50 (H-5', m), 4.16 (H-6', dd, 12, 1.5), 3.76 (H-6', dd, 12, 5), 4.65 (H-1'', d, 8.0), 3.25 (H-2'', dd, 9.0, 8.0), 3.40–3.30 (H-3'', H-4''), 3.45 (H-5'', m), 3.86 (H-6'', dd, 11.5, 2.0), 3.65 (H-6'', dd, 11.5, 6.0); (CD_3OD) 98.9 (C-1), 150.8 (C-3), 104.9 (C-4), 127.1 (C-5), 117.1 (C-6), 70.9 (C-7), 134.9 (C-8), 46.6 (C-9), 118.7 (C-10), 166.3 (C-11), 105.0 (C-1'), 74.5 (C-2')^a, 77.9 (C-3')^b, 71.6 (C-4')^c, 78.1 (C-5')^d, 70.0 (C-6')^e, 100.5 (C-1''), 75.1 (C-2'')^f, 77.4 (C-3'')^g, 71.4 (C-4'')^h, 78.0 (C-5''), 62.8 (C-6''). *Gentiana asclepiadea* (Gentianaceae) (74)

133 JASMOLACTONE A



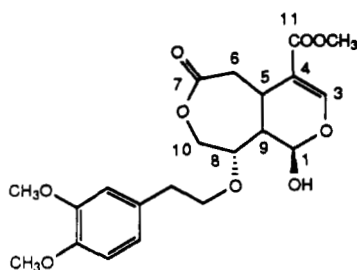
$C_{19}H_{22}O_8$ 378.38 [α] +122.4° ($CHCl_3$) uv 277, 226, 200 (MeOH) (300 MHz $CDCl_3$) 5.20 (H-1, d, 6.9), 7.53 (H-3, d, 1.0), 3.26 (H-5, m), 2.28 (H-6 α , dd, 17.5), 3.32 (H-6 β , dd, 17.5, 4.3), 4.36 (H-8, dd, 3.4, 2.0), 2.53 (H-9, ddd, 6.9, 3.4), 3.95 (H-10 α , d, 9.9), 4.06 (H-10 β , dd, 9.9, 2.0), 3.66 (OMe), 4.27 (H- α , t, 6.8), 2.82 (H- β , t, 6.8), 7.02 (H-2', d, 8.4), 6.73 (H-3', d, 8.4); ($CDCl_3$) 98.9 (C-1), 155.5 (C-3), 105.3 (C-4), 24.8 (C-5), 34.1 (C-6)^a, 172.8 (C-7), 78.4 (C-8), 46.0 (C-9), 71.3 (C-10), 167.4 (C-11), 51.3 (OMe), 65.3 (C- α), 33.9 (C- β)^a, 129.6 (C-1'), 129.9 (C-2'), 115.4 (C-3'), 156.0 (C-4'). *Jasminum multiflorum* (Oleaceae) (75)

134 JASMOLACTONE B



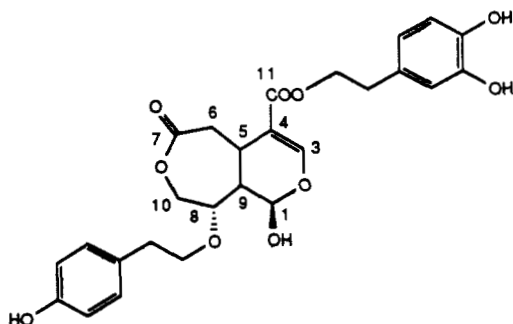
$C_{19}H_{22}O_9$ 394.38 [α] +100.1° (MeOH) uv 280.4, 226.4, 201.2 (MeOH) (300 MHz CD_3OD) 5.18 (H-1, d, 7.0), 7.57 (H-3, d, 1.7), 3.30 (H-5, m), 2.34 (H-6 α , dd, 17.2, 9.8), 3.21 (H-6 β , dd, 17.2, 4.8), 4.49 (H-8, dd, 3.6, 2.2), 2.55 (H-9, ddd, 7.0, 6.5, 3.6), 3.90 (H-10 α , d, 10.0), 4.08 (H-10 β , dd, 10.0, 2.2), 3.65 (OMe), 4.21 (H- α , dt, 7.1, 1.8), 2.78 (H- β , dt, 7.1, 1.8), 6.68 (H-2', d, 2.0), 6.71 (H-5', d, 8.1), 6.54 (H-6', dd, 8.1, 2.0); (CD_3OD) 99.9 (C-1), 156.7 (C-3), 106.4 (C-4), 26.1 (C-5), 35.3 (C-6)^a, 173.8 (C-7), 80.2 (C-8), 47.3 (C-9), 72.1 (C-10), 168.9 (C-11), 51.7 (OMe), 66.5 (C- α), 35.2 (C- β)^a, 130.8 (C-1'), 116.2 (C-2'), 146.0 (C-3'), 144.7 (C-4'), 117.0 (C-5'), 121.2 (C-6'). *Jasminum multiflorum* (Oleaceae) (75)

135 JASMOLACTONE B DIMETHYLATE



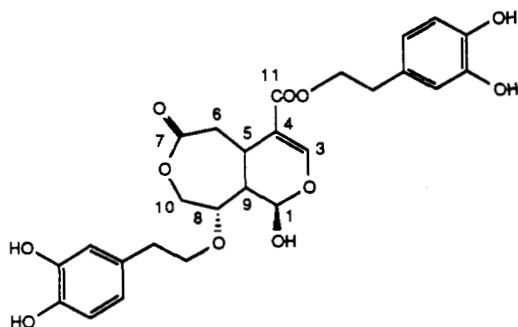
$C_{21}H_{26}O_9$ 422.43 (300 MHz $CDCl_3$) 5.23 (H-1, d, 6.7), 7.54 (H-3, bs), 3.30 (H-5, m), 2.30 (H-6 α , dd, 18.5, 11.5), 3.33 (H-6 β , dd, 18.5), 4.41 (H-8, dd, 3.6, 2.2), 2.62 (H-9, ddd, 6.7, 3.6), 3.97 (H-10, d, 10.0), 3.66 (OMe), 4.29 (H- α , dd, 6.5, 6.4), 4.27 (H- α , dd, 7.0, 6.9), 2.86 (H- β , t, 6.7), 6.79–6.71 (H-2', H-5', H-6'), 3.84, 3.83 (ArOMe); ($CDCl_3$) 98.9 (C-1), 155.3 (C-3), 105.2 (C-4), 25.8 (C-5), 34.6 (C-6), 172.4 (C-7), 78.5 (C-8), 46.4 (C-9), 71.3 (C-10), 167.1 (C-11), 51.5 (OMe), 65.0 (C- α), 34.5 (C- β), 130.4 (C-1'), 111.2 (C-2'), 148.8 (C-3'), 147.6 (C-4'), 112.2 (C-5'), 120.8 (C-6'), 55.8 (ArOMe). CH_2N_2 methylation of jasmolactone B (75)

136 JASMOLACTONE C



$C_{26}H_{28}O_{10}$ 500.50 $[\alpha] +48.6^\circ$ (MeOH) uv 279.2, 223.2, 203.6 (MeOH) (300 MHz Me_2CO-d_6) 5.22 (H-1, d, 6.8), 7.49 (H-3, d, 2.0), 3.28 (H-5, m), 2.32 (H-6 α , dd, 17.0, 10.1), 3.19 (H-6 β , dd, 17.0, 4.2), 4.57 (H-8, dd, 3.6, 2.1), 2.55 (H-9), 3.85 (H-10 α , d, 10.0), 4.08 (H-10 β , dd, 10.0, 2.1), 4.16 (H- α , m), 2.76 (H- β , t, 6.8), 7.08 (H-2', d, 8.4), 6.73 (H-3', d, 8.4), 2.79 (H- β' , t, 6.8), 6.75 (H-2'', H-5''), 6.57 (H-6'', dd, 7.5, 1.7); (CD_3OD) 100.0 (C-1), 156.6 (C-3), 106.8 (C-4), 26.2 (C-5), 35.2 (C-6)^a, 173.9 (C-7), 80.3 (C-8), 47.3 (C-9), 72.1 (C-10), 168.5 (C-11), 66.5 (C- α), 35.3 (C- β)^a, 130.2 (C-1'), 130.9 (C-2'), 116.3 (C-3'), 157.0 (C-4'), 66.2 (C- α'), 35.2 (C- β')^a, 131.0 (C-1''), 116.4 (C-2''), 146.2 (C-3''), 144.8 (C-4''), 117.1 (C-5''), 121.3 (C-6''). *Jasminum multiflorum* (Oleaceae) (75)

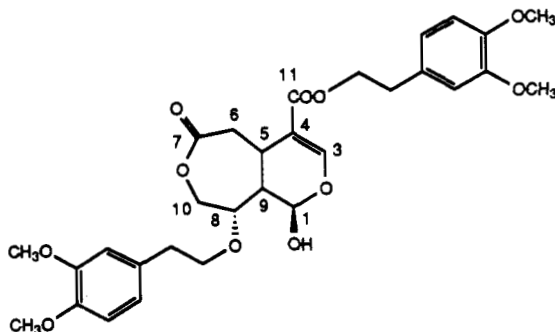
137 JASMOLACTONE D



$C_{26}H_{28}O_{11}$ 516.50 $[\alpha] +28.5^\circ$ (MeOH) uv 281.6, 224.4, 202.8 (MeOH) (300 MHz CD_3OD) 5.20 (H-1, d, 7.1), 7.52 (H-3, bs), 3.27 (H-5, m), 2.29 (H-6 α , dd, 17.3, 11.1), 3.18 (H-6 β , dd, 17.3, 4.3), 4.43 (H-8, bs), 2.53 (H-9, m), 3.91 (H-10 α , d, 9.8), 4.14 (H-10 β , d, 9.8), 4.26 (H- α , t, 6.7), 2.78 (H- β , t, 6.7), 6.70 (H-2', H-5'), 6.55 (H-6', d, 7.7), 4.26 (H- α' , t, 6.7), 2.78 (H- β' , t, 6.7), 6.70 (H-2'', H-5''), 6.57 (H-6'', dd, 7.7, 1.6); (CD_3OD)

99.5 (C-1), 156.4 (C-3), 106.2 (C-4), 25.7 (C-5), 35.1 (C-6), 173.7 (C-7), 79.7 (C-8), 46.8 (C-9), 71.8 (C-10), 168.2 (C-11), 66.2 (C- α), 34.9 (C- β), 130.6 (C-1'), 116.1 (C-2'), 145.6 (C-3'), 144.2 (C-4'), 116.7 (C-5'), 121.1 (C-6'), 65.8 (C- α'), 34.9 (C- β'), 130.6 (C-1''), 116.1 (C-2''), 145.7 (C-3''), 144.3 (C-4''), 116.8 (C-5''), 121.1 (C-6''). *Jasminum multiflorum* (Oleaceae) (75)

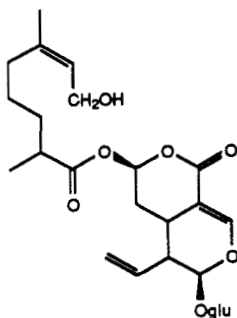
138 JASMOLACTONE D TETRAMETHYLATE



$C_{30}H_{36}O_{11}$ 572.61 (300 MHz $CDCl_3$) 5.22 (H-1, d, 6.7), 7.51 (H-3, bs), 3.24 (H-5, m), 3.31 (H-6, dd), 4.39 (H-8, dd), 2.63 (H-9, ddd), 3.97 (H-10, d, 9.9), 4.27 (H α , H α' , m, 4H), 2.87 (H β , H β' , m, 4H), 6.71–6.79 (H-2', H-5', H-6', H-2'', H-5'', H-6''), 3.85, 3.84, 3.83, 3.82 (ArOMe). CH_2N_2 methylation of jasmolactone D (75)

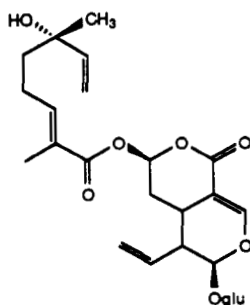
Group 10 (secoiridoids—terpene conjugated)

139 DIHYDROFOLIAMENTHIN



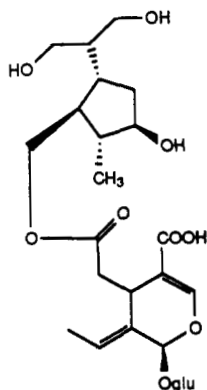
$C_{26}H_{38}O_{12}$ 542.58 (400 MHz pyridine- d_5) 5.85 (H-1, d, 1.6), 7.97 (H-3, d, 2.4), 3.75 (H-5, m), 1.90 (H-6 β , dddd, 14, 5.4, 2.2), 1.85 (H-6 α , td, 14, 13.5, 2.2), 5.70 (H-7, t, 2.2), 5.41 (H-8, dt, 17, 10), 2.77 (H-9, dddd, 10, 5.5, 1.6), 5.12 (H-10, dd, 10.4, 1.8), 5.04 (H-10, dd, 17, 1.8), 5.31 (H-1', d, 7.9), 4.03 (H-2', t, 8.2), 4.23 (H-3', H-4', m), 3.98 (H-5', m), 4.52 (H-6', dd, 12, 2.2), 4.37 (H-6'', dd, 12, 5.3), 2.26 (H-2'', m), 1.33 (H-3'', H-4'', m), 2.03 (H-5'', m), 5.70 (H-7'', t, 6.7), 4.44 (H-8'', dd, 6.7, 1), 0.99 (H-9'', d, 7), 1.68 (H-10'', d); (CD_3OD) 98.1 (C-1), 154.7 (C-3), 103.7 (C-4), 22.2 (C-5), 28.2 (C-6), 92.5 (C-7), 132.4 (C-8), 42.8 (C-9), 120.8 (C-10), 165.2 (C-11), 99.7 (C-1'), 74.0 (C-2'), 77.5 (C-3'), 70.8 (C-4'), 77.7 (C-5'), 62.0 (C-6'), 175.3 (C-1''), 39.6 (C-2''), 33.7 (C-3''), 25.7 (C-4''), 31.9 (C-5''), 138.9 (C-6''), 125.2 (C-7''), 58.8 (C-8''), 16.6 (C-9''), 22.9 (C-10''). *Menyanthes trifoliata* (Gentianaceae) (76)

140 MENTHIAFOLIN



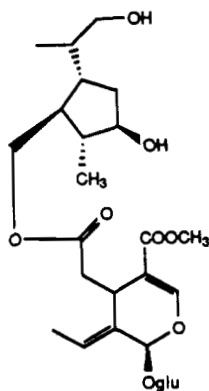
$C_{26}H_{36}O_{12}$ 540.56 (300 MHz CD_3OD) 5.59 (H-1, d, 1.6), 7.66 (H-3, d, 2.4), 3.4 (H-5, m), 1.88–1.95 (H-6, m), 6.62 (H-7, t, 2.2), 5.52 (H-8, dt, 17.3, 9.7), 2.74 (H-9, m), 5.28–5.36 (H-10, dd), 4.71 (H-1', d, 7.8), 3.88 (H-6', dd, 12, 1.7), 3.67 (H-6'', dd, 12, 5.3), 6.87 (H-3'', dt, 7.5, 1.4), 2.24 (H-4'', m), 1.62 (H-5'', m), 5.91 (H-7'', dd, 17.4, 10.7), 5.22 (H-8'', dd, 17.3, 10.8), 5.05 (H-8'', dd, 17.3, 1.5), 1.82 (H-9'', bs), 1.27 (H-10'', s); (CD_3OD) 98.1 (C-1), 154.7 (C-3), 103.8 (C-4), 22.4 (C-5), 28.3 (C-6), 92.9 (C-7), 132.3 (C-8), 42.7 (C-9), 120.9 (C-10), 165.4 (C-11), 99.7 (C-1'), 74.0 (C-2'), 77.5 (C-3'), 70.8 (C-4'), 77.7 (C-5'), 62.0 (C-6'), 166.4 (C-1''), 127.1 (C-2''), 145.8 (C-3''), 24.1 (C-4''), 40.8 (C-5''), 73.0 (C-6''), 145.2 (C-7''), 111.9 (C-8''), 11.6 (C-9''), 27.2 (C-10''). *Menyanthes trifoliata* (Gentianaceae) (76)

141 9"-HYDROXYJASMESOSIDIC ACID



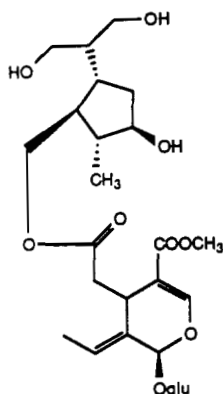
$C_{26}H_{40}O_{14}$ 576.59 $[\alpha] -161.0^\circ$ (MeOH) uv 234 (MeOH) (200 MHz CD_3OD) 5.93 (H-1, bs), 7.54 (H-3, s), 4.00 (H-5, dd, 9.3, 4.4), 2.78 (H-6, dd, 13.9, 4.4), 2.48 (H-6, dd, 14.2, 9.3), 6.11 (H-8, bq, 7.0), 1.76 (H-10, bd, 7.1), 4.83 (H-1', d, 7.6), 1.03 (H-6'', d, 5.9), 4.19 (H-7'', dd, 10.5, 4.6), 3.58 (H-7'', dd, 11.1, 3.0); (CD_3OD) 94.9 (C-1), 155.1 (C-3), 109.6 (C-4), 31.9 (C-5), 41.3 (C-6), 173.4 (C-7), 124.7 (C-8), 130.8 (C-9), 13.7 (C-10), 170.0 (C-11), 100.7 (C-1'), 74.7 (C-2'), 77.9 (C-3'), 71.4 (C-4'), 78.4 (C-5'), 62.7 (C-6'), 46.6 (C-1''), 47.8 (C-2''), 38.6 (C-3''), 36.8 (C-4''), 79.6 (C-5''), 18.4 (C-6''), 68.6 (C-7''), 48.8 (C-8''), 63.3 (C-9''), 62.0 (C-10''). *Jasminum mesnyi* (Oleaceae) (77)

142 JASMESOSIDE



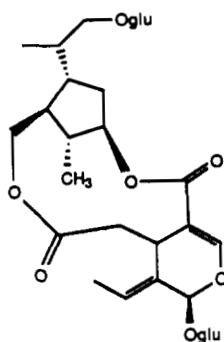
$C_{27}H_{42}O_{13}$ 574.62 $[\alpha] -156.0^\circ$ (MeOH) uv 236 (MeOH) (100 MHz, ?) 5.92 (H-1, bs), 7.53 (H-3, s), 2.70 (H-6, dd, 14.0, 5.0), 2.46 (H-6, dd, 14.0, 8.8), 6.12 (H-8, bq, 7.0), 1.75 (H-10, dd, 7.0, 1.0), 3.72 (COOMe), 0.96 (H-6'', d, 6.5), 1.03 (H-9'', d, 6.0); (CD_3OD) 95.0 (C-1), 155.2 (C-3), 109.4 (C-4), 32.0 (C-5), 41.3 (C-6), 173.3 (C-7), 124.8 (C-8), 130.7 (C-9), 13.7 (C-10), 168.6 (C-11), 52.0 (OMe), 100.8 (C-1'), 74.7 (C-2'), 78.4 (C-3'), 71.5 (C-4'), 77.9 (C-5'), 62.7 (C-6'), 46.8 (C-1''), 48.1 (C-2''), 42.2 (C-3''), 37.8 (C-4''), 79.7 (C-5''), 18.4 (C-6''), 69.1 (C-7''), 41.1 (C-8''), 15.9 (C-9''), 66.5 (C-10''). *Jasminum mesnyi* (Oleaceae) (78)

143 9"-HYDROXYJASMESOSIDE



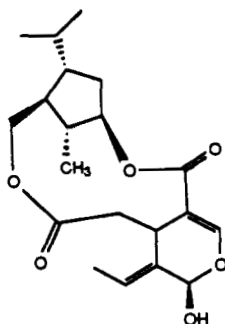
$C_{27}H_{42}O_{14}$ 590.62 $[\alpha] -164.9^\circ$ (MeOH) uv 237 (MeOH) (200 MHz CD_3OD) 5.93 (H-1, bs), 7.53 (H-3, s), 4.01 (H-5, dd, 9.0, 4.2), 2.74 (H-6, dd, 14.2, 4.4), 2.48 (H-6, dd, 14.2, 9.0), 6.12 (H-8, bq, 7.0), 1.75 (H-10, dd, 7.1, 1.0), 3.72 (COOMe), 4.81 (H-1', d, 7.6), 1.04 (H-6'', d, 6.4), 4.20 (H-7'', dd, 10.7, 4.6), 3.58 (H-7'', dd, 11.0, 6.4); (CD_3OD) 95.1 (C-1), 155.2 (C-3), 109.4 (C-4), 32.0 (C-5), 41.3 (C-6), 173.3 (C-7), 124.9 (C-8), 130.7 (C-9), 13.7 (C-10), 168.7 (C-11), 52.0 (OMe), 100.8 (C-1'), 74.8 (C-2'), 78.0 (C-3'), 71.5 (C-4'), 78.5 (C-5'), 62.8 (C-6'), 46.7 (C-1''), 47.8 (C-2''), 38.6 (C-3''), 36.9 (C-4''), 79.7 (C-5''), 18.4 (C-6''), 68.7 (C-7''), 48.9 (C-8''), 63.3 (C-9''), 62.0 (C-10''). *Jasminum mesnyi* (Oleaceae) (77)

144 JASMININ-10''-O-GLUCOSIDE



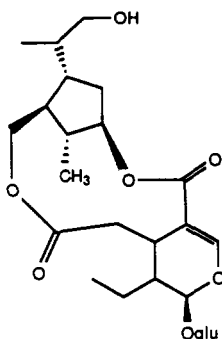
$C_{32}H_{48}O_{17}$ 704.72 mp 153–154° $[\alpha] -236.7^\circ$ (pyridine) uv 238 (MeOH) (200 MHz CD_3OD) 5.95 (H-1, bs), 7.47 (H-3, s), 4.08 (H-5, dd, 11.5, 4.2), 2.50 (H-6, dd, 12.2, 4.2), 2.29 (H-6, t, 12.2), 6.06 (H-8, bdq, 7.1, 1.0), 1.83 (H-10, dd, 7.1, 1.5), 4.81 (H-1', d, 7.8), 4.91 (H-5'', dd, 13.2, 1.2), 1.00 (H-6'', d, 7.6), 1.10 (H-9'', d, 6.6), 4.27 (H-1'', d, 7.6); (CD_3OD) 95.0 (C-1), 154.8 (C-3), 109.8 (C-4), 31.7 (C-5), 44.0 (C-6), 173.4 (C-7), 123.7 (C-8), 131.4 (C-9), 13.3 (C-10), 167.8 (C-11), 100.8 (C-1'), 74.8 (C-2'), 78.0 (C-3'), 71.6 (C-4'), 78.5 (C-5'), 62.8 (C-6'), 44.9 (C-1''), 52.1 (C-2''), 42.5 (C-3''), 36.0 (C-4''), 82.7 (C-5''), 20.7 (C-6''), 67.6 (C-7''), 40.1 (C-8''), 16.2 (C-9''), 75.2 (C-10''), 104.4 (C-1'''), 74.8 (C-2'''), 78.0 (C-3'''), 71.8 (C-4'''), 78.2 (C-5'''), 62.9 (C-6'''). *Jasminum mesnyi* (Oleaceae) (77)

145 AZORICIN (9'-deoxyjasminigenin)



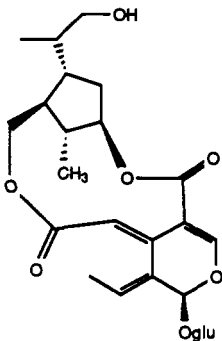
$C_{20}H_{28}O_6$ 364.44 mp 146–148° uv262, 222 (MeOH) (500 MHz CD_3OD) 4.95 (H-1, bs), 7.43 (H-3, s), 3.99 (H-5, dd, 11.5, 2.5), 2.55 (H-6, dd, 13, 3), 2.34 (H-6, dd, 13, 3), 6.01 (H-8, q, 7), 1.80 (H-10, d, 7), 2.25 (H-1', q), 1.77 (H-2', dd, 7, 2.5), 2.34 (H-3', t, 7), 1.96 (H-4', bdd, 13.5, 7), 1.75 (H-4', ddd, 14, 11.5, 3), 4.96 (H-5', d, 4), 1.16 (H-6', d, 7.5), 4.80 (H-7', dd, 12, 2.5), 4.08 (H-7', dd, 12, 2.5), 1.61 (H-8', m), 1.07 (H-9', d, 6.5), 0.99 (H-10', d, 6.5), 4.88 (hydroxyl proton, bs). *Jasminum azoricum* (Oleaceae) (79)

