Review

Naturally Occurring Iridoids, Secoiridoids and Their Bioactivity. An Updated Review, Part 3

Biswanath DINDA,* Debashis ROY CHOWDHURY, and Bikas Chandra MOHANTA

Department of Chemistry, Tripura University; Suryamaninagar, Agartala 799–130, India.
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Naturally occurring new iridoids and secoiridoids published during 2005—2008 are reviewed with available physical and spectral data: mp, $[\alpha]_D$, UV, IR, ^{1}H- and ^{13}C-NMR and plant source. The works on biological and pharmacological activity of naturally occurring iridoids and secoiridoids reported during 2005—2008 are also reviewed. Bioactivities like antibacterial, anticancer, anticoagulant, antifungal, anti-inflammatory, antioxidative, antiprotozoal, hepatoprotective and neuroprotective activities are highlighted.

Key words iridoid; secoiridoid; physical data; spectral data; plant source; bioactivity

This is the third part of a review[1,2] and is mainly a compilation of new iridoids and secoiridoids reported in the literature during mid 2005—2008 as well as a highlight of biological and pharmacological activity of iridoids and secoiridoids published in the said period. The earlier parts of the review[1,2] discussed the new naturally occurring iridoids and secoiridoids reported during 1994—mid 2005 as well as biological and pharmacological activities published in the said period.

Iridoids and secoiridoids are useful phytochemicals in a number of folk medicinal plants and many of them possess significant biological and pharmacological activities. Some of them are chemotaxonomically useful as markers of genus in various plant families. The main aim of this review is for rapid identification of isolated iridoids and secoiridoids by comparison of spectral data as well as to highlight the importance of this class of phytochemicals as pharmaceutical raw materials in the design of several synthetic potent drugs and formulations of herbal drugs.

A number of review articles on plant iridoids and secoiridoids are available. Earlier compilation of plant iridoids and secoiridoids reported upto 1993 is provided in four review articles.[3—6]

Iridoids and secoiridoids are listed in Table 1 in a fashion similar to that of earlier reviews.[1,2] All the compounds are arranged in six groups. Group 1 contains iridoid glycosides with an eight carbon skeleton; Group 2 contains iridoid glycosides with a nine-carbon skeleton and is further divided in to subgroups depending on whether the ninth carbon is attached to C-4 (Group 2a) or C-8 (Group 2b); Group 3 contains iridoid glycosides with ten-carbon skeletons and divided into subgroups; Group 4 contains secoiridoid glycosides; Group 5 contains iridoid aglycones and derivatives and Group 6 contains bis- and tetrakis-iridoid glycosides. The available data for each compound were listed in the following order: name; structure; molecular formula; calculated molecular weight as per atomic weight of most abundant isotopic atoms of C, H, O, N, S, *etc.*; melting point (°C) of crystalline compound; optical rotation, $[\alpha]_D$ (with concentration and solvent); UV (solvent, λ_{max} in nm, log ε); IR (medium, ν_{max} in cm^{-1}); ^{1}H-NMR (spectrometer frequency, solvent); chemical shifts (in δ, ppm starting with H-1 and listed in order) with multiplicities, coupling constants in Hz, assignments; ^{13}C-NMR (spectrometer frequency, solvent); chemical shifts (in δ, ppm, starting with C-1 and listed in order) with assignments; plant source (family); reference(s). The ^{1}H-NMR data have been rounded to the second decimal point and the ^{13}C-NMR data to the first decimal point. Assignment with the same superscript may be interchanged. Data for the derivatives were not listed unless the derivative rather than the free compound isolated in free state.

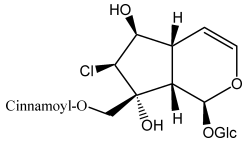
Numbering of the iridoid or secoiridoid skeleton and of the most common functionalities is given in Fig. 1. The sugar or substituent on the C-1 carbon of the aglycone moiety is given the single prime (′) designation, while other substituents are designated as double prime (″), triple prime (‴), *etc.*, according to their substitution position on the main iridoid or secoiridoid skeleton, except in cases of substituents on other substituents. The designation of substituents on other substituents is done by succeeded primes; for instance , a *p*-coumaroyl unit on sugar unit at C-1 will be designated as double prime and a sugar unit on *p*-coumaroyl unit will be designated as triple prime (*e.g.*, **1d**). For bis- and tetrakis-iridoids, the monomeric units are designated as units a,b,c, and d and these units are numbered as per usual numbering. Cinnamoyl, coumaroyl, caffeoyl, feruloyl, isoferuloyl groups are in *trans* configuration unless otherwise indicated. Some abbreviations used in representation of structures are: Glc: β-D-glucopyranosyl; Rha: α-L-rhamnopyranosyl; Me: methyl; OMe: methoxy. Suspected errors in a numbering of a monomeric unit and in multiplicity of proton coupling were corrected if there was some ambiguity in the numbering or multiplicity of proton coupling for a particular compound was observed. All the compounds in Table 1 are alphabeti-

* To whom correspondence should be addressed. e-mail: dindabtu@rediffmail.com

Table 1. List of New Iridoids

Group 1 (8-Carbon skeleton)

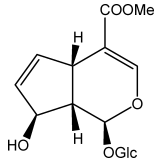
1. Globularioside



$C_{24}H_{29}ClO_{11}$: 528.1398; amorphous solid; $[\alpha]_D^{20}$ −25.0° (c=0.01, MeOH); ^{1}H-NMR (300 MHz, CD_3OD): 5.63 (d, 3.6, H-1), 6.22 (dd, 6.0, 1.5, H-3), 5.06 (dd, 6.0, 3.4, H-4), 2.70 (m, H-5), 3.94 (dd, 7.2, 3.6, H-6), 4.08 (d, 7.2, H-7), 2.63 (dd, 9.9, 3.6, H-9), 4.32 (d, 12.0, H-10), 5.06 (d, 12.0, H-10), 4.75 (d, 7.8, H-1′), 3.18 (m, H-2′), 3.30 (m, H-3′), 3.69 (m, H-4′, 5′), 3.65 (dd, 11.8, 5.8, H-6′), 3.89 (dd, 11.8, 2.0, H-6′), 7.62 (br s, H-2″, 6″), 7.41 (br s, H-3″,5″), 7.40 (br s, H-4″), 7.73 (d, 16.2, H-7″), 6.53 (d, 16.2, H-8″); ^{13}C-NMR (75 MHz, CD_3OD): 96.5 (C-1), 141.7 (C-3), 106.7 (C-4), 39.9 (C-5), 80.5 (C-6), 67.2 (C-7), 84.5 (C-8), 44.6 (C-9), 66.6 (C-10), 101.3 (C-1′), 75.7 (C-2′), 79.6 (C-3′), 72.3 (C-4′), 80.0 (C-5′), 63.6 (C-6′), 136.6 (C-1″), 130.9 (C-2″, 6″), 130.1 (C-3″, 5″), 132.4 (C-4″), 119.6 (C-7″), 147.5 (C-8″). *Globularia alypum* (Globulariaceae).[7]