146 8,9-DIHYDROJASMININ



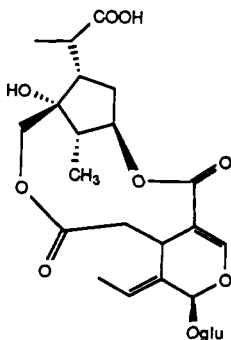
$C_{26}H_{40}O_{12}$ 544.59 mp 135–137° uv 235, 208 (MeOH) (500 MHz $DMSO-d_6$) 4.95 (H-1, bd, 10), 6.58 (H-3, s), 3.5 (H-5, ddd, 11.5, 3, 3), 2.71 (H-6, dd, 13, 11.5), 2.24 (H-6, dd, 13, 3), 2.03 (H-8, dq), 1.21 (H-8, dq), 2.10 (H-9, m), 0.75 (H-10, t), 3.83 (H-1', d, 9), 3.97 (H-2', H-3', m), 3.92 (H-4', dd, 9, 3), 3.66 (H-5', m), 3.71 (H-6', dd, 9, 2), 2.4 (H-1'', m), 1.46 (H-2'', dddd, 7, 2.5, 2, 2), 2.85 (H-3'', dddd, 11.5, 7, 7, 7), 1.72 (H-4'', dd, 13.5, 7), 1.56 (H-4'', ddd, 13.5, 11.5, 3), 5.03 (H-5'', d, 3.5), 0.8 (H-6'', d, 6.5), 4.97 (H-7'', dd, 12, 2.5), 4.08 (H-7'', dd, 12, 2.5), 2.4 (H-8'', m), 4.27 (H-9'', d, 2.5), 0.82 (H-10'', d, 6.5); ($DMSO-d_6$) 93.0 (C-1), 153.4 (C-3), 107.7 (C-4), 34.6 (C-5), 42.4 (C-6), 166.2 (C-7), 20.2 (C-8), 43.1 (C-9), 13.1 (C-10), 170.9 (C-11), 99.1 (C-1'), 73.6 (C-2'), 77.4 (C-3'), 73.3 (C-4'), 76.7 (C-5'), 61.2 (C-6'), 30.0 (C-1''), 37.6 (C-2''), 30.2 (C-3''), 37.6 (C-4''), 51.1 (C-5''), 20.1 (C-6''), 65.1 (C-7''), 50.1 (C-8''), 70.0 (C-9''), 15.7 (C-10''). *Jasminum sambac* (Oleaceae) (80)

147 SAMBACIN (5,6-dehydrojasminin)



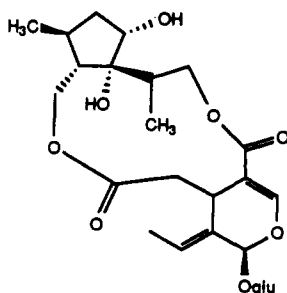
$C_{26}H_{36}O_{12}$ 540.56 mp 150–153° uv 238 (EtOH) (? MHz $DMSO-d_6$) 5.0 (H-1), 7.6 (H-3, s), 7.5 (H-6, s), 6.0 (H-8, q, 6), 1.76 (H-10, d, 7), 3.5–4 (H-6', H-7'', H-9'', 6H), 1.05 (H-6'', H-10'', dd, 8, 4, 6H). *Jasminum sambac* (Oleaceae) (81)

148 JASMISNYIROSIDE



$C_{26}H_{36}O_{14}$ 572.57 mp 230–232° $[\alpha] -228.2$ (MeOH) uv 238–237, 204 (EtOH) (400 MHz CD_3OD) 5.97 (H-1, bs), 7.58 (H-3, s), 3.89 (H-5, dd, 13.5, 5.0), 3.63 (H-6, dd, 13.5, 10.0), 2.62 (H-6, dd, 10.0, 5.0), 6.07 (H-8, bq, 7.0), 1.62 (H-10, dd, 7.0, 1.4), 4.81 (H-1', d, 7.7), 3.41 (H-3', m), 4.04 (H-6', d, 12.0), 3.16 (H-1'', m, 7.7, 2.7), 2.49 (H-3'', m), 1.79 (H-4'', m), 5.02 (H-5'', bd, 2.7), 1.22 (H-6'', d, 7.7), 4.68 (H-7'', d, 11.0), 4.03 (H-7'', d, 11.0), 2.49 (H-8'', m), 0.95 (H-9'', d, 7.0); (CD_3OD) 95.2 (C-1), 155.5 (C-3), 109.8 (C-4), 31.8 (C-5), 44.1 (C-6), 172.5 (C-7), 123.6 (C-8), 131.6 (C-9), 13.3 (C-10), 167.5 (C-11), 100.9 (C-1'), 74.8 (C-2'), 78.5 (C-3'), 71.6 (C-4'), 78.0 (C-5'), 62.8 (C-6'), 47.8 (C-1''), 91.9 (C-2''), 45.0 (C-3''), 37.3 (C-4''), 82.2 (C-5''), 13.3 (C-6''), 64.8 (C-7''), 30.9 (C-8''), 10.8 (C-9''), 180.5 (C-10''). *Jasminum mesnyi* (Oleaceae) (82)

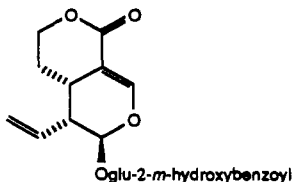
149 compound not named



$C_{26}H_{38}O_{13}$ 558.58 $[\alpha] -150.2^\circ$ (CD_3OD) 35.9 (C-1''), 52.0 (C-2''), 82.2 (C-3''), 74.0 (C-4''), 41.4 (C-5''), 19.5 (C-6''), 64.5 (C-7''), 40.7 (C-8''), 13.3 (C-9''), 66.2 (C-10''). *Jasminum mesnyi* (Oleaceae) (83)

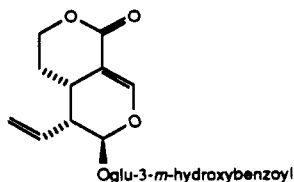
Group 11 (secoiridoids—phenolic conjugated)

150 DESACETYLCENTAPICRIN



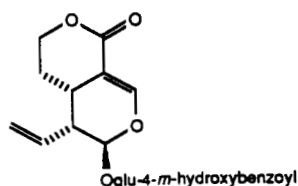
$C_{23}H_{26}O_{11}$ 478.45 (90 MHz pyridine- d_5) 5.58 (H-1, d, 2), 7.68 (H-3, d, 2), 2.7–3.07 (H-5, m), 1.17–1.5 (H-6, m), 4.00–4.30 (H-7, m), 4.80–5.30 (H-8, H-10, m), 2.5 (H-9, bt, 7), 5.43 (H-1', d, 9), 5.82 (H-2', t, 8), 4.31–4.70 (H-3', H-4', H-6', m), 3.62–3.98 (H-5', m), 8.01 (H-2'', bs), 7.67–7.83 (H-4'', m), 7.41 (H-5'', t, 8), 7.36 (H-6'', bs); (CD_3OD) 97.5 (C-1), 153.4 (C-3), 105.9 (C-4), 28.7 (C-5), 25.7 (C-6), 69.4 (C-7), 132.8 (C-8), 43.4 (C-9), 120.9 (C-10), 167.2 (C-11), 97.1 (C-1'), 78.7 (C-2'), 75.4 (C-3')^a, 71.9 (C-4'), 75.5 (C-5')^a, 62.7 (C-6'), 167.5 (C=O), 132.2 (C-1''), 117.1 (C-2''), 121.6 (C-4''), 130.8 (C-5''), 121.7 (C-6''). *Centaurium erythraea* (Gentianaceae) (84)

151 DECENTAPICRIN A



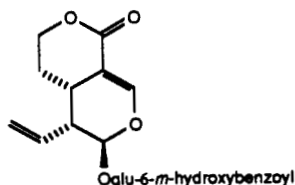
$C_{23}H_{26}O_{11}$ 478.45 mp 245–251° $[\alpha] -203^\circ$ (MeOH) uv 298, 239 (MeOH) (90 MHz pyridine- d_5) 5.75 (H-1, d, 2), 7.88 (H-3, d, 2), 2.83–3.20 (H-5, m), 1.2–1.65 (H-6, m), 4.0–4.30 (H-7, m), 4.86–5.3 (H-8, H-10, m), 2.63 (H-9, bt, 7), 5.37 (H-1', d, 8), 4.35–4.63 (H-2', H-4', H-6', m), 6.10 (H-3', t, 10), 3.7–4.0 (H-5', m), 8.01 (H-2'', bs), 7.67–7.85 (H-4'', m), 7.20–7.40 (H-5'', H-6'', m); (CD_3OD) 98.0 (C-1), 154.0 (C-3), 106.0 (C-4), 28.5 (C-5), 25.9 (C-6), 69.7 (C-7), 133.3 (C-8), 43.8 (C-9), 120.9 (C-10), 167.8 (C-11), 99.7 (C-1'), 73.2 (C-2'), 79.4 (C-3'), 69.7 (C-4'), 78.2 (C-5'), 62.4 (C-6'), 168.4 (C=O), 132.9 (C-1''), 117.3 (C-2''), 158.7 (C-3''), 121.9 (C-4''), 130.4 (C-5''), 121.2 (C-6''). *Centaurium littorale* ssp. *littorale* (Gentianaceae) (84)

152 DECENTAPICRIN B



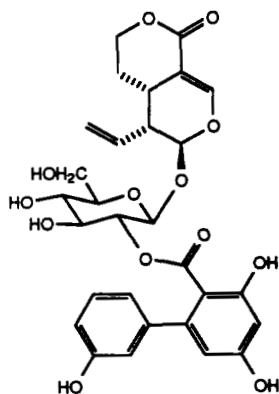
$C_{23}H_{26}O_{11}$ 478.45 $[\alpha] -211^\circ$ (MeOH) uv 300, 241 (MeOH) (90 MHz pyridine- d_5) 5.72 (H-1, d, 2), 7.90 (H-3, d, 2), 2.77–3.20 (H-5, m), 1.2–1.6 (H-6, m), 4.0–4.30 (H-7, m), 4.82–5.30 (H-8, H-10, m), 2.6 (H-9, br, 7), 5.34 (H-1', d, 8), 4.0–4.57 (H-2', H-3', H-6', m), 5.90 (H-4', t, 10), 3.6–4.0 (H-5', m), 8.02 (H-2'', bs), 7.67–7.87 (H-4'', m), 7.30–7.40 (H-5'', H-6'', m); (CD₃OD) 98.1 (C-1), 153.9 (C-3), 106.1 (C-4), 28.5 (C-5), 25.9 (C-6), 69.7 (C-7), 133.3 (C-8), 43.8 (C-9), 120.9 (C-10), 167.4 (C-11), 99.8 (C-1'), 74.9 (C-2'), 76.4 (C-3')^a, 72.8 (C-4'), 75.6 (C-5')^a, 62.3 (C-6'), 168.5 (C=O), 132.3 (C-1''), 117.3 (C-2''), 158.9 (C-3''), 121.5 (C-4'')^b, 130.6 (C-5''), 121.9 (C-6'')^b. *Centaurium littorale* ssp. *littorale* (Gentianaceae) (84)

153 DECENTAPICRIN C



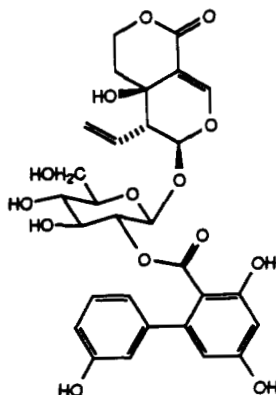
$C_{23}H_{26}O_{11}$ 478.45 $[\alpha] -192^\circ$ (MeOH) uv 299, 240 (MeOH) (90 MHz pyridine- d_5) 5.71 (H-1, d, 2), 7.89 (H-3, d, 2), 2.77–3.10 (H-5, m), 1.17–1.77 (H-6, m), 3.9–4.3 (H-7, m), 4.90–5.6 (H-8, H-10, m), 2.6 (H-9, br, 7), 5.28 (H-1', d, 8), 4.02–4.4 (H-2'–H-4', m), 3.6–4.0 (H-5', m), 5.0–5.2 (H-6', m), 8.00 (H-2'', bs), 7.70–7.86 (H-4'', m), 7.23–7.43 (H-5'', H-6'', m); (CD₃OD) 98.6 (C-1), 153.9 (C-3), 106.0 (C-4), 28.4 (C-5), 25.9 (C-6), 69.7 (C-7), 133.1 (C-8), 43.9 (C-9), 120.9 (C-10), — (C-11), 100.2 (C-1'), 74.7 (C-2'), 77.8 (C-3'), 71.6 (C-4'), 75.7 (C-5'), 64.8 (C-6'), — (C=O), — (C-1''), 117.2 (C-2''), — (C-3''), 121.3 (C-4'')^a, 130.6 (C-5''), 121.6 (C-6'')^a. *Centaurium littorale* ssp. *littorale* (Gentianaceae) (84)

154 AMAROGENTIN



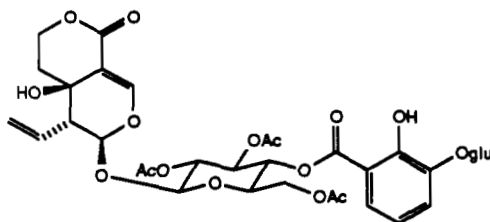
$C_{29}H_{30}O_{13}$ 586.55 (CD₃OD) 96.9 (C-1), 153.6 (C-3), 104.2 (C-4), 28.7 (C-5), 25.8 (C-6), 69.5 (C-7), 132.8 (C-8), 43.4 (C-9), 121.0 (C-10), 167.5 (C-11), 97.3 (C-1'), 74.9 (C-2'), 74.7 (C-3'), 71.7 (C-4'), 78.3 (C-5'), 62.5 (C-6'), 171.4 (C=O), 148.6 (C-1''), 105.6 (C-2''), 163.8 (C-3''), 103.2 (C-4''), 165.9 (C-5''), 112.9 (C-6''), 146.5 (C-1'''), 114.6 (C-2'''), 157.4 (C-3'''), 116.6 (C-4'''), 129.4 (C-5'''), 121.2 (C-6'''). *Suertia japonica* (Gentianaceae) (71,85)

155 AMAROSWERIN



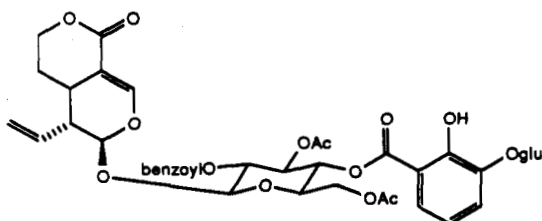
$C_{29}H_{30}O_{14}$ 602.55 (CD_3OD) 98.3 (C-1), 153.7 (C-3), 104.0 (C-4), 64.3 (C-5), 33.5 (C-6), 65.8 (C-7), 133.1 (C-8), 51.8 (C-9), 121.5 (C-10), 167.3 (C-11), 99.0 (C-1'), 75.0 (C-2'), 74.9 (C-3'), 71.3 (C-4'), 78.4 (C-5'), 62.3 (C-6'), 171.9 (C=O), 148.6 (C-1''), 109.4 (C-2''), 163.9 (C-3''), 103.3 (C-4''), 166.3 (C-5''), 112.8 (C-6''), 146.5 (C-1'''), 114.7 (C-2'''), 157.5 (C-3'''), 116.6 (C-4'''), 129.5 (C-5'''), 121.1 (C-6'''). *Suertia japonica* (Gentianaceae) (71,85)

156 GELIDOSIDE



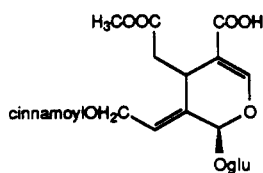
$C_{35}H_{42}O_{21}$ 798.71 no data available. *Gentiana gelida* (Gentianaceae) (86)

157 SCABRASIDE



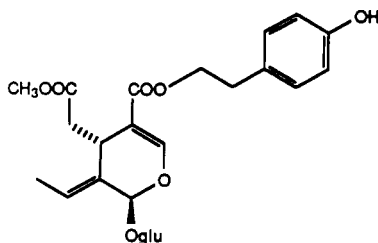
$C_{40}H_{44}O_{20}$ 844.78 $[\alpha] -152.3^\circ$ (MeOH) uv 313, 230, 207 (MeOH) (200 MHz $CDCl_3$) 7.25–7.95 (H-3), 3.46 (H-5, m), 1.55–2.11 (H-6, m), 4.60–5.00 (H-7, m), 5.02–5.37 (H-8, H-10, m), 2.62 (H-9, m), 5.45 (H-1', d, 8), 5.65 (H-2', t, 8), 3.48–3.85 (H-5', H-5''', m), 3.86–4.46 (H-6', H-6''', m), 6.78 (H-5'', t, 8), 7.25–7.95 (H-2''–H-6'', H-4'''–H-6'''), 10.46 (C-2'' hydroxyl proton), 1.86, 2.03 (OAc); ($CDCl_3$) 95.4 (C-1), 150.9 (C-3), 105.2 (C-4), 27.6 (C-5), 24.6 (C-6), 67.6 (C-7), 131.0 (C-8), 42.0 (C-9), 120.8 (C-10), 168.2 (C-11), 95.8 (C-1'), 71.1 (C-2'), 71.6 (C-3'), 69.6 (C-4'), 72.3 (C-5'), 62.2 (C-6'), 163.9 (C''=O), 128.5 (C-1''), 129.4 (C-2''), 128.8 (C-3''), 133.9 (C-4''), 165.1 (C'''=O), 112.6 (C-1'''), 152.0 (C-2'''), 145.6 (C-3'''), 124.2 (C-4'''), 119.4 (C-5'''), 124.1 (C-6'''), 102.3 (C-1'''), 73.3 (C-2'''), 76.1 (C-3'''), 69.9 (C-4'''), 76.1 (C-5'''), 61.6 (C-6'''), 20.6, 20.5 (O=CMe), 170.5, 169.8 (O=CMe). *Gentiana scabra* (Gentianaceae) (87)

158 JASMINOSIDE



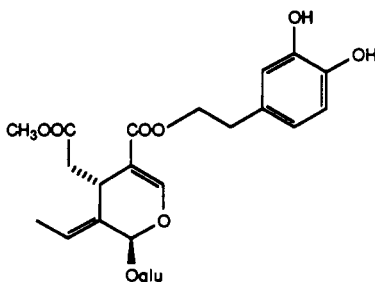
$C_{26}H_{30}O_{13}$ 550.52 mp 116.5–118° $[\alpha] -194.7^\circ$ (MeOH) (90 MHz CD_3OD) 5.99 (H-1, bs), 7.54 (H-3, s), 4.09 (H-5, dd, 9.5, 4.5), 2.88 (H-6, dd, 15.0, 4.5), 2.51 (H-6, dd, 15.0, 9.5), 6.21 (H-8, br, 7.0), 3.64 (COOMe), 6.49 (H- α , d, 16.0), 7.69 (H- β , d, 16.0), 7.22–7.66 (H-2''–H-4''); (CD_3OD) 94.2 (C-1), 154.8 (C-3), 109.2 (C-4), 32.4 (C-5), 40.8 (C-6), 173.2 (C-7), 52.3 (OMe), 124.2 (C-8), 134.1 (C-9), 61.9 (C-10), 169.4 (C-11), 100.8 (C-1'), 74.6 (C-2'), 78.3 (C-3'), 71.3 (C-4'), 77.7 (C-5'), 62.6 (C-6'), 168.1 (C=O), 118.5 (C- α), 146.4 (C- β), 135.5 (C-1''), 129.9 (C-2''), 129.1 (C-3''), 131.4 (C-4''). *Jasminum humile* var. *revolutum* (Oleaceae) (88)

159 ISOLIGUSTROSIDE



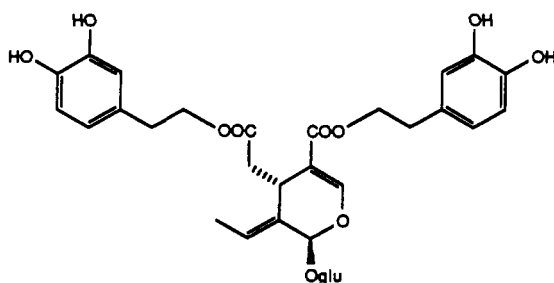
$C_{25}H_{32}O_{12}$ 524.52 pentaacetate mp 45–50° $[\alpha] -122.7^\circ$ ($CHCl_3$) uv 272, 234 (MeOH) (pentaacetate 60 MHz $CDCl_3$) 5.69 (H-1, bs), 7.42 (H-3, s), 4.00 (H-5, bdd, 5.7, 4.8), 6.01 (H-8, bq, 7.0), 1.73 (H-10, dd, 7.0, 1.5), 3.63 (COOMe), 7.13 (H-2'', H-3'', q, 8.8), 2.10 (ArOAc), 2.04 (OAc); (pentaacetate $CDCl_3$) 93.9 (C-1), 153.5 (C-3), 109.0 (C-4), 30.3 (C-5), 39.9 (C-6), — (C-7), 125.1 (C-8), 128.3 (C-9), 13.5 (C-10), 166.5 (C-11), 51.7 (OMe), 97.3 (C-1'), 70.9 (C-2'), 72.8 (C-3'), 68.5 (C-4'), 72.4 (C-5'), 62.0 (C-6'), 64.8 (C- α), 34.7 (C- β), 135.9 (C-1''), 121.9 (C-2''), 130.2 (C-3''), 149.6 (C-4''), 21.1, 20.6 (O=CMe), 171.8, 171.4, 170.9, 170.5 (O=CMe). *Syringa vulgaris* (Oleaceae) (89)

160 ISOOLEUROPEIN



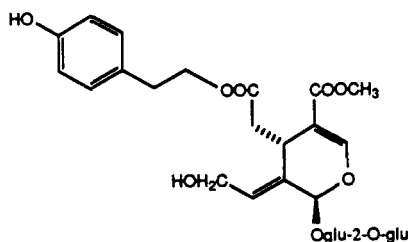
$C_{25}H_{32}O_{13}$ 540.52 hexaacetate $[\alpha] -105.4^\circ$ ($CHCl_3$) uv 272, 235 (MeOH) (hexaacetate 60 MHz $CDCl_3$) 5.69 (H-1, bs), 7.42 (H-3, s), 4.00 (H-5, bdd, 5.7, 4.8), 6.01 (H-8, bq, 7.0), 1.73 (H-10, dd, 7.0, 1.5), 3.62 (COOMe); (hexaacetate $CDCl_3$) 93.9 (C-1), 153.6 (C-3), 108.9 (C-4), 30.4 (C-5), 39.9 (C-6), — (C-7), 125.1 (C-8), 128.3 (C-9), 13.5 (C-10), 166.5 (C-11), 51.6 (OMe), 97.3 (C-1'), 71.0 (C-2'), 72.8 (C-3'), 68.5 (C-4'), 72.5 (C-5'), 62.0 (C-6'), 64.4 (C- α), 34.6 (C- β), 137.1 (C-1''), 123.6 (C-2''), 142.4 (C-3''), 141.1 (C-4''), 124.1 (C-5''), 127.2 (C-6''), 20.6 (O=CMe), 170.9, 170.5, 169.7, 168.6 (O=CMe). *Syringa vulgaris* (Oleaceae) (89)

161 NEOOLEUROPEIN



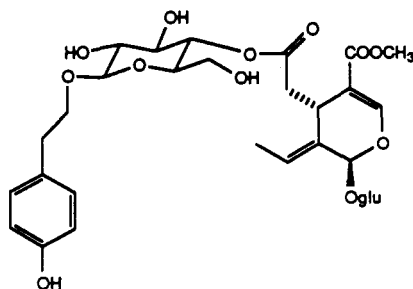
$C_{32}H_{38}O_{15}$ 662.64 octaacetate $[\alpha] -73.5^\circ$ ($CHCl_3$) uv 272, 235 (MeOH) (octaacetate 60 MHz $CDCl_3$) 5.68 (H-1, bs), 7.41 (H-3, s), 3.95 (H-5, bdd, 5.7, 4.8), 5.97 (H-8, bq, 7.0), 1.66 (H-10, dd, 7.0, 1.5); (octaacetate $CDCl_3$) 94.0 (C-1), 153.6 (C-3), 108.9 (C-4), 30.3 (C-5), 40.0 (C-6), 171.1 (C-7), 125.2 (C-8), 128.3 (C-9), 13.5 (C-10), 166.5 (C-11), 97.4 (C-1'), 70.9 (C-2'), 72.8 (C-3'), 68.5 (C-4'), 72.4 (C-5'), 61.9 (C-6'), 64.7, 64.4 (C- α , C- α'), 34.7, 34.5 (C- β , C- β'), 136.9 (C-1'', C-1'''), 123.7 (C-2'', C-2'''), 124.4 (C-3'', C-3'''), 141.1 (C-4'', C-4'''), 124.1 (C-5'', C-5'''), 127.3 (C-6'', C-6'''), 20.7 (O=CMe), 171.3, 170.9, 170.5, 169.7, 168.5 (O=CMe). *Syringa vulgaris* (Oleaceae) (89)