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

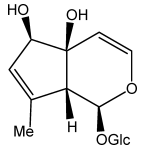
2. Citrifoside



$C_{16}H_{22}O_{10}$: 374.1213; colorless amorphous solid; $[\alpha]_D^{20}$ −56.8° (c=0.105, MeOH); UV (MeOH): 235.4 (3.86); IR (KBr): 3350, 1700, 1635, 1439, 1369, 1286, 1180, 1156, 1072, 1022, 1004; ^{1}H-NMR (500 MHz, DMSO-d_6): 5.28 (d, 4.0, H-1), 7.37 (s, H-3), 3.53 (d, 8.1, H-5), 5.97 (d, 5.2, H-6), 5.72 (d, 5.2, H-7), 4.57 (m, H-8), 2.22 (m, H-9), 3.64 (s, OMe), 4.48 (d, 7.9, H-1′), 2.99 (dd, 8.0, 7.9, H-2′), 3.16 (m, H-3′), 3.07 (m, H-4′), 3.13 (m, H-5′), 3.67 (m, H-6′), 3.45 (dd, 11.8, 5.9, H-6′); ^{13}C-NMR (125 MHz, DMSO-d_6): 95.2 (C-1), 150.8 (C-3), 109.9 (C-4), 37.1 (C-5), 134.0 (C-6), 134.3 (C-7), 76.3 (C-8), 49.5 (C-9), 166.6 (C-11), 51.0 (OMe), 98.7 (C-1′), 73.0 (C-2′), 76.7 (C-3′), 69.9 (C-4′), 77.2 (C-5′), 60.9 (C-6′). *Morinda citrifolia* (Rubiaceae).[8]

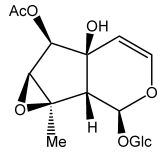
Group 2b (9-Carbon skeleton; ninth carbon on C-8)

3. 7,8-Dehydroharpagide



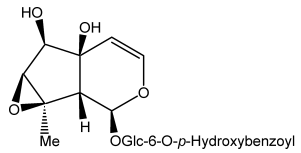
$C_{15}H_{22}O_9$: 346.1263; amorphous powder; $[\alpha]_D^{25}$ −108.0° (c=0.5, MeOH); UV (MeOH): 223 (2.9); IR (KBr): 3500—3100, 2928, 2850, 1640, 1470, 1030—1010, 980; ^{1}H-NMR (500 MHz, $CDCl_3$+drop DMSO-d_6): 5.34 (d, 1.8, H-1), 5.50 (d, 6.7, H-3), 4.90 (dd, 6.7, 2.4, H-4), 4.30 (d, 5.1, H-6), 5.70 (d, 6.3, H-7), 3.00 (d, 3.1, H-9), 1.40 (s, H_3-10), 4.65 (d, 7.6, H-1′), 3.60 (m, H-2′), 3.30 (m, H-3′), 3.40 (m, H-4′), 3.49 (m, H-5′), 3.68 (m, H-6′), 3.58 (m, H-6′); ^{13}C-NMR (125 MHz, $CDCl_3$+drop DMSO-d_6): 96.0 (C-1), 144.2 (C-3), 108.6 (C-4), 74.6 (C-5), 78.4 (C-6), 119.5 (C-7), 134.6 (C-8), 56.9 (C-9), 21.8 (C-10), 101.3 (C-1′), 73.7 (C-2′), 76.4 (C-3′), 70.0 (C-4′), 77.1 (C-5′), 61.5 (C-6′). *Ajuga remota* (Labiatae).[9]

4. 6-*O*-Acetylantirrinoside



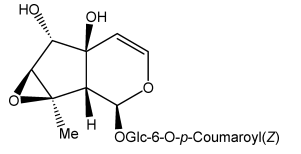
$C_{17}H_{24}O_{11}$: 404.1318; gum; $[\alpha]_D$ −100.0° (c=0.04, MeOH); UV (MeOH): 275 (2.24), 202 (3.61); IR (film): 3411, 2923, 1734, 1375, 1240, 1101, 1076, 1047, 1016, 960; ^{1}H-NMR (500 MHz, CD_3OD): 5.44 (d, 6.0, H-1), 6.32 (d, 6.5, H-3), 4.82 (d, 6.5, H-4), 4.86 (d, 2.0, H-6), 3.39 (d, 2.0, H-7), 2.36 (d, 6.0, H-9), 1.39 (s, H_3-10), 4.57 (d, 8.0, H-1′), 3.14 (m, H-2′), 3.30 (m, H-3′, 5′), 3.15 (m, H-4′), 3.53 (dd, 11.8, 6.5, H-6′), 3.83 (dd, 11.8, 2.5, H-6′), 2.03 (s, Ac); ^{13}C-NMR (125 MHz, CD_3OD): 94.6 (C-1), 143.4 (C-3), 107.5 (C-4), 74.7 (C-5), 79.4 (C-6), 64.2 (C-7), 64.5 (C-8), 53.3 (C-9), 17.4 (C-10), 99.8 (C-1′), 74.7 (C-2′), 77.7 (C-3′), 71.8 (C-4′), 78.6 (C-5′), 63.0 (C-6′), 20.3, 172.0 (Ac). *Kickxia abhaica* (Scrophulariaceae).[10]

5. 6′-*O*-*p*-Hydroxybenzoylantirrinoside



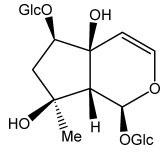
$C_{22}H_{26}O_{12}$: 482.1424; amorphous powder; $[\alpha]_D$ −51.3° (c=0.07, MeOH); UV (MeOH): 320 (3.62), 257 (4.58), 202 (4.82); IR (film): 3420, 3411, 2920, 1701, 1608, 1313, 1279, 1236, 1167, 1101, 1074, 1045, 1012, 771, 617; ^{1}H-NMR (500 MHz, CD_3OD): 4.99 (d, 8.0, H-1), 6.24 (d, 6.0, H-3), 4.77 (d, 6.0, H-4), 3.69 (d, 1.0, H-6), 3.15 (br s, H-7), 2.22 (d, 8.0, H-9), 1.24 (s, H_3-10), 4.62 (d, 8.0, H-1′), 3.16 (m, H-2′), 3.49 (m, H-3′), 3.32 (m, H-4′), 3.33 (m, H-5′), 4.40 (dd, 12.0, 7.0, H-6′), 4.52 (dd, 12.0, 2.5, H-6′), 7.78 (d, 9.0, H-2″, 6″), 6.73 (d, 9.0, H-3″, 5″); ^{13}C-NMR (125 MHz, CD_3OD): 95.6 (C-1), 142.8 (C-3), 107.7 (C-4), 74.8 (C-5), 78.8 (C-6), 66.0 (C-7), 63.0 (C-8), 53.3 (C-9), 17.6 (C-10), 99.9 (C-1′), 74.8 (C-2′), 75.7 (C-3′), 71.8 (C-4′), 77.7 (C-5′), 64.1 (C-6′), 122.2 (C-1″), 132.9 (C-2″, 6″), 132.9 (C-3″, 5″), 163.7 (C-4″), 167.8 (C-7″). *Kickxia abhaica* (Scrophulariaceae).[10]

6. Harprocumbide B (6′-*O*-(*cis*-*p*-Coumaroyl procumbide))



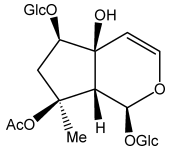
$C_{24}H_{28}O_{12}$: 508.1580; white amorphous powder; ^{1}H-NMR (400 MHz, C_5D_5N): 6.05 (d, 9.2, H-1), 6.67 (d, 6.2, H-3), 5.23 (d, 6.2, H-4), 4.35 (s, H-6), 3.66 (s, H-7), 2.62 (d, 9.2, H-9), 1.81 (s, H_3-10), 5.37 (d, 8.0, H-1′), 4.07 (t, 8.4, H-2′), 4.22 (t, 8.8, H-3′), 4.14 (m, H-4′), 3.97 (dd, 5.2, 2.4, H-5′), 4.89 (dd, 12.0, 2.3, H-6′), 4.83 (dd, 12.0, 5.2, H-6′), 8.02 (d, 8.4, H-2″, 6″), 7.12 (d, 8.4, H-3″, 5″), 6.79 (d, 12.8, H-7″), 5.92 (d, 12.8, H-8″); ^{13}C-NMR (100 MHz, C_5D_5N): 96.0 (C-1), 142.7 (C-3), 105.1 (C-4), 79.6 (C-5), 77.4 (C-6), 65.4 (C-7), 66.2 (C-8), 52.6 (C-9), 17.6 (C-10), 100.1 (C-1′), 74.7 (C-2′), 78.0 (C-3′), 71.0 (C-4′), 75.2 (C-5′), 63.7 (C-6′), 126.3 (C-1″), 133.6 (C-2″, 6″), 115.7 (C-3″, 5″), 160.4 (C-4″), 144.5 (C-7″), 115.8 (C-8″), 166.8 (C-9″). *Harpagophytum procumbens* (Pedaliaceae).[11]