162 HIIRAGILIDE



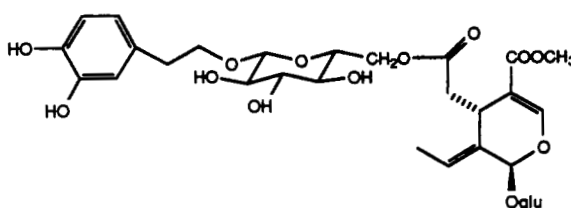
$C_{31}H_{42}O_{18}$ 702.67 nonaacetate mp 70–75° $[\alpha] -153.8^\circ$ ($CHCl_3$) uv 270, 234 (MeOH) (nonaacetate 60 MHz $CDCl_3$) 5.68 (H-1, bs), 7.45 (H-3, s), 5.97 (H-8, br, 6.5), 4.71 (H-10, bd, 6.5), 3.73 (COOMe), 7.11 (H-2'', H-3'', q, 8.8), 2.01–2.12 (OAc, 24H), 2.29 (ArOAc, 3H); (nonaacetate $CHCl_3$) 92.9 (C-1), 153.1 (C-3), 108.8 (C-4), 31.0 (C-5), 40.0 (C-6), 124.6 (C-8), 131.4 (C-9), 60.7 (C-10), 166.6 (C-11), 51.6 (OMe), 97.1 (C-1'), 78.8 (C-2'), 72.6 (C-3'), 68.3 (C-4'), 72.6 (C-5'), 62.0 (C-6'), 101.2 (C-1''), 71.4 (C-2''), 73.1 (C-3''), 68.3 (C-4''), 72.0 (C-5''), 62.0 (C-6''), 65.2 (C- α), 34.4 (C- β), 135.4 (C-1'''), 130.1 (C-2'''), 121.9 (C-3'''), 149.8 (C-4'''), 121.9 (C-5'''), 130.1 (C-6'''), 20.5, 21.1 (O=CMe), 170.9, 170.7, 169.6, 169.2 (C-7, O=CMe). *Osmanthus ilicifolius* (Oleaceae) (90)

163 ISONUEZHENIDE



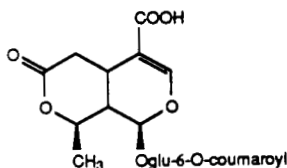
$C_{31}H_{42}O_{17}$ 686.66 $[\alpha] -85^\circ$ (EtOH) uv 280, 227 (EtOH) (400 MHz pyridine- d_5) 6.47 (H-1, bs), 7.75 (H-3, s), 4.36 (H-5, m), 3.02 (H-6, dd, 15.3, 4.3), 2.78 (H-6, dd, 15.8, 9.8), 6.25 (H-8, q, 6.7), 1.77 (H-10, d, 6.7), 3.61 (COOMe), 5.47 (H-1', d, 7.6), 4.91 (H-1'', d, 7.9), 4.07 (H-2'', dd, 9.2, 7.9), 5.53 (H-4'', t, 9.2), 4.23 (H- α , dd, 16.2, 7.6), 3.84 (H- α , dd, 16.7, 7.6), 2.93 (H- β , t, 7.6), 7.11 (H-2''', d, 8.5), 7.06 (H-3''', d, 8.5); (D_2O) 94.9 (C-1), 154.5 (C-3), 108.3 (C-4), 29.8 (C-5), 39.3 (C-6), 172.6 (C-7), 124.8 (C-8), 128.7 (C-9), 13.4 (C-10), 168.8 (C-11), 51.8 (OMe), 99.7 (C-1'), 73.1 (C-2'), 75.7 (C-3'), 69.5 (C-4'), 76.3 (C-5'), 60.7 (C-6'), 102.2 (C-1''), 72.7 (C-2''), 73.8 (C-3''), 71.4 (C-4''), 73.6 (C-5''), 60.5 (C-6''), 70.8 (C- α), 34.3 (C- β), 130.5 (C-1'''), 130.2 (C-2'''), 115.9 (C-3'''), 154.5 (C-4'''). *Ligustrum japonicum* (Oleaceae) (91)

164 NEONUEZHENIDE



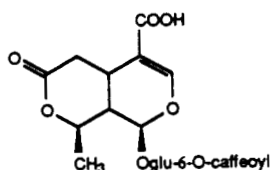
$C_{31}H_{42}O_{18}$ 702.66 nonacetate mp 85–86° $[\alpha] -93.5^\circ$ (CHCl₃) uv 271, 235 (CHCl₃) (nonacetate 60 MHz CDCl₃) 5.71 (H-1, bs), 7.46 (H-3, s), 5.99 (H-8, bq, 6.8), 1.76 (H-10, dd, 7.0, 1.5), 3.72 (COOMe), 4.47 (H-1', d, 6.6), 6.83–7.15 (H-2'', H-5'', H-6''), 2.28 (ArOAc), 2.08, 2.03, 1.99 (OAc); (nonacetate CDCl₃) 94.2 (C-1), 153.4 (C-3), 108.9 (C-4), 30.0 (C-5), 39.9 (C-6), — (C-7), 125.0 (C-8), 128.7 (C-9), 13.5 (C-10), 167.0 (C-11), 51.5 (OMe), 97.4 (C-1'), 71.0 (C-2'), 72.8 (C-3'), 68.5 (C-4'), 72.4 (C-5'), 61.9 (C-6'), 100.9 (C-1''), 71.3 (C-2''), 73.0 (C-3''), 68.8 (C-4''), 72.0 (C-5''), 62.5 (C-6''), 70.0 (C-α), 35.4 (C-β), 137.7 (C-1'''), 123.4 (C-2'''), 142.2 (C-3'''), 140.9 (C-4'''), 124.0 (C-5'''), 127.4 (C-6'''), 21.0, 20.5 (O=CMe), 171.1, 170.8, 170.5, 169.7 (O=CMe). *Ligustrum japonicum* (Oleaceae) (92)

165 IBOTALACTONE A

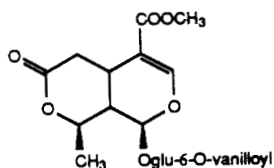


$C_{25}H_{28}O_{13}$ 536.49 mp 138–140° $[\alpha] -41.9^\circ$ (MeOH) uv 321, 300, 227 (MeOH) (400 MHz CD₃OD) 5.32 (H-1, d, 8.3), 7.56 (H-3, s), 3.24 (H-5, m), 2.81 (H-6α, dd, 16.6, 4.0), 2.33 (H-6β, dd, 16.6, 11.7), 4.35–4.38 (H-8), 2.09 (H-9, dd, 8.3, 7.3), 1.42 (H-10, d, 6.4), 4.71 (H-1', d, 8.3), 3.56 (H-5', dd, 11.7, 4.0), 4.60 (H-6', dd, 11.7, 2.4), 4.35–4.38 (H-6', m), 6.34 (H-α, d, 15.6), 7.61 (H-β, d, 15.6), 7.46 (H-2'', d, 8.3), 6.80 (H-3'', d, 8.3); (CD₃OD) 96.6 (C-1), 154.5 (C-3), 109.7 (C-4), 41.9 (C-5), 34.9 (C-6), 174.8 (C-7), 75.7 (C-8), 28.6 (C-9), 21.8 (C-10), 169.5 (C-11), 101.0 (C-1'), 74.7 (C-2'), 77.7 (C-3'), 71.5 (C-4'), 76.0 (C-5'), 63.6 (C-6'), 169.0 (C=O), 114.9 (C-α), 147.1 (C-β), 127.1 (C-1''), 131.4 (C-2''), 116.9 (C-3''), 161.4 (C-4''). *Ligustrum obtusifolium* (Oleaceae) (93)

166 IBOTALACTONE B

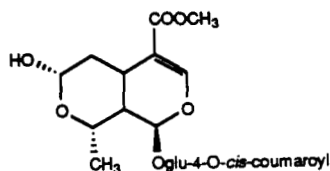


$C_{25}H_{28}O_{14}$ 552.49 pentaacetate mp 70–74° (pentaacetate 400 MHz CDCl₃) 5.28 (H-1, d, 6.3), 7.55 (H-3, d, 2.0), 3.06 (H-5, bdd, 13.2, 8.3), 3.00 (H-6β, dd, 16.6, 13.2), 2.36 (H-6α, dd, 16.6, 8.3), 4.36 (H-8, m), 2.00–2.10 (H-9), 1.49 (H-10, d, 6.4), 4.91 (H-1', d, 8.3), 5.04 (H-2', dd, 9.8, 8.3), 5.28 (H-3', t, 9.8), 5.15 (H-4', t, 9.8), 3.83 (H-5', m), 4.37, 4.35 (H-6'), 6.40 (H-α, d, 16.0), 7.64 (H-β, d, 16.0), 7.53 (H-2'', d, 2.0), 7.23 (H-3'', d, 8.3), 7.41 (H-6'', dd, 8.3, 2.0), 2.06, 2.02, 2.01 (OAc), 2.32, 2.31 (ArOAc); (pentaacetate CDCl₃) 94.2 (C-1), 153.5 (C-3), 109.0 (C-4), 40.6 (C-5), 33.3 (C-6), 72.4 (C-8), 25.5 (C-9), 96.5 (C-1'), 70.6 (C-2'), 73.3 (C-3'), 68.4 (C-4'), 72.5 (C-5'), 61.7 (C-6'), 118.1 (C-α), 143.8 (C-β), 132.9 (C-1''), 123.0 (C-2''), 144.1 (C-3''), 142.5 (C-4''), 124.0 (C-5''), 126.7 (C-6''), 20.7, 20.6 (2×), 20.4 (C-10, O=CMe), 171.0, 170.2, 169.5, 169.4, 169.2, 168.2, 168.1, 166.0 (C-7, C-11, C=O, O=CMe). *Ligustrum obtusifolium* (Oleaceae) (93)

167 6'-O-VANILLOYL-8-*epi*-KINGISIDE

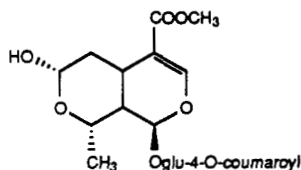
$C_{25}H_{30}O_{14}$ 554.50 uv 292, 260, 235, 227 (MeOH) (300 MHz CD_3OD) 5.20 (H-1, d, 7), 7.53 (H-3, d, 1), 2.94 (H-5, dddd, 12, 7, 4, 1), 2.71 (H-6, dd, 16, 4), 2.04 (H-6, dd, 16, 2), 4.20 (H-8, dq, 7, 6), 2.04 (H-9, t, 7), 1.30 (H-10, d, 6), 3.71 (COOMe), 4.71 (H-1', d, 7.5), 3.21 (H-2', dd, 9, 7.5), 3.37–3.48 (H-3', H-4'), 3.61 (H-5', m), 4.71 (H-6', dd, 12, 2.5), 4.53 (H-6', dd, 12, 5.5), 7.52 (H-2'', d, 2), 6.82 (H-5'', d, 8), 7.54 (H-6'', dd, 8, 2), 3.90 (ArOMe); (CD_3OD) 96.4 (C-1), 154.4 (C-3), 109.3 (C-4), 28.8 (C-5), 34.8 (C-6), 174.5 (C-7), 75.6 (C-8), 41.9 (C-9), 21.6 (C-10), 168.2 (C-11), 51.9 (OMe), 100.8 (C-1'), 74.7 (C-2'), 77.8 (C-3'), 71.7 (C-4'), 76.0 (C-5'), 63.7 (C-6'), 167.9 (C=O), 122.4 (C-1''), 116.0 (C-2''), 148.9 (C-3''), 153.1 (C-4''), 113.8 (C-5''), 125.1 (C-6''), 56.5 (ArOMe). *Gentiana pyrenaica* (Gentianaceae) (94)

168 4'-O-*cis*-p-COUMAROYL-7 α -MORRONISIDE (isolated as 7 α /7 β and *cis*/*trans* mixture)



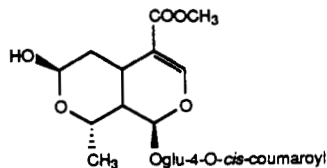
$C_{26}H_{32}O_{13}$ 552.53 uv 310, 230 (MeOH) (400 MHz CD_3OD) 5.84 (H-1, d, 9), 7.52 (H-3, s), 2.93 (H-5, dt, 13, 4.5), 2.03 (H-6, m), 1.18 (H-6, td, 13, 10), 4.86 (H-7, m), 3.96 (H-8, m), 1.78 (H-9, ddd, 9, 5, 2), 1.41 (H-10, d, 7), 3.70 (COOMe), 4.86 (H-1', m), 4.85 (H-4', m), 5.81 (H- α , d, 13), 6.91 (H- β , d, 13), 7.69 (H-2'', d, 8.5), 6.75 (H-3'', d, 8.5); (CD_3OD) 97.1 (C-1), 154.4 (C-3), 110.0 (C-4), 32.0 (C-5), 37.2 (C-6), 96.1 (C-7), 74.1 (C-8), 40.0 (C-9), 19.8 (C-10), 168.7 (C-11), 51.7 (OMe), 100.1 (C-1'), 75.2 (C-2'), 75.7 (C-3'), 72.4 (C-4'), 76.7 (C-5'), 62.5 (C-6'), 167.3 (C=O), 116.1 (C- α), 146.0 (C- β), 127.6 (C-1''), 133.8 (C-2''), 115.8 (C-3''), 160.4 (C-4''). *Gentiana pyrenaica* (Gentianaceae) (95)

169 4'-O-*trans*-p-COUMAROYL-7 α -MORRONISIDE (isolated as 7 α /7 β and *cis*/*trans* mixture)



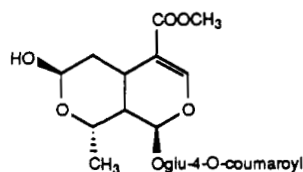
$C_{26}H_{32}O_{13}$ 552.53 uv 310, 230 (MeOH) (400 MHz CD_3OD) 5.84 (H-1, d, 9), 7.52 (H-3, s), 2.93 (H-5, dt, 13, 4.5), 2.03 (H-6, m), 1.18 (H-6, td, 13, 10), 4.86 (H-7, m), 3.96 (H-8, m), 1.78 (H-9, ddd, 9, 5, 2), 1.41 (H-10, d, 7), 3.70 (COOMe), 4.86 (H-1', m), 4.85 (H-4', m), 6.37 (H- α , d, 16), 7.67 (H- β , d, 16), 7.48 (H-2'', d, 8.5), 6.81 (H-3'', d, 8.5); (CD_3OD) 97.1 (C-1), 154.4 (C-3), 110.0 (C-4), 32.0 (C-5), 37.2 (C-6), 96.1 (C-7), 74.1 (C-8), 40.0 (C-9), 19.8 (C-10), 168.7 (C-11), 51.7 (OMe), 100.1 (C-1'), 75.2 (C-2'), 75.7 (C-3'), 72.4 (C-4'), 76.7 (C-5'), 62.5 (C-6'), 168.5 (C=O), 114.8 (C- α), 147.2 (C- β), 127.2 (C-1''), 131.2 (C-2''), 116.9 (C-3''), 161.4 (C-4''). *Gentiana pyrenaica* (Gentianaceae) (95)

170 4'-O-*cis*-p-COUMAROYL-7 β -MORRONISIDE (isolated as 7 α /7 β and *cis*/*trans* mixture)



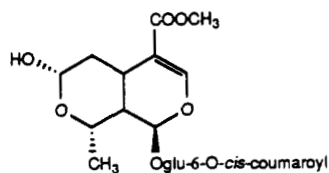
$C_{26}H_{32}O_{13}$ 552.53 uv 310, 230 (MeOH) (400 MHz CD_3OD) 5.89 (H-1, d, 9), 7.51 (H-3, s), 3.14 (H-5, dt, 13, 4.5), 1.90 (H-6, dd, 13, 4.5), 1.50 (H-6, td, 13, 3.5), 5.24 (H-7, d, 3.5), 4.56 (H-8, m), 1.83 (H-9, m), 1.35 (H-10, d, 7), 3.69 (COOMe), 4.86 (H-1', m), 4.85 (H-4', m), 5.81 (H- α , d, 13), 6.91 (H- β , d, 13), 7.69 (H-2'', d, 8.5), 6.75 (H-3'', d, 8.5); (CD_3OD) 95.7 (C-1), 154.4 (C-3), 111.9 (C-4), 27.4 (C-5), 34.6 (C-6), 92.4 (C-7), 65.9 (C-8), 40.6 (C-9), 19.8 (C-10), 168.7 (C-11), 51.7 (OMe), 100.1 (C-1'), 75.2 (C-2'), 75.7 (C-3'), 72.4 (C-4'), 76.7 (C-5'), 62.5 (C-6'), 167.3 (C=O), 116.1 (C- α), 146.0 (C- β), 127.6 (C-1''), 133.8 (C-2''), 115.8 (C-3''), 160.4 (C-4''). *Gentiana pyrenaica* (Gentianaceae) (95)

171 4'-O-*trans*-*p*-COUMAROYL-7 β -MORRONISIDE (isolated as 7 α /7 β and *cis*/*trans* mixture)



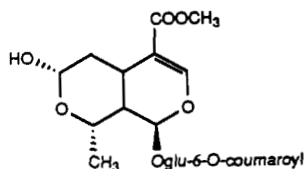
$C_{26}H_{32}O_{13}$ 552.53 uv 310, 230 (MeOH) (400 MHz CD_3OD) 5.89 (H-1, d, 9), 7.51 (H-3, s), 3.14 (H-5, dt, 13, 4.5), 1.90 (H-6, dd, 13, 4.5), 1.50 (H-6, td, 13, 3.5), 5.24 (H-7, d, 3.5), 4.56 (H-8, m), 1.83 (H-9, m), 1.35 (H-10, d, 7), 3.69 (COOMe), 4.86 (H-1', m), 4.85 (H-4', m), 6.37 (H- α , d, 16), 7.67 (H- β , d, 16), 7.48 (H-2'', d, 8.5), 6.81 (H-3'', d, 8.5); (CD_3OD) 95.7 (C-1), 154.4 (C-3), 111.9 (C-4), 27.4 (C-5), 34.6 (C-6), 92.4 (C-7), 65.9 (C-8), 40.6 (C-9), 19.8 (C-10), 168.7 (C-11), 51.7 (OMe), 100.1 (C-1'), 75.2 (C-2'), 75.7 (C-3'), 72.4 (C-4'), 76.7 (C-5'), 62.5 (C-6'), 168.5 (C=O), 114.8 (C- α), 147.2 (C- β), 127.2 (C-1''), 131.2 (C-2''), 116.9 (C-3''), 161.4 (C-4''). *Gentiana pyrenaica* (Gentianaceae) (95)

172 (7*R*)-ISOHAENKEANOSIDE



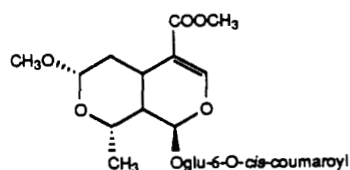
$C_{26}H_{32}O_{13}$ 552.53 (pentaacetate 200 MHz $CDCl_3$) 5.68 (H-1, d, 8.8), 7.45 (H-3, s), 2.85 (H-5, dt, 12.6, 4.6, 4.6), 2.10 (H-6, m, 4.6, 2.3), 1.35 (H-6, m, 12.6, 9.8), 5.75 (H-7, dd, 9.8, 2.3), 3.95 (H-8, dq, 6.8, 2.5), 1.72 (H-9, m, 8.8, 4.6, 2.5), 1.34 (H-10, d, 6.8), 3.72 (COOMe), 5.98 (H- α , d, 12.7), 6.98 (H- β , d, 12.7), 7.67 (H-2'', d, 8.5), 7.10 (H-3'', d, 8.5); (pentaacetate $CDCl_3$) 94.7 (C-1), 152.3 (C-3), 110.2 (C-4), 29.9 (C-5), 32.9 (C-6), 93.7 (C-7), 73.4 (C-8), 38.8 (C-9), 18.7 (C-10), 166.3 (C-11), 51.3 (OMe), 96.6 (C-1'), 70.9 (C-2'), 71.8 (C-3'), 68.5 (C-4'), 72.5 (C-5'), 61.9 (C-6'), 165.0 (C=O), 118.6 (C- α), 143.7 (C- β), 132.0 (C-1''), 131.1 (C-2''), 121.0 (C-3''), 151.0 (C-4''). *Iertia haenkeana* (Rubiaceae) (69)

173 (7*R*)-HAENKEANOSIDE



$C_{26}H_{32}O_{13}$ 552.53 pentaacetate [α] -57° ($CHCl_3$) uv 296, 231 (MeOH) (pentaacetate 200 MHz $CDCl_3$) 5.72 (H-1, d, 8.8), 7.45 (H-3, s), 2.85 (H-5, dt, 12.6, 4.6, 4.6), 2.10 (H-6, m, 4.6, 2.3), 1.35 (H-6, m, 12.6, 9.8), 5.75 (H-7, dd, 9.8, 2.3), 3.95 (H-8, dq, 6.8, 2.5), 1.71 (H-9, m, 8.8, 4.6, 2.5), 1.36 (H-10, d, 6.8), 3.72 (COOMe), 6.41 (H- α , d, 16), 7.68 (H- β , d, 16), 7.56 (H-2'', d, 8.5), 7.13 (H-3'', d, 8.5); (pentaacetate $CDCl_3$) 94.7 (C-1), 152.4 (C-3), 110.2 (C-4), 29.9 (C-5), 32.9 (C-6), 93.7 (C-7), 73.4 (C-8), 38.8 (C-9), 18.7 (C-10), 166.4 (C-11), 51.3 (OMe), 96.6 (C-1'), 70.9 (C-2'), 72.0 (C-3'), 68.5 (C-4'), 72.5 (C-5'), 61.9 (C-6'), 166.1 (C=O), 117.3 (C- α), 144.4 (C- β), 131.8 (C-1''), 129.2 (C-2''), 122.0 (C-3''), 157.1 (C-4''). *Iertia haenkeana* (Rubiaceae) (69)

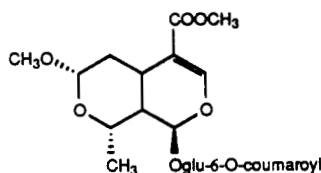
174 (7*R*)-O-METHYLISOHAENKEANOSIDE



$C_{27}H_{34}O_{13}$ 566.56 (tetraacetate 200 MHz $CDCl_3$) 5.59 (H-1, d, 8.5), 7.42 (H-3, s), 2.69 (H-5, dt, 12.5, 4.5, 4.5), 2.05 (H-6, m, 4.5, 2.5), 1.35 (H-6, m, 12.5, 10), 4.40 (H-7, dd, 10, 2.5), 3.82 (H-8, m), 1.70 (H-9, m, 8.5,

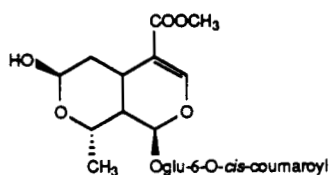
4.5), 1.35 (H-10, d), 3.70 (COOMe), 3.49 (OMe), 5.92 (H- α , d, 12.6), 6.90 (H- β , d, 12.6), 7.56 (H-2", d, 8.6), 7.02 (H-3", d, 8.6); (tetraacetate CDCl₃) 95.2 (C-1), 152.3 (C-3), 110.3 (C-4), 29.9 (C-5), 33.9 (C-6), 102.6 (C-7), 72.5 (C-8), 38.7 (C-9), 19.1 (C-10), 166.5 (C-11), 51.2 (COOMe), 56.0 (OMe), 96.8 (C-1'), 70.8 (C-2'), 72.1 (C-3'), 68.1 (C-4'), 72.2 (C-5'), 61.6 (C-6'), 166.1 (C=O), 118.1 (C- α), 143.9 (C- β), 132.4 (C-1"), 130.8 (C-2"), 121.9 (C-3"), 152.0 (C-4"). *Isertia haenkeana* (Rubiaceae) (69)

175 (7R)-O-METHYLHAENKEANOSIDE



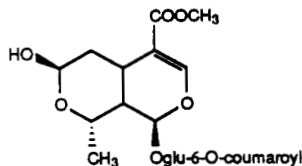
C₂₇H₃₄O₁₃ 566.56 tetraacetate [α] -33° (CHCl₃) uv 296, 231 (MeOH) (tetraacetate 200 MHz CDCl₃) 5.63 (H-1, d, 8.5), 7.48 (H-3, s), 2.69 (H-5, dt, 12.5, 4.5, 4.5), 2.05 (H-6, m, 4.5, 2.5), 1.35 (H-6, m, 12.5, 10), 4.40 (H-7, dd, 10, 2.5), 3.82 (H-8, m), 1.70 (H-9, m, 8.5, 4.5), 1.34 (H-10, d), 3.70 (COOMe), 3.47 (OMe), 6.35 (H- α , d, 16), 7.67 (H- β , d, 16), 7.55 (H-2", d, 8.6), 7.06 (H-3", d, 8.6); (tetraacetate CDCl₃) 95.2 (C-1), 152.3 (C-3), 110.4 (C-4), 29.9 (C-5), 33.9 (C-6), 102.6 (C-7), 72.5 (C-8), 39.1 (C-9), 18.7 (C-10), 166.5 (C-11), 51.2 (COOMe), 56.0 (OMe), 96.8 (C-1'), 70.8 (C-2'), 72.0 (C-3'), 68.4 (C-4'), 72.2 (C-5'), 61.8 (C-6'), 166.1 (C=O), 117.3 (C- α), 144.3 (C- β), 131.8 (C-1"), 129.1 (C-2"), 121.9 (C-3"), 152.0 (C-4"). *Isertia haenkeana* (Rubiaceae) (69)