7. Harpagide 6-*O*-β-glucoside



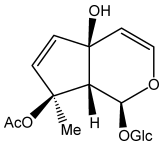
$C_{21}H_{34}O_{15}$: 526.1897; amorphous powder; $[\alpha]_D^{25}$ −57.0° (c=1.0,MeOH); UV (MeOH): 226 (2.4); IR (KBr): 3550—3100, 2920, 2850, 1650, 1475, 1020—1000, 950; ^{1}H-NMR (500 MHz, DMSO-d_6): 5.36 (d, 1.1, H-1), 6.20 (d, 6.7, H-3), 5.94 (dd, 6.7, 1.2, H-4), 5.00 (d, 5.6, H-6), 2.18 (m, H-7), 2.08 (m, H-7), 3.14 (d, 1.6, H-9), 1.23 (s, H_3-10), 4.60 (d, 7.2, H-1′), 3.50 (m, H-2′), 3.39 (m, H-3′), 3.20 (m, H-4′), 3.29 (m, H-5′), 3.56 (m, H-6′), 3.47 (m, H-6′), 4.84 (d, 7.8, H-1″), 3.54 (m, H-2″), 3.44 (m, H-3″), 3.14 (m, H-4″), 3.36 (m, H-5″), 3.68 (m, H-6″), 3.48 (m, H-6″); ^{13}C-NMR (150 MHz, DMSO-d_6): 95.7 (C-1), 146.0 (C-3), 107.8 (C-4), 75.1 (C-5), 76.6 (C-6), 48.3 (C-7), 73.4 (C-8), 55.5 (C-9), 21.4 (C-10), 100.4 (C-1′), 74.0 (C-2′), 76.1 (C-3′), 69.9 (C-4′), 76.8 (C-5′), 61.6 (C-6′), 101.0 (C-1″), 73.6 (C-2″), 76.5 (C-3″), 70.4 (C-4″), 77.0 (C-5″), 60.9 (C-6 ″). *Ajuga remota* (Labiatae).[9]

8. 8-*O*-Acetylharpagide-6-*O*-β-glucoside



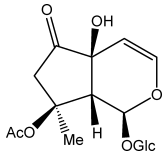
$C_{23}H_{36}O_{16}$: 568.2003; amorphous powder; $[\alpha]_D^{25}$ −85.0° (c=0.5, MeOH); UV (MeOH): 218 (2.8); IR (KBr): 3540, 2930, 2850, 1740, 1645, 1470, 1040—1010, 980; ^{1}H-NMR (500 MHz, DMSO-d_6): 6.35 (d, 1.5, H-1), 6.45 (d, 6.4, H-3), 6.04 (dd, 6.4, 2.0, H-4), 4.90 (d, 4.5, H-6), 2.20 (m, H-7), 2.10 (m, H-7), 3.21 (d, 2.2, H-9) , 1.47 (s, H_3-10), 2.04 (s, OAc), 4.80 (d, 7.6, H-1′), 3.46 (m, H-2′), 3.38 (m, H-3′), 3.25 (m, H-4′), 3.30 (m, H-5′), 3.55 (m, H-6′), 3.41 (m, H-6′), 5.01 (d, 7.5, H-1″), 3.53 (m, H-2″), 3.40 (m, H-3″), 3.18 (m, H-4″), 3.28 (m, H-5″), 3.58 (m, H-6″), 3.44 (m, H-6″); ^{13}C-NMR (125 MHz, DMSO-d_6): 94.8 (C-1), 145.3 (C-3), 108.4 (C-4), 76.0 (C-5), 75.9 (C-6), 48.6 (C-7), 91.2 (C-8), 56.4 (C-9), 23.4 (C-10), 101.0 (C-1′), 74.7 (C-2′), 76.8 (C-3′), 69.8 (C-4′), 76.5 (C-5′), 61.0 (C-6′), 99.9 (C-1″), 74.0 (C-2″), 76.7 (C-3″), 69.4 (C-4″), 60.2 (C-6″), 23.8, 170.3 (OAc). *Ajuga remota* (Labiatae).[9]

9. 6,7-Dehydro-8-acetylharpagide



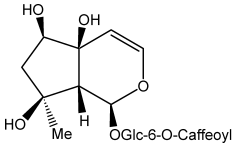
$C_{17}H_{24}O_{10}$: 388.1369; colorless plates; mp >250 °C; $[\alpha]_D^{25}$ −19.0° (c=0.5, MeOH); UV (MeOH): 214 (3.0); IR (KBr): 3450—3100, 2920, 2850, 1735, 1644, 1470, 1050, 890; ^{1}H-NMR (500 MHz, $CDCl_3$+drop DMSO-d_6): 5.40 (d, 2.0, H-1), 5.70 (d, 6.2, H-3), 5.21 (dd, 6.4, 2.2, H-4), 6.02 (d, 9.0, H-6), 5.84 (d, 9.0, H-7), 3.21 (d, 1.8, H-9), 1.37 (s, H_3-10), 2.02 (s, OAc), 4.50 (d, 7.4, H-1′), 3.48 (m, H-2′), 3.55 (m, H-3′), 3.20 (m, H-4′), 3.33 (m, H-5′), 3.70 (m, H-6′), 3.62 (m, H-6′); ^{13}C-NMR (125 MHz, $CDCl_3$+drop DMSO-d_6): 94.8 (C-1), 143.8 (C-3), 107.3 (C-4), 76.0 (C-5), 133.6 (C-6), 128.7 (C-7), 90.5 (C-8), 47.0 (C-9), 23.0 (C-10), 99.0 (C-1′), 74.4 (C-2′), 76.9 (C-3′), 70.4 (C-4′), 77.6 (C-5′), 62.1 (C-6′), 25.4, 169.8 (OAc). *Ajuga remota* (Labiatae).[9]

10. 6-Keto-8-acetylharpagide



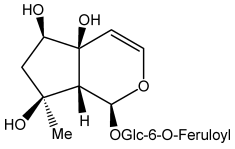
$C_{17}H_{24}O_{11}$: 404.1318; colorless platelets, mp >250 °C; $[\alpha]_D^{25}$ +46.0° (c=1.0, MeOH); UV (MeOH): 208 (3.2); IR (KBr): 3540, 3350, 1740, 1700, 1650, 1470, 1350, 1030—1010, 920, 870; ^{1}H-NMR (500 MHz, $CDCl_3$+drop DMSO-d_6): 5.40 (d, 1.8, H-1), 5.50 (d, 6.1, H-3), 5.10 (dd, 6.1, 2.0, H-4), 2.40 (d, 6.3, H-7), 2.25 (d, 6.3, H-7), 2.90 (d, 1.6, H-9), 1.50 (s, H_3-10), 1.90 (s, OAc), 4.70 (d, 7.5, H-1′), 3.43 (m, H-2′), 3.29 (m,H-3′), 3.36 (m, H-4′), 3.52 (m, H-5′), 3.80 (m, H-6′), 3.68 (m, H-6′); ^{13}C-NMR (125 MHz, $CDCl_3$+drop DMSO-d_6): 95.4 (C-1), 145.0 (C-3), 109.0 (C-4), 73.7 (C-5), 213.1 (C-6), 49.8 (C-7), 87.3 (C-8), 55.9 (C-9), 22.9 (C-10), 99.4 (C-1′), 73.5 (C-2′), 77.3 (C-3′), 71.4 (C-4′), 76.9 (C-5′), 61.5 (C-6′), 24.6, 171.2 (OAc). *Ajuga remota* (Labiatae).[9]