176 (7S)-ISOHAENKEANOSIDE



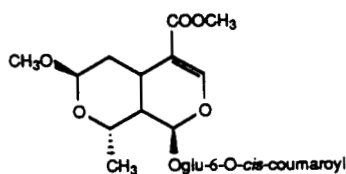
C₂₆H₃₂O₁₃ 552.53 pentaacetate 200 MHz CDCl₃) 5.67 (H-1, d, 8.8), 7.45 (H-3, s), 3.07 (H-5, dt, 12.6, 4.6, 4.6), 2.00 (H-6, m, 4.6), 1.55 (H-6, m, 12.6, 3), 6.14 (H-7, d, 3), 4.25 (H-8, dq, 7, 3), 1.79 (H-9, m, 8.8, 4.6, 3), 1.31 (H-10, d, 7), 3.72 (COOMe), 5.96 (H- α , d, 12.8), 6.98 (H- β , d, 12.8), 7.67 (H-2", d, 8.4), 7.10 (H-3", d, 8.4); (pentaacetate CDCl₃) 94.4 (C-1), 152.5 (C-3), 111.1 (C-4), 25.8 (C-5), 31.2 (C-6), 91.2 (C-7), 67.2 (C-8), 38.6 (C-9), 19.0 (C-10), 166.5 (C-11), 51.4 (OMe), 96.8 (C-1'), 71.0 (C-2'), 72.1 (C-3'), 68.6 (C-4'), 72.6 (C-5'), 61.8 (C-6'), 166.1 (C=O), 118.7 (C- α), 143.9 (C- β), 132.0 (C-1"), 130.8 (C-2"), 121.2 (C-3"), 151.0 (C-4"). *Isertia haenkeana* (Rubiaceae) (69)

177 (7S)-HAENKEANOSIDE



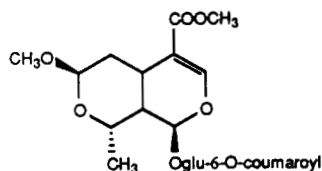
C₂₆H₃₂O₁₃ 552.53 pentaacetate [α] -58° (CHCl₃) uv 296, 231 (MeOH) (pentaacetate 200 MHz CDCl₃) 5.70 (H-1, d, 8.8), 7.44 (H-3, s), 3.07 (H-5, dt, 12.6, 4.6, 4.6), 2.00 (H-6, m, 4.6), 1.55 (H-6, m, 12.6, 3), 6.14 (H-7, d, 3), 4.25 (H-8, dq, 7, 3), 1.79 (H-9, m, 8.8, 4.6, 3), 1.28 (H-10, d, 7), 3.72 (COOMe), 6.40 (H- α , d, 16), 7.68 (H- β , d, 16), 7.57 (H-2", d, 8.6), 7.14 (H-3", d, 8.6); (pentaacetate CDCl₃) 94.4 (C-1), 152.5 (C-3), 111.1 (C-4), 25.8 (C-5), 31.2 (C-6), 91.2 (C-7), 67.2 (C-8), 39.1 (C-9), 18.8 (C-10), 166.5 (C-11), 51.4 (OMe), 96.8 (C-1'), 71.0 (C-2'), 72.1 (C-3'), 68.6 (C-4'), 72.6 (C-5'), 61.8 (C-6'), 166.1 (C=O), 117.3 (C- α), 144.6 (C- β), 131.3 (C-1"), 129.4 (C-2"), 122.1 (C-3"), 152.1 (C-4"). *Isertia haenkeana* (Rubiaceae) (69)

178 (7S)-O-METHYLISOHAENKEANOSIDE

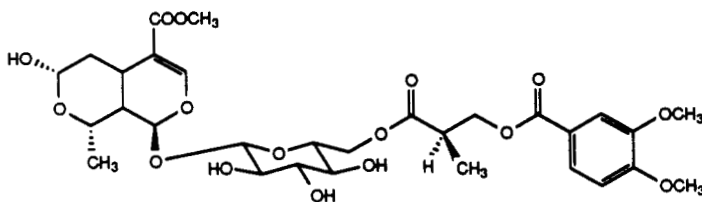


$C_{27}H_{34}O_{13}$ 566.56 (tetraacetate 200 MHz $CDCl_3$) 5.67 (H-1, d, 8.7), 7.42 (H-3, s), 3.05 (H-5, dt, 12.5, 4.5, 4.5), 1.92 (H-6, m, 4.5), 1.42 (H-6, m, 12.5, 3), 4.68 (H-7, d, 3), 4.20 (H-8, dq, 7, 3), 1.69 (H-9, m, 8.7, 4.5, 3), 1.31 (H-10, d, 7), 3.70 (COOMe), 3.31 (OMe), 5.95 (H- α , d, 12.7), 6.96 (H- β , d, 12.7), 7.56 (H-2'', d, 8.6), 7.09 (H-3'', d, 8.6); (tetraacetate $CDCl_3$) 94.5 (C-1), 152.1 (C-3), 111.3 (C-4), 25.8 (C-5), 32.2 (C-6), 97.5 (C-7), 63.9 (C-8), 38.7 (C-9), 18.9 (C-10), 166.4 (C-11), 51.0 (COOMe), 54.3 (OMe), 96.6 (C-1'), 70.8 (C-2'), 71.7 (C-3'), 68.1 (C-4'), 72.4 (C-5'), 61.8 (C-6'), 165.9 (C=O), 118.7 (C- α), 143.9 (C- β), 132.2 (C-1''), 130.8 (C-2''), 121.2 (C-3''), 152.1 (C-4''). *Iseria haenkeana* (Rubiaceae) (69)

179 (7S)-O-METHYLHAENKEANOSIDE

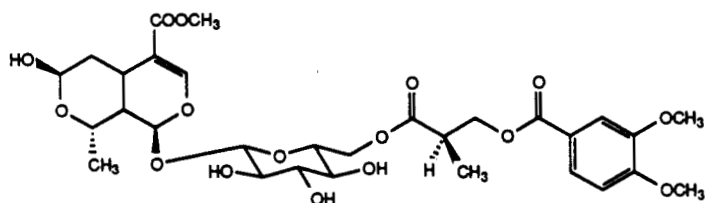


$C_{27}H_{34}O_{13}$ 566.56 tetraacetate [α] -59° ($CHCl_3$) uv 296, 231 (MeOH) (tetraacetate 200 MHz $CDCl_3$) 5.70 (H-1, d, 8.7), 7.42 (H-3, s), 3.05 (H-5, dt, 12.5, 4.5, 4.5), 1.92 (H-6, m, 4.5), 1.42 (H-6, m, 12.5, 3), 4.68 (H-7, d, 3), 4.20 (H-8, dq, 7, 3), 1.69 (H-9, m, 8.7, 4.5, 3), 1.30 (H-10, d, 7), 3.70 (COOMe), 3.31 (OMe), 6.38 (H- α , d, 16), 7.67 (H- β , d, 16), 7.55 (H-2'', d, 8.6), 7.12 (H-3'', d, 8.6); (tetraacetate $CDCl_3$) 94.5 (C-1), 152.1 (C-3), 111.3 (C-4), 25.8 (C-5), 32.2 (C-6), 97.5 (C-7), 63.9 (C-8), 39.0 (C-9), 18.6 (C-10), 166.4 (C-11), 51.0 (COOMe), 54.3 (OMe), 96.6 (C-1'), 70.8 (C-2'), 71.8 (C-3'), 68.4 (C-4'), 72.4 (C-5'), 61.8 (C-6'), 165.9 (C=O), 117.2 (C- α), 144.2 (C- β), 131.7 (C-1''), 129.1 (C-2''), 121.9 (C-3''), 152.1 (C-4''). *Iseria haenkeana* (Rubiaceae) (69)

180 6'-O-[(2R)-METHYL-3-VERATROYLOXYPROPANOYL]-7 α -MORRONISIDE
(isolated as 7 α /7 β mixture)

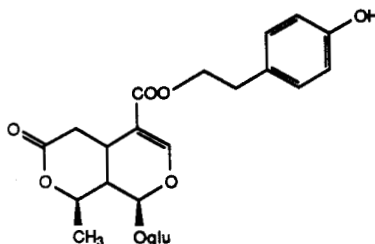
$C_{30}H_{40}O_{16}$ 656.64 uv 290, 255, 240, 225 (MeOH) (400 MHz CD_3OD) 5.77 (H-1, d, 9), 7.48 (H-3, s), 2.79 (H-5, dt, 13, 4.5), 1.99 (H-6, ddd, 13, 4.5, 2.5), 1.17 (H-6, td, 13, 10), 4.78 (H-7, dd, 10, 2.5), 3.94 (H-8, m), 1.74 (H-9, ddd, 9, 4.5, 2.5), 1.36 (H-10, d, 7), 3.71 (COOMe), 4.79 (H-1', d, 8), 4.57 (H-6', dd, 12, 2), 4.24 (H-6', dd, 12, 4.5), 3.03 (H-2'', m), 4.50 (H-3'', dd, 11, 7), 4.42 (H-3'', dd, 11, 5.5), 1.31 (H-4'', d, 7), 7.52 (H-2'', d, 2), 7.03 (H-5'', d, 8.5), 7.65 (H-6'', dd, 8.5, 2), 3.92, 3.88 (ArOMe); (CD_3OD) 96.4 (C-1), 154.4 (C-3), 111.3 (C-4), 31.8 (C-5), 37.1 (C-6), 96.9 (C-7), 73.9 (C-8), 40.1 (C-9), 19.8 (C-10), 168.6 (C-11), 51.7 (COOMe), 100.3 (C-1'), 74.8 (C-2'), 77.8 (C-3'), 71.7 (C-4'), 75.6 (C-5'), 64.8 (C-6'), 175.2 (C-1''), 40.7 (C-2''), 67.0 (C-3''), 14.1 (C-4''), 167.5 (C=O), 123.4 (C-1''), 113.4 (C-2''), 150.2 (C-3''), 155.0 (C-4''), 112.0 (C-5''), 124.9 (C-6''), 56.5 (ArOMe). *Gentiana pyrenaica* (Gentianaceae) (95)

181 6'-O-[(2*R*)-METHYL-3-VERATROYLOXYPROPANOYL]-7 β -MORRONISIDE
(isolated as 7 α /7 β mixture)



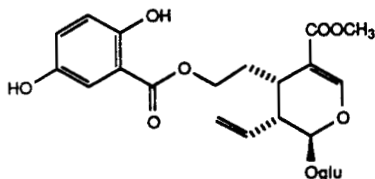
$C_{30}H_{40}O_{16}$ 656.64 uv 290, 255, 240, 225 (MeOH) (400 MHz CD_3OD) 5.78 (H-1, d, 9), 7.47 (H-3, s), 3.10 (H-5, dt, 13, 4.5), 1.83 (H-6, dd, 13, 4.5), 1.43 (H-6, td, 13, 3.5), 5.21 (H-7, d, 3.5), 4.50 (H-8, m), 1.77 (H-9, m), 1.27 (H-10, d, 7), 3.70 (COOMe), 4.76 (H-1', d, 8), 4.60 (H-6', dd, 12, 2), 4.26 (H-6', dd, 12, 4.5), 3.03 (H-2'', m), 4.50 (H-3'', dd, 11, 7), 4.42 (H-3'', dd, 11, 5.5), 1.31 (H-4'', d, 7), 7.52 (H-2''', d, 2), 7.03 (H-5''', d, 8.5), 7.65 (H-6''', dd, 8.5, 2), 3.92, 3.88 (ArOMe); (CD_3OD) 96.1 (C-1), 154.4 (C-3), 111.3 (C-4), 27.2 (C-5), 34.4 (C-6), 92.1 (C-7), 65.6 (C-8), 40.7 (C-9), 19.8 (C-10), 168.6 (C-11), 51.7 (COOMe), 100.3 (C-1'), 74.8 (C-2'), 77.8 (C-3'), 71.8 (C-4'), 75.6 (C-5'), 64.8 (C-6'), 175.2 (C-1''), 40.7 (C-2''), 67.0 (C-3''), 14.1 (C-4''), 167.5 (C=O), 123.4 (C-1'''), 113.4 (C-2'''), 150.2 (C-3'''), 155.0 (C-4'''), 112.0 (C-5'''), 124.9 (C-6'''), 56.5 (ArOMe). *Gentiana pyrenaica* (Gentianaceae) (95)

182 SYRINGALACTONE A (Fliederoside)



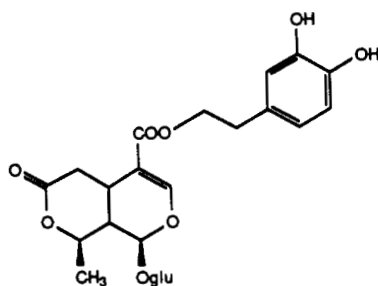
$C_{24}H_{30}O_{12}$ 510.49 pentaacetate mp 64–66° [α] –38.2° ($CHCl_3$) uv 272, 231 (MeOH) (pentaacetate, ? MHz $CDCl_3$) 5.24 (H-1, d, 5.9), 7.37 (H-3, d, 1.0), 4.36 (H-8, dq, 7.3, 6.3), 2.06 (H-9, dd, 7.3, 5.9), 1.48 (H-10, d, 6.3), 4.35 (H- α , t, 6.4), 2.96 (H- β , t, 6.4), 7.22 (H-2'', d, 8.3), 7.04 (H-3'', d, 8.3), 2.29, 2.09, 2.03, 2.01, 1.94 (OAc); (pentaacetate $CDCl_3$) 93.9 (C-1), 151.5 (C-3), 110.1 (C-4), 40.7 (C-5), 33.3 (C-6), 170.6 (C-7)^a, 72.3 (C-8), 25.3 (C-9), 21.1 (C-10)^b, 165.6 (C-11), 96.5 (C-1'), 70.5 (C-2'), 73.2 (C-3'), 68.1 (C-4'), 72.3 (C-5'), 61.5 (C-6'), 64.9 (C- α), 34.5 (C- β), 135.2 (C-1''), 129.8 (C-2''), 121.8 (C-3''), 149.5 (C-4''), 21.1, 20.7, 20.6, 20.5, 20.4 (O=CMe)^b, 170.6, 170.1, 169.6, 169.3, 169.1 (O=CMe)^a. *Syringa vulgaris* (Oleaceae) (96)

183 SYRINGALACTONE B (Lilaciside)



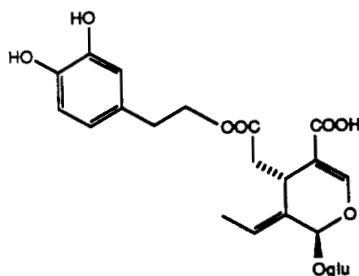
$C_{24}H_{30}O_{13}$ 526.49 hexaacetate mp 58° [α] –35.6° ($CHCl_3$) uv 272, 231 (MeOH) (hexaacetate, ? MHz $CDCl_3$) 5.24 (H-1, d, 5.9), 7.37 (H-3, d, 1.0), 4.36 (H-8, dq, 7.3, 6.3), 2.06 (H-9, dd, 7.3, 5.9), 1.48 (H-10, d, 6.3), 4.35 (H- α , t, 6.4), 2.96 (H- β , t, 6.4), 7.05–7.14 (H-2'', H-5'', H-6'', m), 2.29, 2.28, 2.09, 2.03, 2.01, 1.94 (OAc); (hexaacetate $CDCl_3$) 94.0 (C-1), 151.7 (C-3), 109.9 (C-4), 40.7 (C-5), 33.4 (C-6), 170.7 (C-7)^a, 72.3 (C-8), 25.4 (C-9), 20.9 (C-10)^b, 165.6 (C-11), 96.5 (C-1'), 70.5 (C-2'), 73.3 (C-3'), 68.1 (C-4'), 72.3 (C-5'), 61.5 (C-6'), 64.5 (C- α), 34.4 (C- β), 136.5 (C-1''), 123.5 (C-2''), 142.1 (C-3''), 140.8 (C-4''), 123.9 (C-5''), 126.8 (C-6''), 20.8, 20.7, 20.6 (2 \times), 20.5, 20.4 (O=CMe)^b, 170.6, 170.1, 169.3, 169.1, 168.4, 168.3 (O=CMe)^a. *Syringa vulgaris* (Oleaceae) (96)

184 7-O-GENTISOYLSECOLOGANOL



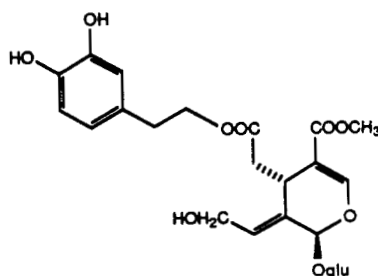
$C_{24}H_{30}O_{13}$ 526.49 uv 335, 235 (MeOH) (300 MHz CD_3OD) 5.59 (H-1, d, 6.5), 7.51 (H-3, s), 2.97 (H-5, bdd, 13, 6), 2.11 (H-6, dt, 15, 6), 1.99 (H-6, ddd, 15, 13, 6), 4.35 (H-7, t, 6), 5.82 (H-8, ddd, 17, 10.5, 8.5), 2.69 (H-9, ddd, 8.5, 6.5, 6), 5.33 (H-10, dd, 17, 1.5), 5.25 (H-10, dd, 10.5, 1.5), 3.68 (COOMe), 4.71 (H-1', d, 8), 3.20–3.90 (H-2'–H-6'), 6.78 (H-3'', d, 9), 6.97 (H-4'', dd, 9, 3), 7.23 (H-6'', d, 3); (CD_3OD) 97.8 (C-1), 153.8 (C-3), 111.5 (C-4), 30.2 (C-5), 31.7 (C-6), 65.0 (C-7), 135.7 (C-8), 45.4 (C-9), 119.6 (C-10), 169.2 (C-11), 51.7 (OMe), 100.3 (C-1'), 74.7 (C-2'), 78.1 (C-3'), 71.6 (C-4'), 78.4 (C-5'), 62.9 (C-6'), 171.8 (C=O), 113.5 (C-1''), 156.1 (C-2''), 115.6 (C-3''), 118.9 (C-4''), 150.7 (C-5''), 125.0 (C-6''). *Gentiana verna* (Gentianaceae) (61)

185 DEMETHYLOLEUROPEIN



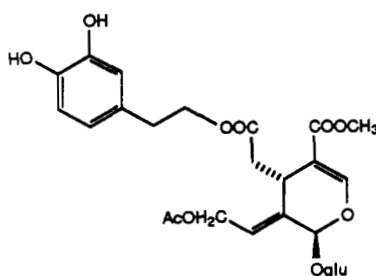
$C_{24}H_{30}O_{13}$ 526.49 mp 147–149° [α] –123.5° (EtOH) uv 282.8, 230.8 (EtOH) (? MHz CD_3OD) 5.87 (H-1, s), 7.57 (H-3, s), 6.03 (H-8, q, 7), 1.66 (H-10, d, 7), 4.14 (H- α , t, 7), 2.73 (H- β , t, 7), 6.41–6.77 (H-2'', H-5'', H-6''); (CD_3OD) 95.0 (C-1), 155.0 (C-3), 109.3 (C-4), 31.6 (C-5), 41.0 (C-6), 173.2 (C-7), 124.6 (C-8), 130.4 (C-9), 13.3 (C-10), 169.8 (C-11), 100.7 (C-1'), 74.5 (C-2'), 78.0 (C-3'), 71.2 (C-4'), 77.6 (C-5'), 62.4 (C-6'), 66.7 (C- α), 35.1 (C- β), 130.6 (C-1''), 116.3 (C-2''), 145.9 (C-3''), 144.6 (C-4''), 116.9 (C-5''), 121.2 (C-6''). *Olea europaea* (Oleaceae) (66)

186 10-HYDROXYOLEUROPEIN



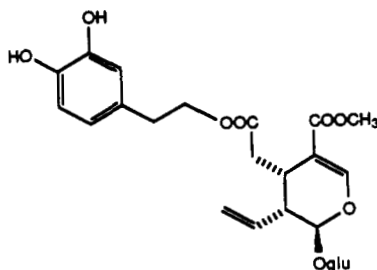
$C_{24}H_{32}O_{14}$ 556.52 [α] –153.7° (MeOH) uv 282, 231 (EtOH) (60 MHz CD_3OD) 5.78 (H-1, bs), 7.49 (H-3, s), 6.08 (H-8, br, 6.0), 3.70 (COOMe), 4.20 (H- α , t, 7.0), 2.78 (H- β , t, 7.0), 6.50–6.95 (H-2'', H-5'', H-6''); (CD_3OD) 94.9 (C-1), 155.1 (C-3), 109.4 (C-4), 32.4 (C-5), 41.4 (C-6), 173.1 (C-7), 129.5 (C-8), 131.2 (C-9), 59.3 (C-10), 168.5 (C-11), 52.0 (OMe), 100.1 (C-1'), 74.8 (C-2'), 78.5 (C-3'), 71.6 (C-4'), 78.0 (C-5'), 62.9 (C-6'), 66.9 (C- α), 35.4 (C- β), 130.8 (C-1''), 116.6 (C-2''), 146.3 (C-3''), 145.0 (C-4''), 117.2 (C-5''), 121.4 (C-6''). *Ligustrum japonicum* (Oleaceae) (97)

187 10-ACETOXYOLEUROPEIN



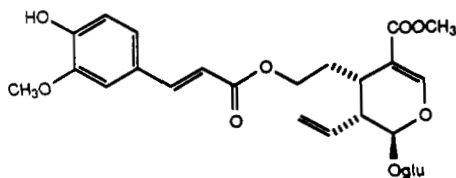
$C_{27}H_{34}O_{15}$ 598.56 $[\alpha] -191.1^\circ$ (MeOH) (100 MHz DMSO- d_6) 6.00 (H-8, br, 7), 4.67 (H-10, dd, 7, 3); (CD₃OD) 94.3 (C-1), 154.9 (C-3), 109.1 (C-4), 32.4 (C-5), 41.1 (C-6), 172.8 (C-7)^a, 124.4 (C-8), 133.9 (C-9), 61.8 (C-10), 168.3 (C-11), 52.0 (OMe), 100.9 (C-1'), 74.7 (C-2'), 78.4 (C-3'), 71.4 (C-4'), 77.9 (C-5'), 62.7 (C-6'), 66.9 (C- α), 35.4 (C- β), 130.7 (C-1''), 116.4 (C-2''), 146.2 (C-3''), 144.9 (C-4''), 117.1 (C-5''), 121.3 (C-6''), 20.8 (O=CMe), 172.6 (O=CMe)^a. *Osmanthus fragrans* (Oleaceae) (68,88)

188 OLEUROSIDE

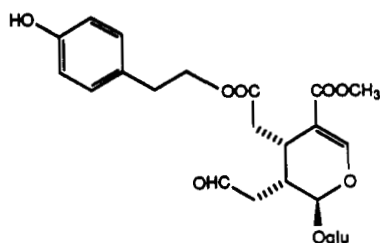


$C_{25}H_{32}O_{13}$ 540.52 $[\alpha] -83.7^\circ$ (MeOH) uv 290, 283, 230 (MeOH) (200 MHz CD₃OD) 5.45 (H-1, d, 4.2), 7.46 (H-3, d, 1.7), 3.22 (H-5, m), 2.87 (H-6, dd, 16.1, 5.4), 2.30 (H-6, dd, 16.1, 8.8), 5.57 (H-8, bdt, 18.2, 9.3), 2.70 (H-9, ddd, 9.3, 4.4, 4.2), 5.15 (H-10, dd, 9.3, 1.5), 5.14 (H-10, dd, 18.2, 1.5), 3.65 (COOMe), 4.66 (H-1', d, 7.6), 3.90 (H-6', bd, 11.3), 4.18 (H- α , t, 6.8), 2.76 (H- β , t, 6.8), 6.67 (H-2'', d, 2.0), 6.70 (H-5'', d, 7.8), 6.55 (H-6'', dd, 7.8, 2.0); (CD₃OD) 97.5 (C-1), 153.7 (C-3), 110.0 (C-4), 29.0 (C-5), 35.5 (C-6'), 174.3 (C-7), 134.4 (C-8), 45.3 (C-9), 120.6 (C-10), 168.8 (C-11), 51.7 (OMe), 100.0 (C-1'), 74.6 (C-2'), 78.3 (C-3'), 71.5 (C-4'), 78.0 (C-5'), 62.7 (C-6'), 66.7 (C- α), 35.4 (C- β)^a, 130.9 (C-1''), 117.1 (C-2''), 146.2 (C-3''), 144.9 (C-4''), 116.5 (C-5''), 121.3 (C-6''). *Olea europaea* (Oleaceae) (98)