11. 6-*O*-Caffeoylharpagide



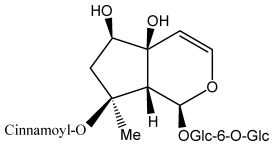
$C_{24}H_{30}O_{13}$: 526.1686; pale brown amorphous powder; $[\alpha]_D^{26}$ −37.6° (c=1.0, MeOH); UV (MeOH): 312 (2.60), 227 (2.48), 203 (2.56); IR (KBr): 3394, 1697, 1607, 1605, 1520, 1033;^{1}H-NMR (400 MHz, CD_3OD): 5.65 (d, 1.2, H-1), 6.32 (d, 6.4, H-3), 4.93 (dd, 6.4, 1.4, H-4), 3.67 (t, 3.9, H-6), 1.85 (dd, 13.7, 4.6, H-7), 1.75 (dd, 13.8, 3.0, H-7), 2.54 (s, H-9), 1.18 (s, H_3-10), 4.59 (d, 7.9, H-1′), 3.25 (t, 8.9, H-2′), 3.39 (t, 7.4, H-3′), 3.40 (t, 7.4, H-4′), 3.54—3.57 (m, H-5′), 4.48 (dd, 12.0, 2.1, H-6′), 4.35 (dd, 12.0, 5.8, H-6′), 7.03 (d, 2.0, H-2″), 6.76 (d, 8.2, H-5″), 6.93 (dd, 8.2, 2.0, H-6″), 7.56 (d, 15.9, H-7″), 6.28 (d, 15.9, H-8″); ^{13}C-NMR (100 MHz, CD_3OD): 93.1 (C-1), 142.5 (C-3), 108.4 (C-4), 72.8 (C-5), 78.3 (C-6), 46.9 (C-7), 78.4 (C-8), 59.5 (C-9), 25.0 (C-10), 99.2 (C-1′), 74.4 (C-2′), 77.4 (C-3′), 71.7 (C-4′), 76.7 (C-5′), 64.5 (C-6′), 127.7 (C-1″), 115.2 (C-2″), 146.8 (C-3″), 149.6 (C-4″), 116.5 (C-5″), 123.1 (C-6″), 147.2 (C-7″), 114.8 (C-8″), 169.1 (C-9″). *Scrophularia ningpoensis* (Scrophulariaceae).[12]

12. 6′-*O*-Feruloylharpagide



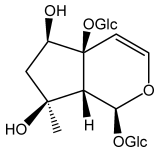
$C_{25}H_{32}O_{13}$: 540.1842; brown amorphous powder; $[\alpha]_D^{26}$ −35.2° (c=1.0, MeOH); UV (MeOH): 325 (2.61), 235 (2.48), 204 (2.58); IR (KBr): 3417, 1601, 1516; ^{1}H-NMR (400 MHz, CD_3OD): 5.65 (d, 1.2, H-1), 6.30 (d, 6.4, H-3), 4.93 (dd, 6.4, 1.5, H-4), 3.67 (t, 3.9, H-6), 1.84 (dd, 13.7, 4.6, H-7), 1.73 (dd, 13.7, 3.2, H-7), 2.54 (s, H-9), 1.17 (s, H_3-10), 4.59 (d, 7.9, H-1′), 3.24 (t, 9.0, H-2′), 3.41 (t, 6.2, H-3′), 3.40 (t, 6.2, H-4′), 3.54—3.58 (m, H-5′), 4.48 (dd, 12.0, 2.2, H-6′), 4.36 (dd, 12.0, 5.8, H-6′), 7.16 (d, 1.9, H-2″), 6.79 (d, 8.2, H-5″), 7.05 (dd, 8.2, 1.9, H-6″), 7.62 (d, 15.9, H-7″), 6.38 (d, 15.9, H-8″), 3.87 (s, MeO-3″); ^{13}C-NMR (100 MHz, CD_3OD): 93.1 (C-1), 142.5 (C-3), 108.4 (C-4), 72.7 (C-5), 78.3 (C-6), 46.9 (C-7), 78.4 (C-8), 59.5 (C-9), 25.0 (C-10), 99.2 (C-1′), 74.4 (C-2′), 77.4 (C-3′), 71.7 (C-4′), 75.6 (C-5′), 64.5 (C-6′), 127.6 (C-1″), 117.7 (C-2″), 149.3 (C-3″), 150.6 (C-4″), 116.5 (C-5″), 124.2 (C-6″), 147.1 (C-7″), 115.2 (C-8″), 169.1 (C-9″), 56.4 (MeO-3″). *Scrophularia ningpoensis* (Scrophulariaceae).[12]