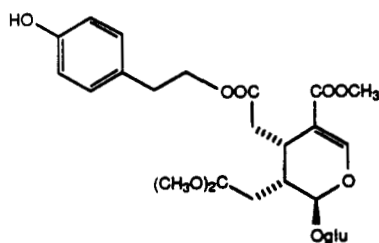
189 METHYLGRANDIFLOROSIDE



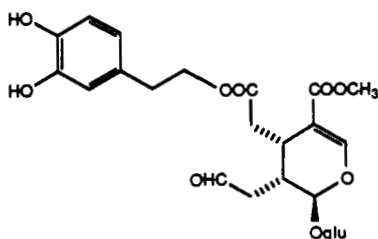
$C_{27}H_{34}O_{13}$ 566.56 (pentaacetate 270 MHz CDCl₃) 5.3 (H-1), 7.38 (H-3, bs), 2.87 (H-5, dddd, 5, 1), 2.28 (H-6, m), 1.73 (H-6, m), 4.27, 4.15 (H-7), 5.63 (H-8, ddd, 17.5, 9, 9), 2.70 (H-9, ddq, 9, 5, 1.5), 5.3, 5.2 (H-10), 3.70 (COOMe), 4.89 (H-1', d, 8), 5.02 (H-2', dd, 9, 8), 5.23 (H-3', t, 9), 5.11 (H-4', t, 9), 3.70 (H-5'), 4.30 (H-6', dd, 12.5, 4.5), 4.15 (H-6', dd, 12.5, 2.5), 6.30 (H- α , d, 16), 7.61 (H- β , d, 16), 7.26 (H-2'', d, 1.5), 6.98 (H-5'', d, 8.5), 7.40 (H-6'', dd, 8.5, 1.5), 3.87 (ArOMe), 2.09, 2.03, 2.01, 1.94 (OAc), 2.33 (ArOAc); (pentaacetate CDCl₃) 96.3 (C-1)^a, 150.7 (C-3), 110.1 (C-4), 28.1 (C-5), 27.8 (C-6), 62.4 (C-7)^b, 132.8 (C-8), 43.1 (C-9), 120.3 (C-10), 167.0 (C-11)^c, 51.3 (OMe), 96.0 (C-1')^a, 70.6 (C-2'), 72.6 (C-3'), 68.3 (C-4'), 72.3 (C-5'), 61.8 (C-6')^b, 166.9 (C=O)^c, 116.8 (C- α), 143.5 (C- β), 127.7 (C-1''), 112.4 (C-2''), 152.8 (C-3''), 140.1 (C-4''), 127.6 (C-5''), 122.1 (C-6''), 56.0 (ArOMe), 20.7, 20.6 (3 \times), 20.2 (O=CMe), 170.6, 170.1, 169.3 (2 \times), 168.9, 168.7 (O=CMe). *Exacum tetragonum* (Gentianaceae) (99)

190 LIGUSTALOSIDE B (contaminated by acetal, hemi-acetal, and hydrate forms)

$C_{25}H_{32}O_{13}$ 540.52 $[\alpha] -120.0^\circ$ (MeOH) uv 284, 277, 240, 226 (?) (60 MHz CD_3OD) 7.45 (H-3, bs), 9.58 (H-10, bs), 3.65 (COOMe), 4.20 (H- α , t, 7.0), 2.83 (H- β , t, 7.0), 6.88 (H-2", H-3"); (CD_3OD) 97.8 (C-1), 154.1 (C-3), 110.6 (C-4), 30.8 (C-5), 36.5 (C-6), 174.3 (C-7), 42.0 (C-8), 37.4 (C-9), 202.7 (C-10), 168.9 (C-11), 51.8 (OMe), 100.8 (C-1'), 74.8 (C-2'), 78.4 (C-3'), 71.6 (C-4'), 78.0 (C-5'), 62.8 (C-6'), 66.9 (C- α), 35.2 (C- β), 130.1 (C-1"), 130.9 (C-2"), 116.4 (C-3"), 157.0 (C-4"). *Ligustrum japonicum* (Oleaceae) (97)

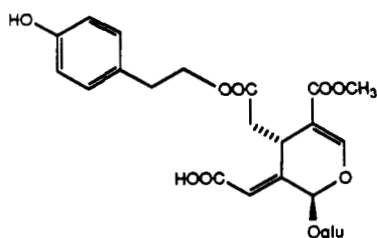
191 LIGUSTALOSIDE B DIMETHYL ACETAL

$C_{27}H_{38}O_{14}$ 586.59 $[\alpha] -125.5^\circ$ (MeOH) (60 MHz CD_3OD) 5.42 (H-1, d, 7.3), 7.48 (H-3, s), 3.64 (COOMe), 3.35 (OMe, 6H), 4.19 (H- α , t, 7.0), 2.82 (H- β , t, 7.0), 6.89 (H-2", H-3", q, 8.6); (CD_3OD) 98.2 (C-1), 154.4 (C-3), 110.6 (C-4), 30.7 (C-5), 36.5 (C-6), 174.7 (C-7), 35.0 (C-8), 37.2 (C-9), 98.6 (C-10), 169.1 (C-11), 52.0 (OMe), 100.8 (C-1'), 74.7 (C-2'), 78.2 (C-3'), 71.5 (C-4'), 77.9 (C-5'), 62.8 (C-6'), 66.9 (C- α), 35.0 (C- β), 130.2 (C-1"), 131.1 (C-2"), 116.5 (C-3"), 157.0 (C-4"). *Ligustrum ovalifolium* (Oleaceae) (97)

192 LIGUSTALOSIDE A (contaminated by acetal, hemi-acetal, and hydrate forms)

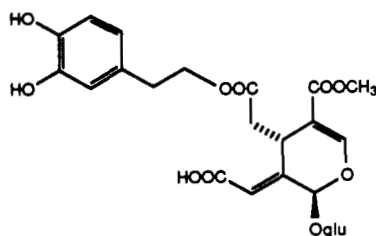
$C_{25}H_{32}O_{14}$ 556.52 $[\alpha] -120.1^\circ$ (MeOH) uv 282, 231 (?) (60 MHz CD_3OD) 7.48 (H-3, bs), 9.63 (H-10, bs), 3.65 (COOMe), 4.21 (H- α , t, 7.0), 2.78 (H- β , t, 7.0), 6.42-6.85 (H-2", H-5", H-6"); (CD_3OD) 97.9 (C-1), 154.1 (C-3), 110.6 (C-4), 30.8 (C-5), 36.6 (C-6), 174.3 (C-7), 42.0 (C-8), 37.3 (C-9), 202.8 (C-10), 168.9 (C-11), 51.8 (OMe), 100.8 (C-1'), 74.8 (C-2'), 78.4 (C-3'), 71.7 (C-4'), 78.0 (C-5'), 62.8 (C-6'), 66.9 (C- α), 35.4 (C- β), 130.9 (C-1"), 116.5 (C-2")^a, 146.2 (C-3"), 144.9 (C-4"), 117.1 (C-5")^a, 121.3 (C-6"). *Ligustrum japonicum* (Oleaceae) (97)

193 LIGUSTROSIDIC ACID



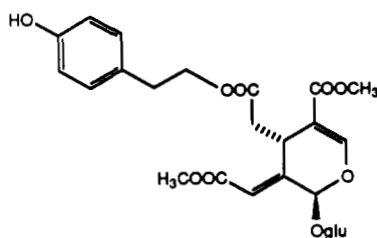
$C_{25}H_{30}O_{14}$ 554.50 pentaacetate $[\alpha] -130.2^\circ$ ($CHCl_3$) uv 271, 233 (MeOH) (pentaacetate 60 MHz $CDCl_3$) 5.92 (H-1, bd, 1.5), 7.49 (H-3, s), 6.27 (H-8, bs), 3.73 (COOMe), 6.58 (COOH, bs), 7.12 (H-2", H-3", q, 8.9), 2.04 (OAc, 12H), 2.29 (ArOAc); (pentaacetate $CDCl_3$) 93.2 (C-1), 152.8 (C-3), 108.2 (C-4), 31.3 (C-5), 39.4 (C-6), — (C-7), 118.9 (C-8), 147.9 (C-9), — (C-10), 166.6 (C-11), 51.7 (OMe), 97.4 (C-1'), 71.0 (C-2'), 72.7 (C-3'), 68.4 (C-4'), 72.5 (C-5'), 61.9 (C-6'), 65.2 (C- α), 34.4 (C- β), 135.7 (C-1"), 130.1 (C-2"), 121.9 (C-3"), 149.8 (C-4"), 20.6 (O=CMe), 171.7, 171.0, 170.6, 169.7, 168.8 (O=CMe). *Ligustrum japonicum* (Oleaceae) (92)

194 OLEUROPEINIC ACID



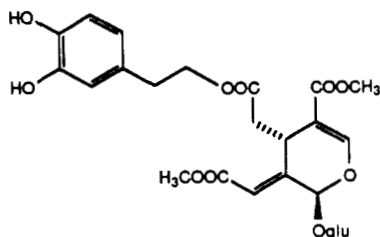
$C_{25}H_{30}O_{15}$ 570.50 hexaacetate $[\alpha] -120.3^\circ$ ($CHCl_3$) uv 271, 235 ($CHCl_3$) (hexaacetate 60 MHz $CDCl_3$) 5.91 (H-1, bd, 1.5), 7.49 (H-3, s), 6.28 (H-8, bs), 3.72 (COOMe), 6.58 (COOH, bs), 6.83–7.15 (H-2", H-5", H-6"), 2.08, 2.04, 2.03 (OAc, 12H), 2.28 (ArOAc, 6H); (hexaacetate $CDCl_3$) 93.2 (C-1), 152.8 (C-3), 108.2 (C-4), 31.2 (C-5), 39.4 (C-6), — (C-7), 118.9 (C-8), 147.7 (C-9), — (C-10), 166.6 (C-11), 51.7 (OMe), 97.5 (C-1'), 71.0 (C-2'), 72.7 (C-3'), 68.4 (C-4'), 72.5 (C-5'), 61.9 (C-6'), 64.7 (C- α), 34.3 (C- β), 137.0 (C-1"), 123.6 (C-2"), 142.3 (C-3"), 141.1 (C-4"), 124.0 (C-5"), 127.2 (C-6"), 20.6 (O=CMe), 171.6, 171.0, 170.5, 169.7, 168.7, 168.0 (O=CMe). *Ligustrum japonicum* (Oleaceae) (92)

195 LIGUSTROSIDIC ACID METHYL ESTER



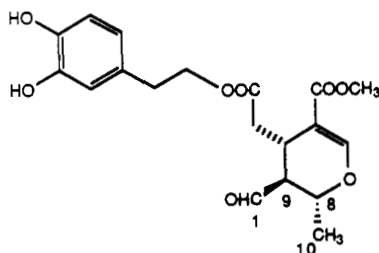
$C_{26}H_{32}O_{14}$ 568.53 pentaacetate uv 271, 233 (MeOH) (pentaacetate 60 MHz $CDCl_3$) 5.92 (H-1, bd, 1.5), 7.49 (H-3, s), 6.27 (H-8, dd, 1.5, 0.7), 3.74, 3.73 (COOMe), 7.12 (H-2", H-3", q, 8.9), 2.04 (OAc, 12H), 2.29 (ArOAc); (pentaacetate $CDCl_3$) 93.3 (C-1), 152.8 (C-3), 108.2 (C-4), 31.3 (C-5), 39.4 (C-6), — (C-7), 119.0 (C-8), 147.1 (C-9), 166.3 (C-10), 166.6 (C-11), 51.7 (OMe), 97.4 (C-1'), 71.0 (C-2'), 72.7 (C-3'), 68.4 (C-4'), 72.4 (C-5'), 61.9 (C-6'), 65.1 (C- α), 34.4 (C- β), 135.7 (C-1"), 130.1 (C-2"), 121.9 (C-3"), 149.8 (C-4"), 20.6 (O=CMe), 171.7, 170.6, 169.7 (O=CMe). CH_2N_2 methylation of ligustrosidic acid (92)

196 OLEUROPEINIC ACID METHYL ESTER



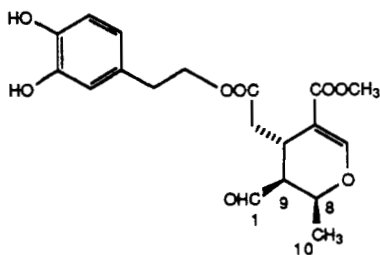
$C_{26}H_{32}O_{15}$ 584.53 hexaacetate uv 271, 235 (MeOH) (hexaacetate 60 MHz $CDCl_3$) 5.91 (H-1, bd, 1.5), 7.50 (H-3, s), 6.28 (H-8, dd, 1.5, 0.7), 3.74, 3.73 (COOMe), 6.83–7.15 (H-2'', H-5'', H-6''), 2.05, 2.04, 2.03 (OAc, 12H), 2.29, 2.28 (ArOAc, 6H); (hexaacetate $CDCl_3$) 93.3 (C-1), 152.8 (C-3), 108.2 (C-4), 31.2 (C-5), 39.4 (C-6), — (C-7), 119.0 (C-8), 146.9 (C-9), 166.3 (C-10), 166.6 (C-11), 51.7 (OMe), 97.5 (C-1'), 71.0 (C-2'), 72.7 (C-3'), 68.4 (C-4'), 72.5 (C-5'), 61.9 (C-6'), 64.7 (C- α), 34.3 (C- β), 136.9 (C-1''), 123.6 (C-2''), 142.4 (C-3''), 141.1 (C-4''), 124.0 (C-5''), 127.2 (C-6''), 20.6 (O=CMe), 171.5, 170.5, 169.7 (O=CMe). CH_2N_2 methylation of oleuropeinic acid (92)

197 compound not named



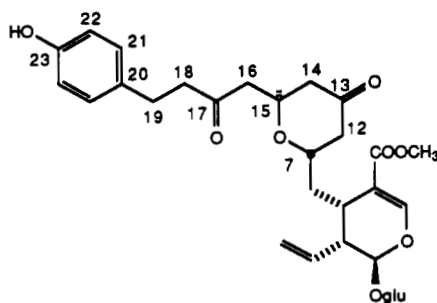
$C_{19}H_{22}O_8$ 378.38 $[\alpha] +35.7^\circ$ ($CHCl_3$) uv 280, 230 (MeOH) (200 MHz $CDCl_3$) 9.50 (H-1, d, 1.8), 7.57 (H-3, d, 1.4), 3.38 (H-5, m, 8.6, 5.5, 3.5, 1.1), 2.88 (H-6, dd, 16.2, 8.6), 2.53 (H-6, dd, 16.2, 3.5), 4.46 (H-8, ddq, 6.6, 5.5, 1.1), 2.57 (H-9, dt, 5.5, 1.8), 1.38 (H-10, d, 6.6), 3.72 (COOMe), 4.28 (H- α , dt, 11.0, 6.6), 4.26 (H- α , dt, 11.0, 6.6), 2.80 (H- β , br, 6.6), 6.78 (H-2', d, 2.0), 6.74 (H-5', d, 8.0), 6.60 (H-6', dd, 8.0, 2.0); ($CDCl_3$) 199.6 (C-1), 153.4 (C-3), 129.9 (C-4), 26.8 (C-5), 36.9 (C-6), 171.5 (C-7), 70.5 (C-8), 54.1 (C-9), 19.1 (C-10), 167.1 (C-11), 51.3 (OMe), 65.0 (C- α), 34.0 (C- β), 106.1 (C-1'), 115.0 (C-2'), 143.2 (C-3'), 142.5 (C-4'), 115.8 (C-5'), 120.8 (C-6'). *Olea europaea* (Oleaceae) (65)

198 compound not named

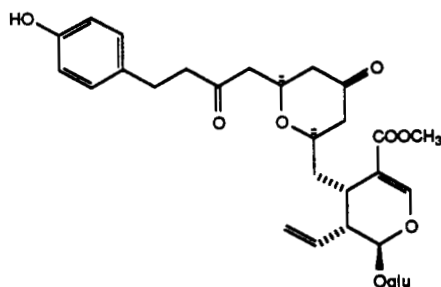


$C_{19}H_{22}O_8$ 378.38 $[\alpha] -44.0^\circ$ ($CHCl_3$) uv 280, 230 (MeOH) (200 MHz $CDCl_3$) 9.61 (H-1, dd, 2.1, 1.0), 7.66 (H-3, bs, 0.9, 0.5), 3.37 (H-5, m, 11.2, 2.6, 1.3), 2.86 (H-6, dd, 16.0, 11.2), 2.22 (H-6, dd, 16.0, 2.6), 4.18 (H-8, m, 6.7, 2.5, 1.0), 2.62 (H-9, m, 2.5, 2.1, 1.3, 0.5), 1.56 (H-10, d, 6.7), 3.74 (COOMe), 4.37, 4.20 (H- α , m), 2.82 (H- β , m), 6.85 (H-2', d, 2.0), 6.81 (H-5', d, 8.0), 6.63 (H-6', dd, 8.0, 2.0); ($CDCl_3$) 200.0 (C-1), 156.9 (C-3), 130.1 (C-4), 28.1 (C-5), 38.9 (C-6), 170.9 (C-7), 69.6 (C-8), 50.9 (C-9), 17.8 (C-10), 167.1 (C-11), 51.6 (OMe), 65.4 (C- α), 34.2 (C- β), 106.3 (C-1'), 115.1 (C-2'), 143.3 (C-3'), 142.9 (C-4'), 116.2 (C-5'), 121.0 (C-6'). *Olea europaea* (Oleaceae) (65)

199 HYDRANGENOSIDE A

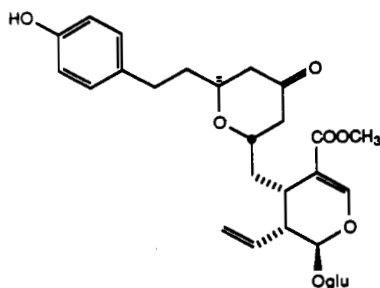


$C_{31}H_{40}O_{13}$ 620.65 $[\alpha] -85.2^\circ$ (MeOH) uv 276, 238, 226 (MeOH) (100 MHz CD_3OD) 7.47 (H-3, s), 3.68 (COOMe), 2.10–3.00 (H-12, H-14, H-16), 2.80 (H-18, H-19, bs), 6.62–7.10 (H-21, H-22); (CD_3OD) 97.5 (C-1), 153.6 (C-3), 111.7 (C-4), 29.6 (C-5), 35.9 (C-6), 69.5 (C-7)^a, 135.4 (C-8), 45.2 (C-9), 119.9 (C-10), 168.9 (C-11), 51.8 (OMe), 46.1 (C-12)^b, 209.5 (C-13)^c, 46.9 (C-14)^b, 72.2 (C-15)^a, 47.1 (C-16)^b, 210.0 (C-17)^c, 48.0 (C-18)^b, 29.6 (C-19), 133.0 (C-20), 130.2 (C-21), 116.1 (C-22), 156.2 (C-23), 99.8 (C-1'). *Hydrangea macrophylla* var. *macrophylla* (Saxifragaceae) (100)

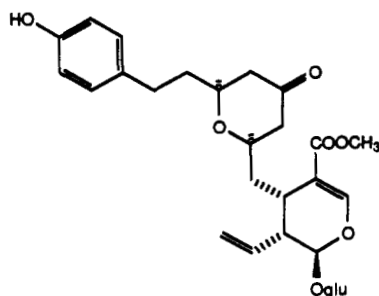
200 HYDRANGENOSIDE B (7-*epi*-Hydrangenoside A)

$C_{31}H_{40}O_{13}$ 620.65 $[\alpha] -80.0^\circ$ (MeOH) uv 279, 227.5 (MeOH) (100 MHz CD_3OD) 7.44 (H-3, s), 1.72 (H-6, m), 3.67 (COOMe), 2.78 (H-18, H-19, bs), 6.68–7.01 (H-21, H-22); (pentaacetate $CDCl_3$) 95.3 (C-1)^a, 150.1 (C-3), 111.0 (C-4), 26.1 (C-5), 34.3 (C-6), 72.8 (C-7)^b, 132.9 (C-8), 42.5 (C-9), 120.1 (C-10), 166.5 (C-11), 51.0 (OMe), 45.0 (C-12)^c, 205.7 (C-13)^d, 46.8 (C-14)^c, 73.7 (C-15)^b, 47.8 (C-16)^c, 206.3 (C-17)^d, 48.4 (C-18)^c, 28.8 (C-19), 138.3 (C-20), 129.1 (C-21), 121.2 (C-22), 148.7 (C-23), 95.8 (C-1')^a. *Hydrangea macrophylla* var. *macrophylla* (Saxifragaceae) (100)

201 HYDRANGENOSIDE C

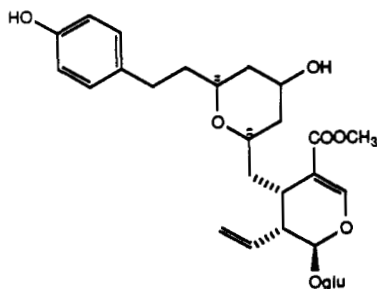


$C_{29}H_{38}O_{12}$ 578.61 $[\alpha] -94.7^\circ$ (MeOH) uv 280, 227 (MeOH) (100 MHz CD_3OD) 7.47 (H-3, s), 1.78 (H-6, m), 3.68 (COOMe), 6.73–7.07 (H-19, H-20); (pentaacetate $CDCl_3$) 96.0 (C-1)^a, 150.8 (C-3), 111.6 (C-4), 27.5 (C-5), 34.4 (C-6)^b, 70.2 (C-7)^c, 133.2 (C-8), 44.1 (C-9), 120.5 (C-10), 167.0 (C-11), 51.2 (OMe), 46.7 (C-12)^d, 207.1 (C-13), 47.0 (C-14)^d, 71.6 (C-15)^c, 35.1 (C-16)^b, 30.8 (C-17), 138.9 (C-18), 129.5 (C-19), 121.5 (C-20), 149.0 (C-21), 96.3 (C-1')^a. *Hydrangea macrophylla* var. *macrophylla* (Saxifragaceae) (100)

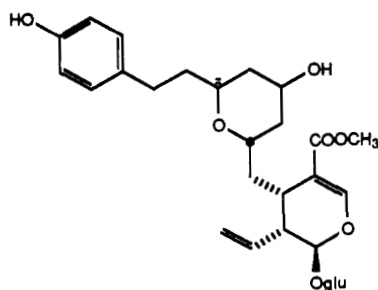
202 HYDRANGENOSIDE D (7-*epi*-Hydrangenoside C)

$C_{29}H_{38}O_{12}$ 578.61 mp 186–187° $[\alpha] -126.3^\circ$ (MeOH) uv 278, 227 (MeOH) (100 MHz CD_3OD) 5.33 (H-1, d, 1.5), 7.47 (H-3, s), 3.68 (COOMe), 2.70 (H-12, H-14), 6.75–7.08 (H-19, H-20); (pentaacetate $CDCl_3$) 95.6 (C-1)^a, 150.5 (C-3), 111.2 (C-4), 25.5 (C-5), 34.0 (C-6)^b, 75.2 (C-7)^c, 133.0 (C-8), 42.3 (C-9), 120.6 (C-10), 166.7 (C-11), 51.1 (OMe), 48.2 (C-12)^d, 206.7 (C-13), 51.1 (C-14)^d, 77.7 (C-15)^e, 37.1 (C-16)^b, 30.4 (C-17), 138.9 (C-18), 129.6 (C-19), 121.5 (C-20), 149.0 (C-21), 96.2 (C-1')^a, *Hydrangea macrophylla* var. *macrophylla* (Saxifragaceae) (100)

203 HYDRANGENOSIDE E

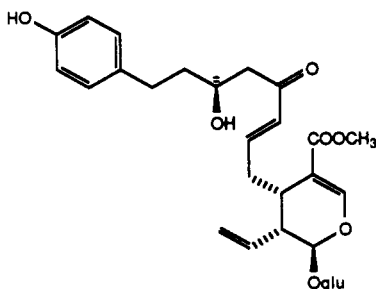


$C_{29}H_{40}O_{12}$ 580.63 $[\alpha] -108.7^\circ$ (MeOH) uv 285, 277.5, 225 (MeOH) (100 MHz CD_3OD) 7.38 (H-3, s), 1.48 (H-6, m), 3.64 (COOMe), 1.48 (H-12, H-14, H-16), 4.06 (H-13, m), 2.62 (H-17, t, 7), 6.70–7.03 (H-19, H-20), 4.64 (H-1', d); (CD_3OD) 100.0 (C-1), 152.9 (C-3), 112.1 (C-4), 28.5 (C-5), 35.8 (C-6), 69.9 (C-7)^a, 135.6 (C-8), 44.7 (C-9), 120.0 (C-10), 169.4 (C-11), 51.7 (OMe), 39.2 (C-12)^b, 65.4 (C-13), 40.9 (C-14)^b, 71.6 (C-15)^a, 39.7 (C-16)^b, 31.7 (C-17), 134.5 (C-18), 130.7 (C-19), 116.3 (C-20), 156.3 (C-21). *Hydrangea scandens* (Saxifragaceae) (100)

204 HYDRANGENOSIDE F (7-*epi*-Hydrangenoside E)

$C_{29}H_{40}O_{12}$ 580.63 $[\alpha] -87.0^\circ$ (MeOH) uv 277.5, 226.5 (MeOH) (100 MHz CD_3OD) 7.42 (H-3, s), 1.75 (H-6, m), 3.68 (COOMe), 1.75 (H-12, H-14, H-16), 2.57 (H-17, m), 6.70–7.07 (H-19, H-20). *Hydrangea scandens* (Saxifragaceae) (100)

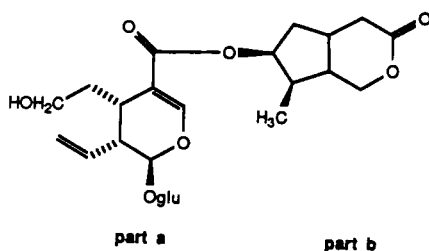
205 HYDRANGENOSIDE G



$C_{29}H_{38}O_{12}$ 578.61 $[\alpha] -104.1^\circ$ (MeOH) uv 278.5, 227 (MeOH) (100 MHz CD_3OD) 7.43 (H-3, s), 2.62 (H-5, H-6, H-9), 3.60 (COOMe), 5.96 (H-12, d, 16), 2.62 (H-14, m), 1.68 (H-16, m), 2.62 (H-17, m), 6.68–6.96 (H-19, H-20), 4.62 (H-1', d, 8); (CD_3OD) 97.5 (C-1)^a, 153.9 (C-3), 110.2 (C-4), 33.3 (C-5), 31.8 (C-6)^b, 148.4 (C-7), 135.0 (C-8), 45.1 (C-9), 120.1 (C-10), 168.9 (C-11), 51.9 (OMe), 132.9 (C-12), 201.7 (C-13), — (C-14), — (C-15), 33.8 (C-16)^b, 40.3 (C-17)^b, 134.0 (C-18), 130.3 (C-19), 116.2 (C-20), 156.1 (C-21), 100.0 (C-1')^a. *Hydrangea scandens* (Saxifragaceae) (100)

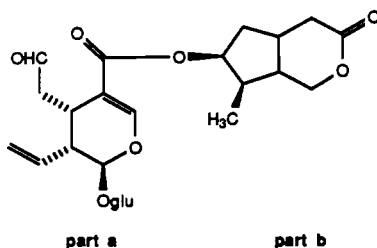
Group 12 (bis-secoiridoids)

206 ABELIOSIDE B



$C_{25}H_{36}O_{12}$ 528.55 pentaacetate mp 211–213° $[\alpha] -38^\circ$ ($CHCl_3$) uv 232 (EtOH) (pentaacetate 200 MHz $CDCl_3$) 5.2–5.4 (H-1_a), 7.34 (H-3_a, d, 1.5), 2.6–3.0 (H-5_a), 4.04–4.3 (H-7_a), 5.60 (H-8_a, dt, 18, 9), 2.6–3.0 (H-9_a), 5.2–5.4 (H-10_a), 4.90 (H-1'_a, d, 8), 5.03 (H-2'_a, dd, 9, 8), 5.2–5.4 (H-3'_a), 5.13 (H-4'_a, t, 9), 4.0–4.3 (H-6'_a), 4.31 (H-6'_a, dd, 12, 4), 4.0–4.3 (H-1_b), 4.35 (H-1_b, dd, 11.5, 4), 2.42 (H-4_b, dd, 15, 4), 2.6–3.0 (H-4_b, H-5_b), 5.2–5.4 (H-7_b), 1.05 (H-10_b, d, 6.5), 2.12, 2.06, 2.04, 2.02, 1.95 (OAc); (pentaacetate $CDCl_3$) 96.3 (C-1_a), 150.8 (C-3_a), 111.0 (C-4_a), 27.6 (C-5_a), 75.5 (C-6_a), 62.1 (C-7_a), 132.6 (C-8_a), 42.9 (C-9_a), 120.4 (C-10_a), 166.0 (C-11_a), 96.0 (C-1'_a), 70.6 (C-2'_a), 72.4 (C-3'_a), 68.2 (C-4'_a), 72.2 (C-5'_a), 61.6 (C-6'_a), 68.2 (C-1_b), 172.8 (C-3_b), 34.4 (C-4_b), 32.8 (C-5_b), 39.1 (C-6_b), 78.4 (C-7_b), 40.4 (C-8_b), 42.5 (C-9_b), 13.1 (C-10_b), 20.7, 20.6 (2×), 20.4 (O=CMe), 171.1, 170.7, 169.4 (2×), 168.0 (O=CMe). *Abelia grandiflora* (Caprifoliaceae) (101)

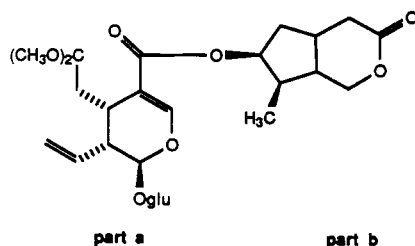
207 ABELIOSIDE A



$C_{25}H_{34}O_{12}$ 526.54 $[\alpha] -38^\circ$ (MeOH) uv 236 (EtOH) (200 MHz D_2O) 5.51 (H-1_a, d, 6.5), 7.53 (H-3_a, s), 3.2–3.5 (H-5_a, m), 2.53 (H-6_a, bdd, 17.5, 8), 2.7–3.0 (H-6_a, m), 9.70 (H-7_a, bs), 5.66 (H-8_a, dt, 18, 9), 2.7–3.0 (H-9_a, m), 5.26 (H-10_a, bd, 18), 5.25 (H-10_a, bd, 9), 4.69 (H-1'_a, d, 8), 3.91 (H-6'_a, bd, 12), 3.67 (H-6'_a, dd, 12, 5), 4.43 (H-1_b, dd, 11.5, 4), 4.21 (H-1_b, dd, 11.5, 3.5), 2.38 (H-4_b, dd, 15, 4), 2.7–3.0 (H-4_b, H-5_b), 2.12 (H-6_b, bd, 14, 8), 1.45 (H-6_b, ddd, 14, 10, 4), 5.21 (H-7_b, br, 3.5), 2.0–2.3 (H-8_b, H-9_b), 1.03 (H-10_b, d, 6.5); (tetraacetate $CDCl_3$) 95.9 (C-1_a), 151.1 (C-3_a), 109.7 (C-4_a), 25.5 (C-5_a), 43.4 (C-6_a), 200.3 (C-7_a), 132.3 (C-8_a), 43.7 (C-9_a),

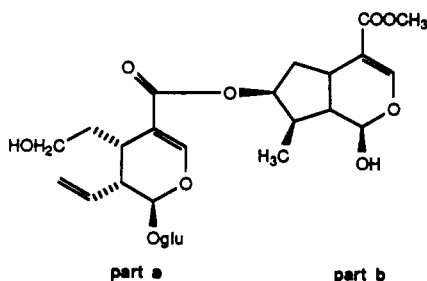
121.2 (C-10_a), 165.8 (C-11_a), 95.9 (C-1'_a), 70.7 (C-2'_a), 72.3 (C-3'_a), 68.1 (C-4'_a), 72.3 (C-5'_a), 61.6 (C-6'_a), 68.1 (C-1_b), 172.8 (C-3_b), 34.4 (C-4_b), 32.8 (C-5_b), 39.1 (C-6_b), 78.4 (C-7_b), 40.5 (C-8_b), 42.5 (C-9_b), 13.1 (C-10_b), 20.7, 20.4 (3×) (O=CMe), 170.6, 170.4, 169.4, 168.9 (O=CMe). *Abelia grandiflora* (Caprifoliaceae) (101)

208 ABELIOSIDE A DIMETHYL ACETAL



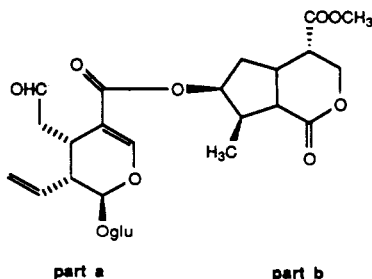
C₂₇H₄₀O₁₃ 572.61 [α]_D²⁰ -39° (MeOH) uv 235 (EtOH) (200 MHz D₂O) 5.62 (H-1_a, d, 6.5), 7.54 (H-3_a, s), 2.9-3.0 (H-5_a), 1.85-1.95 (H-6_a, m), 4.61 (H-7_a, dd, 7, 4.5), 5.80 (H-8_a, dt, 18, 9), 2.76 (H-9_a, m), 5.42 (H-10_a, bd, 18), 5.39 (H-10_a, bd, 9), 4.87 (H-1'_a, d, 8), 3.32, 3.30 (OMe), 4.52 (H-1_b, dd, 11.5, 4), 4.35 (H-1_b, dd, 11.5, 3.5), 2.85 (H-4_b, dd, 15, 7), 2.50 (H-4_b, dd, 15, 4), 2.9-3.0 (H-5_b, m), 2.22 (H-6_b, bd, 14, 8), 1.53 (H-6_b, ddd, 14, 10, 4), 5.22 (H-7_b, br, 3.5), 2.13 (H-8_b, m), 2.35 (H-9_b, m), 1.08 (H-10_b, d, 6.5); (tetraacetate CDCl₃) 96.3 (C-1_a), 150.3 (C-3_a), 111.5 (C-4_a), 27.0 (C-5_a), 31.4 (C-6_a), 102.5 (C-7_a), 133.2 (C-8_a), 43.3 (C-9_a), 120.1 (C-10_a), 166.0 (C-11_a), 96.0 (C-1'_a), 70.6 (C-2'_a), 72.4 (C-3'_a), 68.2 (C-4'_a), 72.2 (C-5'_a), 61.7 (C-6'_a), 68.2 (C-1_b), 172.7 (C-3_b), 34.3 (C-4_b), 32.7 (C-5_b), 39.1 (C-6_b), 78.2 (C-7_b), 40.4 (C-8_b), 42.4 (C-9_b), 13.0 (C-10_b), 53.4, 51.6 (OMe), 20.6, 20.5, 20.3 (2×) (O=CMe), 170.5, 170.1, 169.2, 168.7 (O=CMe). *Abelia grandiflora* (Caprifoliaceae) artifact (101)

209 LACINIATOSIDE V



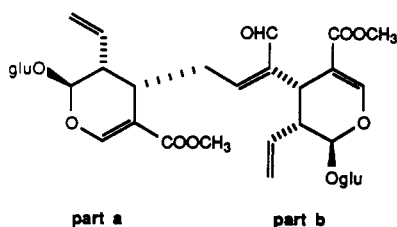
C₂₇H₃₈O₁₄ 586.59 [α]_D²⁰ -98° (MeOH) uv 237 (?) (300 MHz Me₂CO-*d*₆) 5.56 (H-1_a, d, 6.9), 7.52 (H-3_a, d, 1.0), 2.88 (H-5_a, t, 6.5, 5.5), 1.83 (H-6_a, ddt, 14, 7, 6.5), 1.72 (H-6_a, dq, 14, 7, 7), 3.58 (H-7_a), 5.79 (H-8_a, ddd, 17.5, 10.5, 8.1), 2.64 (H-9_a, dddd, 8.1, 6.9, 0.9, 0.7), 5.30 (H-10_a, ddd, 17.5, 1.8, 0.9), 5.21 (H-10_a, ddd, 10.5, 1.8, 0.7), 4.74 (H-1'_a, d, 8), 3.24 (H-2'_a, dd, 8.9, 8), 3.3-3.5 (H-3'_a-H-5'_a), 3.88 (H-6'_a, dd, 12), 3.67 (H-6'_a), 4.0-4.4 (sugar hydroxyl protons), 5.00 (H-1_b, t, 6.5, 6.4), 7.42 (H-3_b, d, 1.4), 3.13 (H-5_b, dddd, 9.2, 8.9, 7.1, 1.4), 2.33 (H-6_b, ddd, 14, 7.1, 1.6), 1.66 (H-6_b, ddd, 14, 9.2, 4.8), 5.24 (H-7_b, td, 5.4, 4.8, 1.6), 2.17 (H-8_b, pd, 7.1, 7.1, 5.4), 1.93 (H-9_b, ddd, 8.9, 7.1, 6.5), 1.09 (H-10_b, d, 7.1), 3.67 (COOMe), 6.40 (C-1_b hydroxyl proton, d); (Me₂CO-*d*₆) 97.5 (C-1_a), 152.9 (C-3_a), 111.7 (C-4_a), 30.6 (C-5_a), 33.9 (C-6_a), 60.6 (C-7_a), 135.9 (C-8_a), 44.9 (C-9_a), 118.9 (C-10_a), 167.6 (C-11_a), 100.0 (C-1'_a), 74.4 (C-2'_a), 77.9 (C-3'_a)^a, 71.4 (C-4'_a), 77.7 (C-5'_a)^a, 62.7 (C-6'_a), 96.6 (C-1_b), 153.0 (C-3_b), 111.5 (C-4_b), 33.3 (C-5_b), 40.4 (C-6_b), 77.3 (C-7_b), 41.3 (C-8_b), 48.1 (C-9_b), 14.3 (C-10_b), 168.3 (C-11), 51.3 (OMe). *Dipsacus laciniatus* (Dipsacaceae) (102)

210 SCAEVOLOSIDE



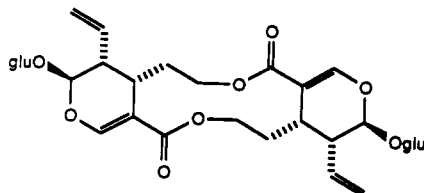
$C_{27}H_{36}O_{14}$ 584.57 tetraacetate $[\alpha] -36^\circ$ (CH_2Cl_2) uv 232 (MeOH) (tetraacetate 270 MHz $CDCl_3$) 5.32 (H-1_a, d, 3), 7.40 (H-3_a, d, 2), 3.32 (H-5_a, dddd, 9, 7, 5, 2), 2.88 (H-6_a, ddd, 18, 5, 1), 2.44 (H-6_a, ddd, 18, 7, 1), 9.73 (H-7_a, t, 1), 5.52 (H-8_a, ddd, 18, 9, 8), 2.79 (H-9_a, m), 5.2–5.4 (H-10_a, m), 4.92 (H-1'_a, d, 8), 5.03 (H-2'_a, dd, 9, 8), 5.2–5.4 (H-3'_a, m), 5.12 (H-4'_a, t, 9), 3.76 (H-5'_a, m), 4.29 (H-6'_a, dd, 12, 4), 4.16 (H-6'_a, dd, 12, 2), 4.48 (H-3_b, dd, 12, 4), 4.30 (H-3_b, dd, 12, 10), 2.55 (H-4_b, td, 10, 4), 3.01 (H-5_b, tdd, 11, 10, 7), 2.20 (H-6_b, ddd, 14, 7, 1), 1.54 (H-6_b, ddd, 14, 11, 4), 5.31 (H-7_b, td, 4, 1), 2.50 (H-8_b, m), 2.73 (H-9_b, dd, 11, 10), 1.20 (H-10_b, d, 7), 3.77 (COOMe), 1.95–2.11 (OAc); (tetraacetate $CDCl_3$) 95.9 (C-1_a), 151.2 (C-3_a), 109.0 (C-4_a), 25.6 (C-5_a), 43.5 (C-6_a), 200.2 (C-7_a), 132.1 (C-8_a), 43.6 (C-9_a), 121.0 (C-10_a), 165.6 (C-11_a), 95.9 (C-1'_a), 70.7 (C-2'_a), 72.3 (C-3'_a), 68.1 (C-4'_a), 72.4 (C-5'_a), 61.7 (C-6'_a), 172.9 (C-1_b), 67.2 (C-3_b), 45.7 (C-4_b)^a, 37.3 (C-5_b), 38.8 (C-6_b), 77.2 (C-7_b), 42.5 (C-8_b), 46.6 (C-9_b)^a, 14.4 (C-10_b), 171.1 (C-11), 52.5 (OMe), 20.7, 20.6 (2 \times), 20.3 (O=CMe), 170.5, 170.2, 169.2, 168.9 (O=CMe). *Scaevola racemigera* (Goodeniaceae) (103)

211 CENTAUROSIDE



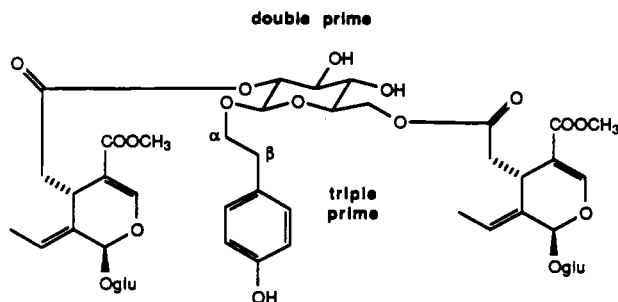
$C_{34}H_{46}O_{19}$ 758.73 $[\alpha] -130^\circ$ (MeOH) uv 233 (MeOH) (100 MHz CD_3OD) 7.49 (H-3_a, d, 1), 6.70 (H-7_a, t, 8.0), 7.54 (H-3_b, s), 9.02 (H-7_b, s), 3.72, 3.62 (COOMe); (DMSO- d_6) 95.4 (C-1_a), 150.7 (C-3_a), 107.1 (C-4_a), 29.6 (C-5_a), 28.3 (C-6_a), 155.2 (C-7_a), 133.7 (C-8_a), 43.1 (C-9_a), 118.6 (C-10_a), 166.2 (C-11_a), 95.5 (C-1_b), 152.3 (C-3_b), 108.7 (C-4_b), 31.5 (C-5_b), 140.8 (C-6_b), 193.8 (C-7_b), 134.0 (C-8_b), 44.0 (C-9_b), 119.6 (C-10_b), 166.5 (C-11), 51.0, 50.6 (OMe). *Erythraea centaurium* (Gentianaceae) (104)

212 LISIANTHOSIDE



$C_{32}H_{44}O_{18}$ 716.70 no data available. *Lisianthus jefensis* (Gentianaceae) (105)

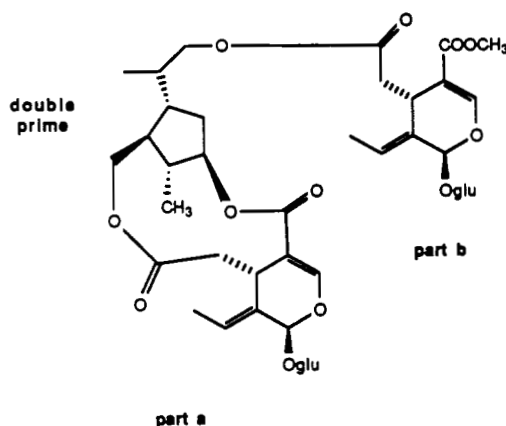
213 OLEONUEZHENIDE



$C_{48}H_{64}O_{27}$ 1073.02 $[\alpha] +62.3^\circ$ (EtOH) uv 280, 230 (EtOH) (400 MHz pyridine- d_5) 6.42, 6.29 (H-1, bs), 7.73, 7.69 (H-3, s), 3.02 (H-6, dd, 14.3, 4.0), 2.81 (H-6, dd, 14.3, 4.8), 2.75 (H-6, dd, 14.3, 8.5), 2.46 (H-6, dd, 14.3, 7.7), 6.18, 6.14 (H-8, q's, 7.0), 1.73, 1.69 (H-10, d's, 7.0), 3.64, 3.61 (COOMe), 5.50, 5.47 (H-1', d's, 7.7), 4.85 (H-1'', d, 8.1), 5.44 (H-2'', dd, 9.6, 8.1), 4.87 (H-6'', m), 4.22 (H- α , dd, 16.2, 7.7), 3.85 (H- α , dd, 16.2, 7.7), 2.97 (H- β , dd, 13.2, 7.7), 2.94 (H- β , dd, 13.2, 7.7), 7.25 (H-2''', d, 8.5), 7.14 (H-3''', d, 8.5); (D₂O) 94.7, 94.8 (C-1), 154.4 (C-3, 2 \times), 108.2 (C-4, 2 \times), 29.8, 30.2 (C-5), 39.4, 40.0 (C-6), 171.0, 173.0 (C-7), 124.6, 124.8 (C-8), 129.8 (C-9, 2 \times), 12.7, 12.8 (C-10), 168.4 (C-11, 2 \times), 51.7 (OMe, 2 \times), 99.6 (C-1', 2 \times), 72.8 (C-2', 2 \times), 76.4 (C-

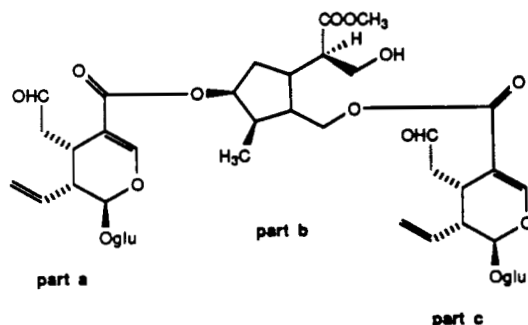
3', 2×), 69.6 (C-4', 2×), 75.8 (C-5', 2×), 60.8 (C-6', 2×), 100.2 (C-1''), 73.9 (C-2''), 73.9 (C-3''), 70.0 (C-4''), 73.4 (C-5''), 63.9 (C-6''), 70.2 (C-α), 34.3 (C-β), 130.1 (C-1'''), 129.8 (C-2'''), 115.2 (C-3'''), 154.4 (C-4'''). *Ligustrum japonicum* (Oleaceae) (91)

214 JASMOSIDE



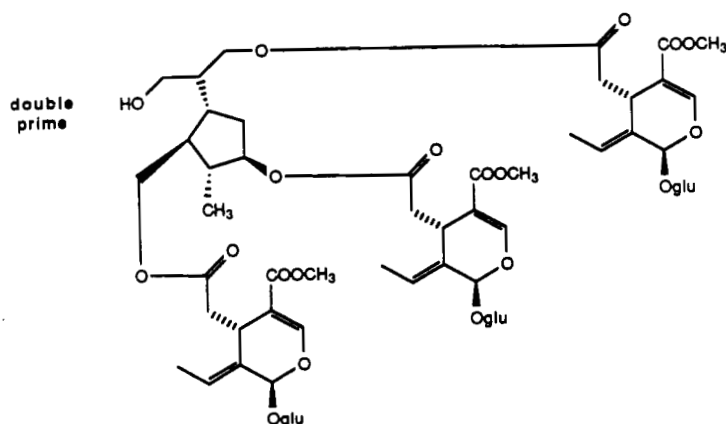
$C_{43}H_{60}O_{22}$ 928.93 $[\alpha] -236.4^{\circ}$ (MeOH) uv 237 (MeOH) (100 MHz CD_3OD) 5.95 (H-1_a, bs), 7.47 (H-3_a, s), 6.05 (H-8_a, bq, 7.0), 1.76 (H-10_a, bd, 7.0), 5.95 (H-1_b, bs), 7.53 (H-3_b, s), 6.11 (H-8_b, bq, 7.0), 1.76 (H-10_b, bd, 7.0), 1.01 (H-6'', d, 7.5), 1.09 (H-9'', d, 7.0), 3.71 (COOMe); (CD_3OD) 95.0 (C-1_a), 154.9 (C-3_a), 109.6 (C-4_a), 31.6 (C-5_a), 44.0 (C-6_a), 173.2 (C-7_a), 123.6 (C-8_a), 131.3 (C-9_a), 13.3 (C-10_a), 167.6 (C-11_a), 100.8 (C-1'_a, C-1'_b), 74.7 (C-2'_a, C-2'_b), 78.4 (C-3'_a, C-3'_b), 71.5 (C-4'_a, C-4'_b), 77.9 (C-5'_a, C-5'_b), 62.7 (C-6'_a, C-6'_b), 95.1 (C-1_b), 155.1 (C-3_b), 109.4 (C-4_b), 31.9 (C-5_b), 41.3 (C-6_b), 173.2 (C-7_b), 124.7 (C-8_b), 130.7 (C-9_b), 13.8 (C-10_b), 168.5 (C-11_b), 52.5 (OMe), 44.8 (C-1''), 52.0 (C-2''), 42.4 (C-3''), 36.1 (C-4''), 82.5 (C-5''), 20.8 (C-6''), 67.4 (C-7''), 39.6 (C-8''), 16.4 (C-9''), 69.7 (C-10''). *Jasminum mesnyi* (Oleaceae) (78)

215 PULOSARIOSIDE



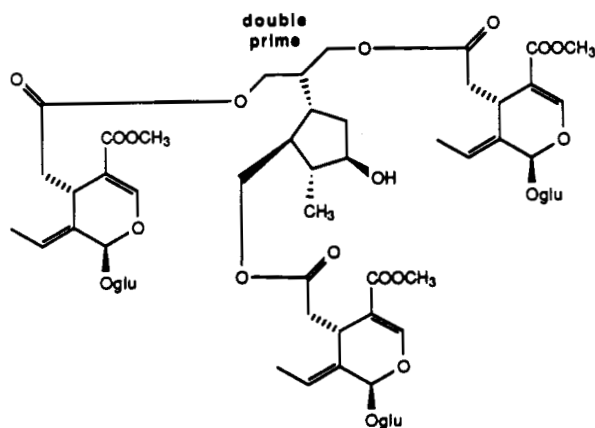
$C_{43}H_{60}O_{23}$ 944.93 mp 132° $[\alpha] -94^{\circ}$ (MeOH) uv 230 (MeOH) (pyridine- d_5) 96.6 (C-1_a), 152.7 (C-3_a), 109.1 (C-4_a), 27.3 (C-5_a), 44.4 (C-6_a), 200.6 (C-7_a), 133.9 (C-8_a), 49.3 (C-9_a), 119.6 (C-10_a), 166.5 (C-11_a), 64.3 (C-1_b), 62.9 (C-3_b), 46.1 (C-4_b), 41.0 (C-5_b), 36.0 (C-6_b), 76.3 (C-7_b), 37.5 (C-8_b), 44.3 (C-9_b), 14.5 (C-10_b), 174.8 (C-11_b), 96.6 (C-1_c), 152.7 (C-3_c), 108.9 (C-4_c), 26.9 (C-5_c), 44.1 (C-6_c), 200.6 (C-7_c), 133.9 (C-8_c), 49.3 (C-9_c), 119.6 (C-10_c), 166.3 (C-11_c). *Alyxia reinwardtii* (Apocynaceae) (106)

216 SAMBACOSIDE A



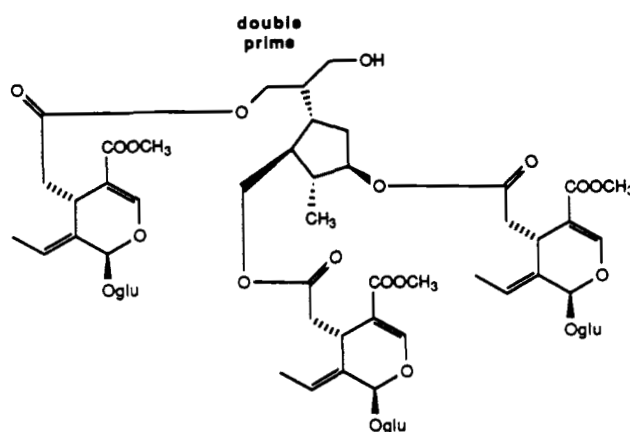
$C_{61}H_{86}O_{34}$ 1363.33 $[\alpha] -226.6^\circ$ (MeOH) uv 237 (MeOH) (200 MHz CD_3OD) 5.93 (H-1, bs, 3H), 7.53 (H-3, s, 3H), 6.09 (H-8, bq, 7.0, 3H), 1.75 (H-10, bd, 7.0, 9H), 3.72 (COOMe, 9H), 4.81 (H-1', d, 8.0, 3H), 4.65 (H-5'', m, 1H), 1.06 (H-6'', d, 7.0, 3H); (CD_3OD) 95.2 (C-1, 3 \times), 155.2 (C-3, 3 \times), 109.4 (C-4, 3 \times), 31.9 (C-5, 3 \times), 41.3 (C-6, 3 \times), 173.2, 173.0 (C-7), 124.9, 124.8 (C-8), 130.9, 130.8, 130.7 (C-9), 13.8 (C-10, 3 \times), 168.6 (C-11, 3 \times), 52.1 (OMe, 3 \times), 100.8 (C-1'), 74.8 (C-2'), 78.4 (C-3'), 71.5, 71.4 (C-4'), 77.9 (C-5'), 62.8, 62.7 (C-6'), 44.2 (C-1''), 49.8 (C-2''), 40.0 (C-3''), 34.8 (C-4''), 83.2 (C-5''), 19.0 (C-6''), 68.1 (C-7''), 44.5 (C-8''), 62.5 (C-9''), 64.4 (C-10''). *Jasminum sambac* (Oleaceae) (107)

217 SAMBACOSIDE E



$C_{61}H_{86}O_{34}$ 1363.33 $[\alpha] -208.5^\circ$ (MeOH) uv 237 (MeOH) (200 MHz CD_3OD) 5.93 (H-1, bs, 3H), 7.53 (H-3, s, 3H), 2.74 (H-6, dd, 14.0, 5.0, 2H), 2.72 (H-6, dd, 14.0, 5.0, 1H), 2.50 (H-6, dd, 14.0, 9.0, 1H), 2.48 (H-6, dd, 14.0, 9.0, 2H), 6.11 (H-8, bq, 7.0, 3H), 1.75 (H-10, bd, 7.0, 9H), 3.71 (COOMe, 9H), 4.81 (H-1', d, 8.0, 3H), 1.05 (H-6'', d, 6.0, 3H); (CD_3OD) 95.2 (C-1, 3 \times), 155.2 (C-3, 3 \times), 109.4 (C-4, 3 \times), 31.9 (C-5, 3 \times), 41.3 (C-6, 3 \times), 173.2, 173.0 (C-7), 124.9, 124.8 (C-8), 130.9, 130.8, 130.7 (C-9), 13.8 (C-10, 3 \times), 168.6 (C-11, 3 \times), 52.1 (OMe, 3 \times), 100.8 (C-1'), 74.8 (C-2'), 78.4 (C-3'), 71.5, 71.4 (C-4'), 77.9 (C-5'), 62.8, 62.7 (C-6'), 46.5 (C-1''), 49.8 (C-2''), 39.5 (C-3''), 37.0 (C-4''), 79.4 (C-5''), 18.4 (C-6''), 68.2 (C-7''), 41.8 (C-8''), 65.6 (C-9''), 64.2 (C-10''). *Jasminum sambac* (Oleaceae) (107)

218 SAMBACOSIDE F

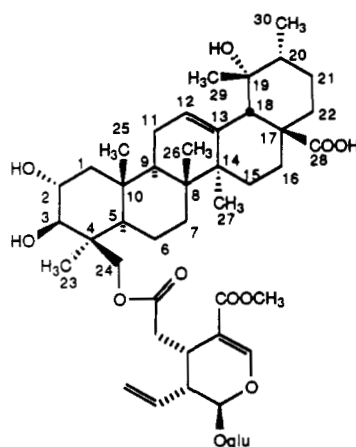


$C_{61}H_{86}O_{34}$ 1363.33 $[\alpha] -215.7^\circ$ (MeOH) uv 237 (MeOH) (200 MHz CD_3OD) 5.93 (H-1, bs, 3H), 7.53 (H-3, s, 3H), 2.75 (H-6, dd, 14.0, 5.0, 2H), 2.67 (H-6, dd, 14.0, 5.0, 1H), 2.49 (H-6, dd, 14.0, 9.0, 3H), 6.11 (H-8, bq, 7.0, 3H), 1.75 (H-10, bd, 7.0, 9H), 3.72 (COOMe, 9H), 4.82 (H-1', d, 8.0, 3H), 4.66 (H-5'', m, 1H), 1.06 (H-6'', d, 7.0, 3H); (CD_3OD) 95.2 (C-1, 3 \times), 155.2 (C-3, 3 \times), 109.4 (C-4, 3 \times), 31.9 (C-5, 3 \times), 41.3 (C-6, 3 \times), 173.2, 173.0 (C-7), 124.9, 124.8 (C-8), 130.9, 130.8, 130.7 (C-9), 13.8 (C-10, 3 \times), 168.6 (C-11, 3 \times), 52.1 (OMe, 3 \times), 100.8 (C-1'), 74.8 (C-2'), 78.4 (C-3'), 71.5, 71.4 (C-4'), 77.9 (C-5'), 62.8, 62.7 (C-6'), 44.3 (C-1''), 49.3 (C-2''), 40.3 (C-3''), 34.9 (C-4''), 83.1 (C-5''), 18.9 (C-6''), 68.2 (C-7''), 44.3 (C-8''), 65.8 (C-9''), 61.0 (C-10'').

Jasminum sambac (Oleaceae) (107)

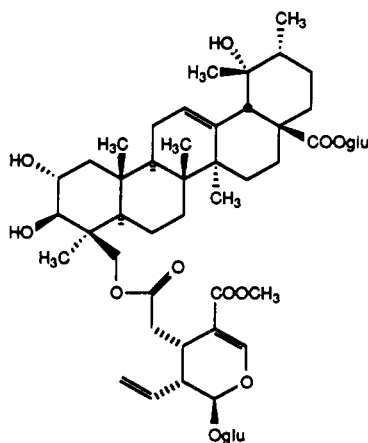
Group 13 (other seco-iridoids)

219 DESFONTAINIC ACID



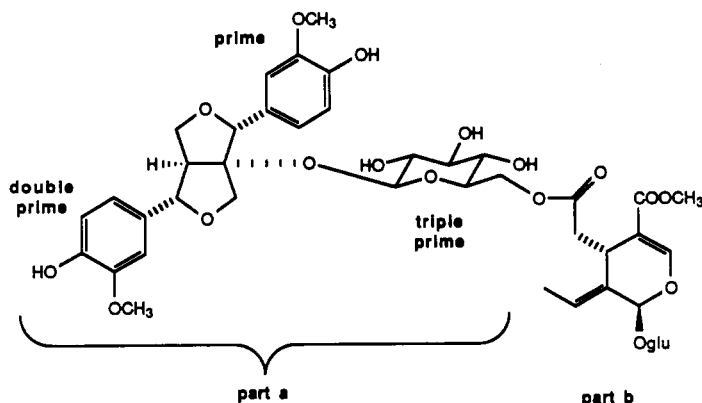
$C_{47}H_{70}O_{16}$ 891.07 uv 236 (MeOH) (360 MHz CD_3OD) 5.48 (H-1, d, 7), 7.38 (H-3, s), 2.90 (H-5, m), 5.70 (H-8, ddd, 18, 16, 10), 2.52 (H-9, bs), 5.16 (H-10, m), 4.61 (H-1', d, 8), 3.20 (H-2'-H-5'), 3.79 (H-6', dd, 12, 2), 3.59 (H-6', dd, 12, 4), 3.62 (COOMe), 4.24 (H-2B'', split t, 10, 4), 3.05 (H-3 α ', d, 10), 2.28 (H-5 α ', split t, 13, 4.5), 5.22 (H-12'', bt), 2.52 (H-18B'', bs), 1.20, 1.18, 1.10, 0.96, 0.74 (H-23'', H-25''-H-29'', s, 3H each), 3.82 (H-24'', d, 11), 3.28 (H-24'', d, 11), 0.82 (H-30'', d, 6); ($CDCl_3$) 95.6 (C-1), 151.8 (C-3), 109.8 (C-4), 28.5 (C-5), 34.9 (C-6), 170.0 (C-7), 133.7 (C-8), 46.4 (C-9), 117.3 (C-10), 167.7 (C-11), 50.0 (OMe), 98.0 (C-1'), 72.5 (C-2'), 76.9 (C-3'), 69.5 (C-4'), 76.2 (C-5'), 60.7 (C-6'), 44.3 (C-1''), 61.1 (C-2''), 85.3 (C-3''), 39.0 (C-4''), 53.6 (C-5''), 18.0 (C-6''), 32.4 (C-7''), 40.7 (C-8''), 47.7 (C-9''), 36.9 (C-10''), 24.9 (C-11''), 126.3 (C-12''), 138.9 (C-13''), 40.9 (C-14''), 28.6 (C-15''), 25.1 (C-16''), 47.8 (C-17''), 54.7 (C-18''), 72.2 (C-19''), 43.4 (C-20''), 27.8 (C-21''), 37.5 (C-22''), 22.9 (C-23''), 69.0 (C-24''), 16.2 (C-25''), 14.7 (C-26''), 22.3 (C-27''), 183.7 (C-28''), 24.8 (C-29''), 15.6 (C-30''). *Desfontainia spinosa* (Loganiaceae) (108)

220 DESFONTAINOSIDE



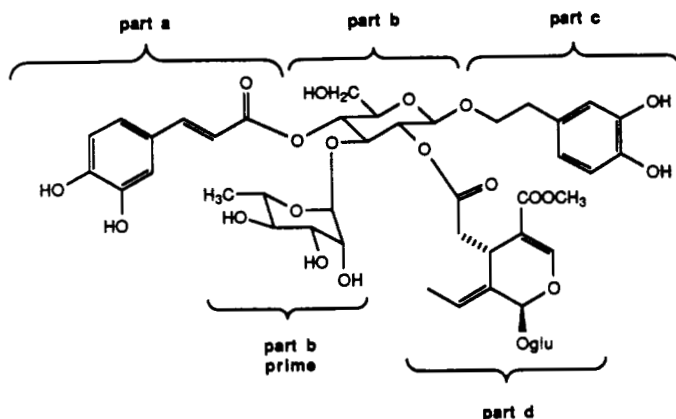
$C_{53}H_{80}O_{21}$ 1053.21 uv 236 (MeOH) (360 MHz CD_3OD) 5.49 (H-1, d, 7), 7.38 (H-3, s), 2.91 (H-5, m), 5.70 (H-8, ddd, 18, 16, 10), 2.52 (H-9), 5.21 (H-10, m), 5.15 (H-10, dd, 10, 1), 4.61 (H-1', d, 8), 3.10–3.30 (H-2'–H-5', H-24'', H-2'''–H-5''', m, 9H), 3.58 (H-6', m, 2H), 3.62 (COOMe), 4.20 (H-2β'', split t, 10, 4), 3.05 (H-3α'', d, 10), 2.52 (H-5α'', m), 5.18 (H-12'', coarse t), 2.42 (H-18β'', bs), 1.24, 1.20, 1.11, 0.97, 0.66 (H-23'', H-25''–H-29'', s, 3H each), 3.83 (H-24'', d, 11), 0.83 (H-30'', d, 6), 5.21 (H-1''', d, 8), 3.80 (H-6''', dd, 12, 2), 3.70 (H-6''', dd, 12, 2); (CD_3OD) 97.6 (C-1), 154.0 (C-3), 111.9 (C-4), 29.6 (C-5), 34.3 (C-6), 170.0 (C-7), 136.1 (C-8), 45.5 (C-9), 119.3 (C-10), 169.7 (C-11), 52.0 (OMe), 100.2 (C-1'), 74.7 (C-2'), 78.3 (C-3'), 71.6 (C-4'), 78.6 (C-5'), 62.8 (C-6'), 46.5 (C-1''), 63.2 (C-2''), 87.3 (C-3''), 39.0 (C-4''), 54.9 (C-5''), 18.9 (C-6''), 30.8 (C-7''), 41.3 (C-8''), 51.5 (C-9''), 36.9 (C-10''), 25.0 (C-11''), 129.5 (C-12''), 139.8 (C-13''), 42.8 (C-14''), 30.0 (C-15''), 26.5 (C-16''), 48.0 (C-17''), 56.7 (C-18''), 73.6 (C-19''), 43.0 (C-20''), 27.2 (C-21''), 38.3 (C-22''), 26.7 (C-23''), 71.0 (C-24''), 17.8 (C-25''), 16.6 (C-26''), 24.8 (C-27''), 178.0 (C-28''), 27.1 (C-29''), 17.6 (C-30''), 95.8 (C-1'''), 73.9 (C-2'''), 78.0 (C-3'''), 71.1 (C-4'''), 78.5 (C-5'''), 62.5 (C-6'''). *Desfontainia spinosa* (Loganiaceae) (108)

221 SAMBACOLIGNOSIDE



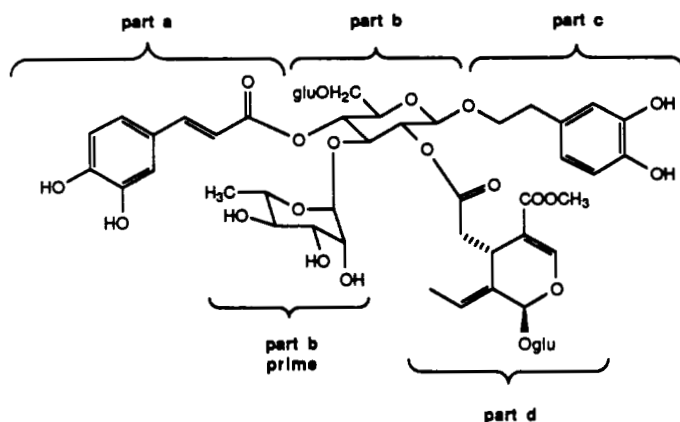
$C_{43}H_{54}O_{22}$ 922.89 $[\alpha] -97.1^\circ$ (MeOH) uv 280, 233 (MeOH) (400 MHz CD_3OD) 4.72 (H-2_a, s), 4.48 (H-4_a, dd, 9.0, 8.0), 3.82 (H-4_a, dd, 9.0, 6.0), 4.81 (H-6_a, d, 5.5), 4.36 (H-8_a, d, 10.5), 3.96 (H-8_a, d, 10.5), 7.07 (H-2'_a, d, 2.0), 6.80 (H-5'_a, d, 8.0), 6.88 (H-6'_a, dd, 8.0, 2.0), 7.04 (H-2''_a, d, 2.0), 6.74 (H-5''_a, d, 8.0), 6.86 (H-6''_a, dd, 8.0, 2.0), 3.89, 3.85 (ArOMe), 4.39 (H-1''_a, d, 8.0), 3.01 (H-2''_a, t, 8.0), 4.21 (H-6''_a, dd, 12.0, 1.5), 4.04 (H-6''_a, dd, 12.0, 6.5), 5.89 (H-1_b, bs), 7.51 (H-3_b, s), 3.97 (H-5_b, dd, 9.0, 4.5), 2.66 (H-6_b, dd, 14.5, 4.5), 2.38 (H-6_b, dd, 14.5, 9.0), 6.07 (H-8_b, dq, 7.0, 0.8), 1.65 (H-10_b, dd, 7.0, 1.5), 3.67 (COOMe), 4.82 (H-1'_b, d, 8.0), 3.88 (H-6'_b, dd, 12.0, 1.5), 3.66 (H-6'_b, dd, 12.0, 6.0); (CD_3OD) 99.2 (C-1_a), 89.4 (C-2_a), 72.1 (C-4_a), 60.4 (C-5_a), 87.6 (C-6_a), 73.8 (C-8_a), 128.8 (C-1'_a), 113.8 (C-2'_a), 148.5 (C-3'_a), 147.4 (C-4'_a), 115.4 (C-5'_a), 122.1 (C-6'_a), 56.7 (ArOMe), 133.2 (C-1''_a), 111.0 (C-2''_a), 149.4 (C-3''_a), 147.4 (C-4''_a), 116.3 (C-5''_a), 120.1 (C-6''_a), 56.7 (ArOMe), 100.1 (C-1''_a), 74.9 (C-2''_a)^a, 78.2 (C-3''_a)^b, 71.6 (C-4''_a), 75.2 (C-5''_a), 65.1 (C-6''_a), 95.0 (C-1_b), 155.1 (C-3_b), 109.4 (C-4_b), 31.8 (C-5_b), 41.3 (C-6_b), 172.9 (C-7_b), 125.1 (C-8_b), 130.5 (C-9_b), 13.8 (C-10_b), 168.7 (C-11_b), 52.0 (COOMe), 100.8 (C-1'_b), 74.8 (C-2'_b)^a, 78.5 (C-3'_b)^b, 71.6 (C-4'_b), 78.0 (C-5'_b), 62.8 (C-6'_b). *Jasminum sambac* (Oleaceae) (109)

222 OLEOACTEOSIDE



$C_{46}H_{58}O_{25}$ 1010.96 mp 158–161° [α] –122.9° (MeOH) uv 333, 290, 221, 205 (MeOH) (400 MHz CD_3OD) 6.25 (H- α_a , d, 16.0), 7.58 (H- β_a , d, 16.0), 7.04 (H-2 $_a$, d, 2.0), 6.73 (H-5 $_a$, d, 8.0), 6.96 (H-6 $_a$, dd, 8.0, 2.0), 4.38 (H-1 $_b$, d, 7.8), 5.47 (H-1' $_b$, d, 2.0), 1.07 (H-6' $_b$, d, 6.4), 2.79 (H- β_c , br, 7.3), 6.69 (H-2 $_c$, d, 2.0), 6.67 (H-5 $_c$, d, 8.0), 6.55 (H-6 $_c$, dd, 8.0, 2.0), 5.61 (H-1 $_d$, bs), 7.44 (H-3 $_d$, s), 2.10 (H-6 $_d$, dd, 16.1, 3.4), 1.94 (H-6 $_d$, dd, 16.1, 8.3), 5.98 (H-8 $_d$, bq, 7.3), 1.66 (H-10 $_d$, dd, 7.3, 1.5), 3.70 (COOMe); (CD_3OD) 127.5 (C-1 $_a$), 114.2 (C-2 $_a$), 75.8 (C-2 $_b$), 77.6 (C-3 $_b$), 70.2 (C-4 $_b$), 76.7 (C-5 $_b$), 62.3 (C-6 $_b$), 104.2 (C-1' $_b$), 69.9 (C-2' $_b$), 72.3 (C-3' $_b$), 75.4 (C-4' $_b$), 67.8 (C-5' $_b$), 18.1 (C-6' $_b$), 131.5 (C-1 $_c$), 116.8 (C-2 $_c$), 144.7 (C-3 $_c$), 146.1 (C-4 $_c$), 117.1 (C-5 $_c$), 121.3 (C-6 $_c$), 72.3 (C- α_c), 36.6 (C- β_c), 95.5 (C-1 $_d$), 155.1 (C-3 $_d$), 109.2 (C-4 $_d$), 30.7 (C-5 $_d$), 41.0 (C-6 $_d$), 172.9 (C-7 $_d$), 124.7 (C-8 $_d$), 130.9 (C-9 $_d$), 13.7 (C-10 $_d$), 168.8 (C-11 $_d$), 52.0 (COOMe), 100.9 (C-1' $_d$), 74.8 (C-2' $_d$), 78.2 (C-3' $_d$), 71.5 (C-4' $_d$), 77.9 (C-5' $_d$), 62.7 (C-6' $_d$). *Syringa reticulata* (Oleaceae) (110)

223 OLEOECHINACOSIDE



$C_{52}H_{68}O_{30}$ 1173.10 pentadecaacetate mp 108–110° [α] –57.6° ($CHCl_3$) uv 280 (MeOH) (pentadecaacetate 400 MHz $CDCl_3$) 6.34 (H- α_a , d, 16.1), 7.63 (H- β_a , d, 16.1), 7.37–7.42 (H-2 $_a$), 7.24 (H-5 $_a$, d, 8.3), 7.37–7.42 (H-6 $_a$), 4.35 (H-1 $_b$, d, 7.8), 4.79 (H-1' $_b$, d, 1.5), 1.00 (H-6' $_b$, d, 6.0), 4.55 (H-1'' $_b$, d, 7.8), 2.86 (H- β_c , br, 5.7), 7.05–7.10 (H-2 $_c$, H-5 $_c$, H-6 $_c$), 5.66 (H-1 $_d$, bs), 7.42 (H-3 $_d$, s), 2.60 (H-6 $_d$, dd, 16.6, 3.4), 2.34 (H-6 $_d$, dd, 16.6, 8.8), 5.96 (H-8 $_d$, bq, 6.8), 1.74 (H-10 $_d$, dd, 6.8, 1.5), 3.70 (COOMe), 2.31, 2.30, 2.29, 2.27, 2.09, 2.08, 2.03, 2.02 (4 \times), 2.01, 1.98, 1.95, 1.89 (OAc); (pentadecaacetate $CDCl_3$) 132.7 (C-1 $_a$), 122.9 (C-2 $_a$), 143.9 (C-3 $_a$), 142.6 (C-4 $_a$), 124.1 (C-5 $_a$), 126.5 (C-6 $_a$), 118.1 (C- α_a), 144.5 (C- β_a), 165.2 (C- α_c), 100.5 (C-1 $_b$), 70.9 (C-2 $_b$), 81.1 (C-3 $_b$), 68.1 (C-4 $_b$), 72.0 (C-5 $_b$), 68.3 (C-6 $_b$), 99.2 (C-1' $_b$), 69.7 (C-2' $_b$), 70.0 (C-3' $_b$), 71.8 (C-4' $_b$), 67.3 (C-5' $_b$), 17.4 (C-6' $_b$), 100.8 (C-1'' $_b$), 71.2 (C-2'' $_b$), 73.8 (C-3'' $_b$), 70.2 (C-4'' $_b$), 72.7 (C-5'' $_b$), 61.8 (C-6'' $_b$), 137.6 (C-1 $_c$), 123.2 (C-2 $_c$), 141.8 (C-3 $_c$), 140.6 (C-4 $_c$), 123.9 (C-5 $_c$), 127.3 (C-6 $_c$), 68.5 (C- α_c), 35.3 (C- β_c), 94.2 (C-1 $_d$), 153.1 (C-3 $_d$), 108.4 (C-4 $_d$), 29.4 (C-5 $_d$), 39.0 (C-6 $_d$), 125.1 (C-8 $_d$), 128.3 (C-9 $_d$), 13.7 (C-10 $_d$), 166.9 (C-11 $_d$), 51.4 (COOMe), 97.5 (C-1' $_d$), 70.7 (C-2' $_d$), 72.6 (C-3' $_d$), 68.3 (C-4' $_d$), 72.3 (C-5' $_d$), 61.5 (C-6' $_d$), 20.9, 20.7, 20.6, 20.3 (O=CMe), 170.6, 170.3, 170.2, 170.1, 169.4, 168.3, 168.1, 167.9 (C-7 $_d$, O=CMe). *Syringa reticulata* (Oleaceae) (110)

TABLE 2. Alphabetical Compound Index.

Abelioside A [207]	Dihydropenstemide [17]
Abelioside A dimethyl acetal [208]	β -Dihydroplumericinic acid glucosyl ester [42]
Abelioside B [206]	Dihydropenstemide [20]
10-Acetoxyeuropein [187]	Dolichodial [91]
2'- <i>O</i> -Acetyldihydropenstemide [18]	Dolicholactone [71]
2'- <i>O</i> -Acetylpatrinoside [23]	Ebuloside [6]
13- <i>O</i> -Acetylplumieride [48]	8- <i>epi</i> -Dihydropenstemide [16]
7- <i>O</i> -Acetylsecologanol [112]	7- <i>epi</i> -Hydrangenoside A [200]
2'- <i>O</i> -Acetylswertiamarin [128]	7- <i>epi</i> -Hydrangenoside C [202]
10- <i>O</i> -Acetylviburnalloside [28]	7- <i>epi</i> -Hydrangenoside E [204]
Actinidialactone [101]	8- <i>epi</i> -Kingside [124]
Allamancin [38]	8- <i>epi</i> -Valeroside [8]
Allamcidin A [33]	7- <i>epi</i> -Vogelose [130]
Allamcidin B [34]	Epoxycerberidol [84]
Allamcidin B β -D-glucose [44]	11-Ethoxyviburnal [77]
Allamcin [36]	Eucommioside I [96]
Allaneroside [49]	Eucommioside II [95]
Allodolicholactone [72]	Flideroside [182]
3- <i>O</i> -Allosylcerberidol [82]	2'- <i>O</i> -Foliamenthoyldihydropenstemide [19]
3- <i>O</i> -Allosylcyclocerberidol [87]	Furcatoside A [26]
3- <i>O</i> -Allosylepoxycerberidol [85]	Furcatoside B [25]
Alpigenoside [109]	Furcatoside C [24]
Amarogentin [154]	Gelidoside [156]
Amaroswerin [155]	Gelsemiol [97]
6'- <i>O</i> -Apiosylebuloside [7]	Gelsemiol-1-glucoside [98]
Azoricin [145]	Gelsemiol-3-glucoside [99]
3,10-Bis- <i>O</i> -allosylcerberidol [83]	Gentiogenal [107]
Boonein [56]	Gentiopical [107]
13- <i>O</i> -Caffeoylplumieride [53]	Gentiopicroside [131]
Centaurosides [211]	7- <i>O</i> -Gentisoylsecologanol [184]
Cerberic acid [80]	Gibboside [70]
Cerberidol [81]	6'- <i>O</i> - β -D-Glucosylgentiopicroside [132]
Cerberinic acid [78]	(7 <i>R</i>)-Haenkeanoside [173]
Cerbinal [79]	(7 <i>S</i>)-Haenkeanoside [177]
Confertoside [21]	Hiiragilide [162]
4'- <i>O</i> - <i>cis</i> - <i>p</i> -Coumaroyl-7 α -morroneiside [168]	Hydrangenoside A [199]
4'- <i>O</i> - <i>trans</i> - <i>p</i> -Coumaroyl-7 α -morroneiside [169]	Hydrangenoside B [200]
4'- <i>O</i> - <i>cis</i> - <i>p</i> -Coumaroyl-7 β -morroneiside [170]	Hydrangenoside C [201]
4'- <i>O</i> - <i>trans</i> - <i>p</i> -Coumaroyl-7 β -morroneiside [171]	Hydrangenoside D [202]
13- <i>O</i> -Coumaroylplumieride [50]	Hydrangenoside E [203]
Cyclocerberidol [86]	Hydrangenoside F [204]
Decentapicrin A [151]	Hydrangenoside G [205]
Decentapicrin B [152]	9"-Hydroxyjasmoside [143]
Decentapicrin C [153]	9"-Hydroxyjasmosidic acid [141]
Deglucoserrulatoside [12]	(7 <i>R</i>)-10-Hydroxymorroneiside [125]
Deglucosyl plumieride [35]	(7 <i>S</i>)-10-Hydroxymorroneiside [126]
Dehydroiridodial- β -D-gentiobioside [90]	10-Hydroxyeulose dimethyl ester [119]
Dehydroiridomyrmecin [61]	10-Hydroxyeuropein [186]
5,6-Dehydrojasminin [147]	Ibotalactone A [165]
Demethyloluropein [185]	Ibotalactone B [166]
1-Deoxyeucommiol [94]	Iridodial- β -D-gentiobioside [89]
9'-Deoxyjasminogenin [145]	Isoactinidialactone [102]
10-Deoxypatrinoside [3]	Isoallamandicin [40]
10-Deoxypatrinoside aglycone [2]	Isodehydroiridomyrmecin [62]
10-Deoxypenstemide [1]	Isodihydroepinepetalactone [65]
13-Deoxylumieride [43]	Isodolichodial [92]
Desacetylcentapicrin [150]	Isoepiiridomyrmecin [63]
Desfontainic acid [219]	(7 <i>R</i>)-Isohaenkeanoside [172]
Desfontainoside [220]	(7 <i>S</i>)-Isohaenkeanoside [176]
2',3'- <i>O</i> -Diacylfurcatoside C [28]	Isoligustrosides [159]
8,9-Didehydro-7-hydroxydolichodial [93]	Isononepetalactone [60]
Dideroside [110]	Isonuezhenide [163]
7,7- <i>O</i> -Dihydroebuloside [5]	Isoeuropein [160]
Dihydroepinepetalactone [64]	8-Isoplumieride [46]
Dihydrofoliamenthin [139]	Isosweroside [108]
8,9-Dihydrojasminin [146]	Jasmoside [142]

- Jasminin-10''-O-glucoside [144]
 Jasminoside [158]
 Jasmisnyiroside [148]
 Jasmolactone A [133]
 Jasmolactone B [134]
 Jasmolactone B dimethylate [135]
 Jasmolactone C [136]
 Jasmolactone D [137]
 Jasmolactone D tetramethylate [138]
 Jasmoside [214]
 Jiofuran [104]
 Jioglutolide [66]
 Kingiside aglycone [106]
 Laciniatoside V [209]
 Latifonin [73]
 Ligustalloside A [192]
 Ligustalloside B [190]
 Ligustalloside B dimethyl acetal [191]
 Ligustrosidic acid [193]
 Ligustrosidic acid methyl ester [195]
 Lilacoside [183]
 Lisianthoside [212]
 Menthiatofin [140]
 Mentzetriol [88]
 7 α -Methoxysweroside [129]
 3-O-Methylallamancin [39]
 3-O-Methylallamcin [37]
 Methyl glucooleoside [118]
 Methylgrandifloroside [189]
 (7*R*)-O-Methylhaenkeanoside [175]
 (7*S*)-O-Methylhaenkeanoside [179]
 (7*R*)-O-Methylisohaenkeanoside [174]
 (7*S*)-O-Methylisohaenkeanoside [178]
 (7*R*)-O-Methylmorrioniside [122]
 (7*S*)-O-Methylmorrioniside [123]
 Methyl syramuraldehydate [105]
 6'-O-[(2*R*)-Methyl-3-veratroxyloxypropanoyl]-
 7 α -morrioniside [180]
 6'-O-[(2*R*)-Methyl-3-veratroxyloxypropanoyl]-
 7 β -morrioniside [181]
 7 α -Morrioniside [120]
 7 β -Morrioniside [121]
 Nardostachin [4]
 Neoneuzhenide [164]
 Neoeuropein [161]
 4 $\alpha\alpha$, 7 α , 7 $\alpha\alpha$ -Nepetalactone [57]
 4 $\alpha\alpha$, 7 α , 7 $\alpha\beta$ -Nepetalactone [58]
 4 $\alpha\beta$, 7 α , 7 $\alpha\beta$ -Nepetalactone [59]
 Nepetariaside [100]
 Nepetaside [69]
 Norviburtinal [76]
 Oleoacteoside [222]
 Oleoëchinacoside [223]
 Oleoneuzhenide [213]
 Oleoside dimethyl ester [117]
 Oleuropeinic acid [194]
 Oleuropeinic acid methyl ester [196]
 Oleurosides [188]
 Oruwacin [41]
 Oxysporone [55]
 Patrinalloside [22]
 Penstebioside [14]
 Penstemide aglycone [11]
 Plumenoside [42]
 Plumiepoxyde [47]
 1 α -Plumieride [45]
 Plumieride coumarate [50]
 Plumieride coumarate glucoside [51]
 Plumieridine [35]
 Posoquenine [74]
 1 α -Protoplumericin A [52]
 Protoplumericin A [51]
 Protoplumericin B [54]
 Pulosarioside [215]
 Rehmaglutin C [103]
 Sambacin [147]
 Sambacolognoside [221]
 Sambacoside A [216]
 Sambacoside E [217]
 Sambacoside F [218]
 Scabraside [157]
 Scaevoloside [210]
 Secologanin dimethyl acetal [113]
 Secologanol [111]
 Secologanoside [114]
 Secologanoside dimethyl ester [116]
 Secoxyloganin [115]
 Serrulatolloside [10]
 Serrulatolloside aglycone [9]
 Serrulatolloside [15]
 Serruloside [13]
 Strypsinolactone [75]
 Suspensolide A [30]
 Suspensolide A aglycone [29]
 Suspensolide B [31]
 Suspensolide C [32]
 Swertiamarin [127]
 Syringalactone A [182]
 Syringalactone B [183]
 6'-O-Vanilloyl-8-*epi*-kingiside [167]
 Viburnalloside [27]
 Villosol [67]
 Villosolloside [68]

TABLE 3. Molecular Formula Index.

C ₇ H ₈ O ₄	55	Oxysporone	C ₁₀ H ₆ O ₄	78	Cerberinic acid
C ₉ H ₆ O ₂	76	Norviburtinal	C ₁₀ H ₁₀ O ₄	107	Gentiogenol
C ₉ H ₁₂ O ₄	104	Jiofuran	C ₁₀ H ₁₂ O ₄	93	8,9-Didehydro-7-hydroxy-dolichodial
C ₉ H ₁₂ O ₅	103	Rehmaglutin C	C ₁₀ H ₁₁ O ₂	57	4 $\alpha\alpha$, 7 α , 7 $\alpha\alpha$ -Nepetalactone
C ₉ H ₁₁ O ₃	56	Boonein		58	4 $\alpha\alpha$, 7 α , 7 $\alpha\beta$ -Nepetalactone
	88	Mentzetriol		59	4 $\alpha\beta$, 7 α , 7 $\alpha\beta$ -Nepetalactone
C ₉ H ₁₄ O ₄	66	Jioglutolide		60	Isoneonepetalactone
C ₉ H ₁₆ O ₃	81	Cerberidol		61	Dehydroiridomyrmecin
	94	1-Deoxyeucommiol		62	Isodehydroiridomyrmecin
C ₉ H ₁₆ O ₄	84	Epoxyerberidol		71	Dolicholactone
	86	Cycloerberidol			

	72	Allodolicholactone	$C_{19}H_{30}O_{11}$	113	Secologanin dimethy acetal
	91	Dolichodial	$C_{20}H_{24}O_{11}$	42	Plumenoside
	92	Isodolichodial	$C_{20}H_{28}O_6$	145	Azoricin
	101	Actinidialactone	$C_{20}H_{32}O_6$	4	Nardostachin
	102	Isoactinidialactone	$C_{21}H_{18}O_8$	41	Oruwacin
$C_{10}H_{16}O_2$	63	Isoepiiridomyrmecin	$C_{21}H_{26}O_9$	135	Jasmolactone B dimethylate
	64	Dihydroepineperalactone	$C_{21}H_{26}O_{11}$	43	13-Deoxyplumieride
	65	Isodihydroepineperalactone	$C_{21}H_{26}O_{12}$	45	1 α -Plumieride
$C_{10}H_{16}O_4$	67	Villosol		46	8-Isoplumieride
	97	Gelsemiol	$C_{21}H_{26}O_{13}$	47	Plumiepoide
$C_{11}H_8O_4$	79	Cerbinal	$C_{21}H_{28}O_{12}$	44	Allamcidin B β -D-glucose
$C_{11}H_8O_5$	80	Cerberic acid	$C_{21}H_{30}O_{10}$	13	Serrulolide
$C_{11}H_{14}O_6$	105	Methyl syramuraldehydate	$C_{21}H_{32}O_9$	1	10-Deoxypentemide
	106	Kingiside aglycone		12	Deglucoserrulatoside
$C_{11}H_{14}O_7$	74	Posoquenin	$C_{21}H_{32}O_{10}$	6	Ebuloside
$C_{11}H_{16}O_7$	73	Larifonin		10	Serrulatolide
$C_{12}H_{12}O_3$	77	11-Ethoxyviburtinal		20	Dihydroserrulolide
$C_{12}H_{16}O_7$	75	Strypinolactone	$C_{21}H_{34}O_{10}$	3	10-Deoxyparrinoside
$C_{13}H_{14}O_5$	36	Allamcin		5	7,7-O-Dihydroebuloside
$C_{14}H_{16}O_5$	37	3-O-Methylallamcin		16	8- <i>epi</i> -Dihydropentemide
$C_{15}H_{16}O_7$	35	Plumieridine		17	Dihydropentemide
	40	Isoallamandicin	$C_{21}H_{34}O_{11}$	8	8- <i>epi</i> -Valeroside
$C_{15}H_{18}O_7$	33	Allamcidin A		22	Patrinalloside
	34	Allamcidin B	$C_{21}H_{36}O_{13}$	83	3,10-Bis-O-allosylcerberidol
$C_{15}H_{18}O_8$	38	Allamancin	$C_{22}H_{30}O_{14}$	132	6'-O- β -D-Glucosylgentio-
$C_{15}H_{22}O_5$	9	Serrulatolide aglycone			picroside
	11	Pentemide aglycone	$C_{22}H_{34}O_{12}$	90	Dehydroiridodial- β -D-
$C_{15}H_{24}O_5$	2	10-Deoxyparrinoside aglycone			gentiobioside
$C_{15}H_{26}O_8$	82	3-O-Allosylcerberidol	$C_{22}H_{36}O_{12}$	89	Iridodial- β -D-gentiobioside
$C_{15}H_{26}O_9$	85	3-O-Allosylepoxycerberidol	$C_{23}H_{26}O_{11}$	150	Desacetylcentapicrin
	87	3-O-Allosylcyclocerberidol		151	Decentapicrin A
	95	Eucommioside II		152	Decentapicrin B
	96	Eucommioside I		153	Decentapicrin C
$C_{16}H_{20}O_8$	39	3-O-Methylallamancin	$C_{23}H_{28}O_{13}$	48	13-O-Acetylplumieride
$C_{16}H_{20}O_9$	131	Gentiopicroside	$C_{23}H_{34}O_{16}$	118	Methyl glucooleoside
$C_{16}H_{22}O_9$	108	Isosweroside	$C_{23}H_{36}O_{11}$	18	2'-O-Acetyldihydropentemide
$C_{16}H_{22}O_{11}$	114	Secologanoside	$C_{23}H_{36}O_{12}$	23	2'-O-Acetylpatrinoside
	127	Swertiamarin		24	Furcatoside C
$C_{16}H_{26}O_8$	69	Nepetaside	$C_{24}H_{30}O_{12}$	182	Syringalactone A
$C_{16}H_{26}O_9$	68	Villosolide	$C_{24}H_{30}O_{13}$	183	Syringalactone B
	70	Gibboside		184	7-O-Gentisoylsecologanol
	98	Gelsemiol-1-glucoside		185	Demethyloleuropein
	99	Gelsemiol-3-glucoside	$C_{24}H_{32}O_{14}$	186	10-Hydroxyoleuropein
$C_{16}H_{28}O_8$	100	Nepetariaside	$C_{25}H_{28}O_{13}$	165	Ibotalactone A
$C_{17}H_{24}O_{10}$	129	7 α -Methoxysweroside	$C_{25}H_{28}O_{14}$	166	Ibotalactone B
	130	7- <i>epi</i> -Vogeloside	$C_{25}H_{30}O_{14}$	167	6'-O-Vanilloyl-8- <i>epi</i> -kingiside
$C_{17}H_{24}O_{11}$	115	Secoxyloganin		193	Ligustrosidic acid
	124	8- <i>epi</i> -Kingiside	$C_{25}H_{30}O_{15}$	194	Oleuropeinic acid
$C_{17}H_{26}O_{10}$	111	Secologanol	$C_{25}H_{32}O_{12}$	159	Isoligustroside
$C_{17}H_{26}O_{11}$	120	7 α -Morrnonside	$C_{25}H_{32}O_{13}$	160	Isooleuropein
	121	7 β -Morrnonside		188	Oleurosides
$C_{17}H_{26}O_{12}$	125	(7R)-10-Hydroxymorrnonside		190	Ligustalolide B
	126	(7S)-10-Hydroxymorrnonside	$C_{25}H_{32}O_{14}$	192	Ligustalolide A
$C_{18}H_{24}O_{11}$	128	2'-O-Acetylswertiamarin	$C_{25}H_{34}O_{12}$	207	Abelioside A
$C_{18}H_{26}O_{11}$	116	Secologanoside dimethyl ester	$C_{25}H_{36}O_{12}$	206	Abelioside B
	117	Oleoside dimethyl ester	$C_{25}H_{36}O_{14}$	32	Suspensolide C
$C_{18}H_{26}O_{12}$	119	10-Hydroxyoleoside dimethyl ester	$C_{25}H_{38}O_{13}$	27	Viburnalloside
			$C_{25}H_{38}O_{14}$	30	Suspensolide A
$C_{18}H_{28}O_{11}$	122	(7R)-O-Methylmorrnonside	$C_{26}H_{28}O_{10}$	136	Jasmolactone C
	123	(7S)-O-Methylmorrnonside	$C_{26}H_{28}O_{11}$	137	Jasmolactone D
$C_{18}H_{28}O_{12}$	109	Alpigenoside	$C_{26}H_{30}O_{13}$	158	Jasminoside
$C_{19}H_{22}O_8$	133	Jasmolactone A	$C_{26}H_{32}O_{13}$	168	4'-O- <i>cis</i> -p-Coumaroyl-7 α -
	197	compound not named			morrnonside
	198	compound not named		169	4'-O- <i>trans</i> -p-Coumaroyl-7 α -
$C_{19}H_{22}O_9$	134	Jasmolactone B			morrnonside
$C_{19}H_{28}O_9$	29	Suspensolide A aglycone		170	4'-O- <i>cis</i> -p-Coumaroyl-7 β -
$C_{19}H_{28}O_{11}$	112	7-O-Acetylsecologanol			morrnonside
$C_{19}H_{28}O_{13}$	110	Diderroside		171	4'-O- <i>trans</i> -p-Coumaroyl-7 β -

		morroniside	$C_{30}H_{32}O_{15}$	53	13- <i>O</i> -Caffeoylplumieride
	172	(7 <i>R</i>)-Isohaenkeanoside	$C_{30}H_{34}O_{15}$	49	Allaneroside
	173	(7 <i>R</i>)-Haenkeanoside	$C_{30}H_{36}O_{11}$	138	Jasmolactone D tetramethylate
	176	(7 <i>S</i>)-Isohaenkeanoside	$C_{30}H_{40}O_{16}$	180	6'- <i>O</i> -[(2 <i>R</i>)-Methyl-3-veratroyl-oxypyrpanoyl]-7α-morroniside
	177	(7 <i>S</i>)-Haenkeanoside			
$C_{26}H_{32}O_{14}$	195	Ligustrosidic acid methyl ester			
$C_{26}H_{32}O_{15}$	196	Oleuropeinic acid methyl ester			
$C_{26}H_{36}O_{12}$	140	Menthiafolin		181	6'- <i>O</i> -[(2 <i>R</i>)-Methyl-3-veratroyl-oxypyrpanoyl]-7β-morroniside
	147	Sambacin			
$C_{26}H_{36}O_{14}$	148	Jasminyroside	$C_{31}H_{40}O_{13}$	199	Hydrangenoside A
$C_{26}H_{38}O_{12}$	139	Dihydrofoliamenthin		200	Hydrangenoside B
$C_{26}H_{38}O_{13}$	149	compound not named	$C_{31}H_{42}O_{17}$	163	Isonuezhenide
$C_{26}H_{40}O_{12}$	146	8,9-Dihydrojasminin	$C_{31}H_{42}O_{18}$	162	Hiiraglide
$C_{26}H_{40}O_{14}$	7	6'- <i>O</i> -Apiosylebuloside		164	Neonuezhenide
	141	9'-Hydroxyjasmesosidic acid	$C_{31}H_{48}O_{12}$	19	2'- <i>O</i> -foliamenthoyldihydropensternide
$C_{27}H_{34}O_{13}$	174	(7 <i>R</i>)- <i>O</i> -Methylisoaenkeanoside			
	175	(7 <i>R</i>)- <i>O</i> -Methylhaenkeanoside	$C_{32}H_{38}O_{15}$	161	Neoleuropein
	178	(7 <i>S</i>)- <i>O</i> -Methylisoaenkeanoside	$C_{32}H_{42}O_{14}$	25	Furcatoride B
	179	(7 <i>S</i>)- <i>O</i> -Methylhaenkeanoside		26	Furcatoride A
	189	Methylgrandifloroside	$C_{32}H_{44}O_{18}$	212	Lisianthoside
$C_{27}H_{34}O_{15}$	187	10-Acetoxyoleuropein	$C_{32}H_{48}O_{17}$	144	Jasminin-10'- <i>O</i> -glucoside
$C_{27}H_{36}O_{14}$	210	Scaevoloside	$C_{34}H_{44}O_{16}$	31	Suspensolide B
$C_{27}H_{38}O_{14}$	191	Ligustalide B dimethyl acetal	$C_{34}H_{46}O_{19}$	211	Centaurosides
	209	Laciniatoside V	$C_{35}H_{42}O_{21}$	156	Gelidoside
$C_{27}H_{40}O_{13}$	208	Abelioside A dimethyl acetal	$C_{36}H_{42}O_{19}$	51	Protoplumericin A
$C_{27}H_{40}O_{14}$	28	2',3'- <i>O</i> -Diacetylfurcatoride C		52	1α-Protoplumericin A
$C_{27}H_{42}O_{13}$	142	Jasmesoside	$C_{36}H_{42}O_{20}$	54	Protoplumericin B
$C_{27}H_{42}O_{14}$	15	Serrulatoside	$C_{40}H_{44}O_{20}$	157	Scabraside
	143	9'-Hydroxyjasmesoside	$C_{43}H_{54}O_{22}$	221	Sambacolognoside
$C_{27}H_{42}O_{15}$	14	Penstebioside	$C_{43}H_{60}O_{22}$	214	Jasmoside
$C_{27}H_{44}O_{15}$	21	Confertoside	$C_{43}H_{60}O_{23}$	215	Pulosarioside
$C_{29}H_{30}O_{13}$	154	Amarogentin	$C_{46}H_{58}O_{25}$	222	Oleoacteoside
$C_{29}H_{30}O_{14}$	155	Amaroswerin	$C_{47}H_{70}O_{16}$	219	Desfontainic acid
$C_{29}H_{38}O_{12}$	201	Hydrangenoside C	$C_{48}H_{64}O_{27}$	213	Oleonuezhenide
	202	Hydrangenoside D	$C_{52}H_{68}O_{30}$	223	Oleoecchinacoside
	205	Hydrangenoside G	$C_{53}H_{80}O_{21}$	220	Desfontainoside
$C_{29}H_{40}O_{12}$	203	Hydrangenoside E	$C_{61}H_{86}O_{34}$	216	Sambacoside A
	204	Hydrangenoside F		217	Sambacoside E
$C_{30}H_{32}O_{14}$	50	Plumieride coumarate		218	Sambacoside F

TABLE 4. Plant Index.

Actinidiaceae		Eucommiaceae	
<i>Actinidia</i>	60, 61, 62, 63, 64, 65, 89, 90, 101, 102	<i>Eucommia</i>	94, 96
Apocynaceae		Gentianaceae	
<i>Allamanda</i>	33, 34, 36, 37, 38, 39, 40, 44, 47, 48, 49, 50, 51, 54	<i>Centaurium</i>	150, 151, 152, 153
<i>Alstonia</i>	56	<i>Erythraea</i>	211
<i>Alyxia</i>	215	<i>Exacum</i>	189
<i>Cerbera</i>	78, 79, 80, 81, 82, 83, 84, 85, 86, 87	<i>Gentiana</i>	111, 112, 131, 132, 156, 157, 167, 168, 169, 170, 171, 180, 181, 184
<i>Plumeria</i>	42, 43, 45, 46, 52, 53	<i>Lisianthus</i>	212
Bignoniaceae		<i>Menyanthes</i>	139, 140
<i>Kigelia</i>	76	<i>Suertia</i>	127, 128, 154, 155
Caprifoliaceae		Goodeniaceae	
<i>Abelia</i>	206, 207, 208	<i>Scaevola</i>	210
<i>Lonicera</i>	109, 113, 114, 115, 130	Labiatae	
<i>Sambucus</i>	5, 6, 7, 108, 120, 121	<i>Centranthus</i>	77, 93
<i>Viburnum</i>	18, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32	<i>Nepeta</i>	57, 58, 59, 69, 100
Cornaceae		<i>Teucrium</i>	71, 72, 91, 92
<i>Aucuba</i>	95	Loasaceae	
Dipsacaceae		<i>Mentzelia</i>	88
<i>Dipsacus</i>	209	Loganiaceae	
		<i>Desfontainia</i>	219, 220
		<i>Gelsemium</i>	97, 98, 99

<i>Strychnos</i>	75, 106	<i>Gardenia</i>	79
Oleaceae		<i>Isertia</i>	172, 173, 174, 175, 176, 177, 178, 179
<i>Jasminum</i>	133, 134, 136, 137, 141, 142, 143, 144, 145, 146, 147, 148, 149, 158, 214, 216, 217, 218, 221	<i>Morinda</i>	41
<i>Ligustrum</i>	118, 124, 163, 164, 165, 166, 186, 190, 191, 192, 193, 194, 213	<i>Nauclea</i>	110
<i>Olea</i>	117, 185, 188, 197, 198	<i>Posoqueria</i>	73, 74
<i>Osmantibus</i>	162, 187	Saxifragaceae	
<i>Syringa</i>	105, 159, 160, 161, 182, 183, 222, 223	<i>Hydrangea</i>	199, 200, 201, 202, 203, 204, 205
Rubiaceae		Scrophulariaceae	
<i>Cruckshanksia</i>	129	<i>Penstemon</i>	2, 3, 5, 8, 9, 10, 13, 14, 15, 17, 19, 20, 21, 22
<i>Galium</i>	125, 126	<i>Rebmannia</i>	66, 103, 104
		Valerianaceae	
		<i>Nardostachys</i>	4
		<i>Patrinia</i>	67, 68, 70

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