13. 6′-*O*-Glucopyranosylharpagoside



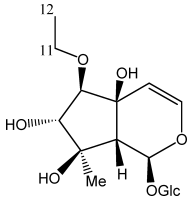
$C_{30}H_{40}O_{16}$: 656.2316; pale brown amorphous powder; $[\alpha]_D^{26}$ +11.6° (c=1.0, MeOH); UV (MeOH): 279 (2.35), 222 (2.27), 216 (2.31), 204 (2.37); IR (KBr): 3421, 1701, 1632, 1601, 1516; ^{1}H-NMR (400 MHz, CD_3OD): 6.19 (d, 1.2, H-1), 6.39 (d, 6.4, H-3), 4.93 (dd, 6.4, 1.6, H-4), 3.74 (t, 3.4, H-6), 2.24 (d, 15.1, H-7), 1.99 (dd, 15.4, 4.4, H-7), 2.92 (s, H-9), 1.53 (s, H_3-10), 6.63 (d, 7.9, H-1′), 3.23 (t, 9.1, H-2′), 3.43—3.46 (m, H-3′), 3.38 (t, 7.4, H-4′), 3.52—3.56 (m, H-5′), 4.20 (dd, 12.0, 1.8, H-6′), 3.89 (dd, 12.0, 6.5, H-6′), 4.59 (d, 7.9, H-1″), 3.23 (t, 9.1, H-2″), 3.40—3.42 (m, H-3″), 3.38 (t, 7.4, H-4″), 3.53 (d, 9.1, H-5″), 3.90 (dd, 12.0, 2.3, H-6″), 3.68 (dd, 12.0, 5.8, H-6″), 7.57—7.61 (m, H-2‴, 6‴), 7.36—7.40 (m, H-3‴, 5‴), 7.39—7.41 (m, H-4‴), 7.70 (d, 16.0, H-7‴), 6.50 (d, 16.0, H-8‴); ^{13}C-NMR (100 MHz, CD_3OD): 94.3 (C-1), 143.8 (C-3), 107.0 (C-4), 73.6 (C-5), 77.7 (C-6), 46.3 (C-7), 88.5 (C-8), 55.4 (C-9), 22.9 (C-10), 99.3 (C-1′), 74.4 (C-2′), 77.7 (C-3′), 71.7 (C-4′), 77.7 (C-5′), 69.6 (C-6′), 104.6 (C-1″), 75.4 (C-2″), 77.7 (C-3″), 71.7 (C-4″), 77.7 (C-5″), 62.8 (C-6″), 136.0 (C-1‴), 129.2 (C-2‴, 6‴), 130.0 (C-3‴, 5‴), 131.3 (C-4‴), 146.0 (C-7‴), 120.3 (C-8‴), 168.3 (C-9‴). *Scrophularia ningpoensis* (Scrophulariaceae).[12]

14. 5-*O*-β-Glucopyranosylharpagide



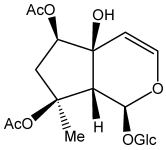
$C_{21}H_{34}O_{15}$: 526.1897; amorphous powder, $[\alpha]_D^{21}$ −33.1° (c=0.45, MeOH); ^{1}H-NMR (400 MHz, CD_3OD): 5.75 (d, 1.5, H-1), 6.39 (d, 6.6, H-3), 5.15 (d, 6.6, H-4), 3.93 (dd, 3.8, 3.2, H-6), 1.85 (br s, H_2-7), 2.76 (d, 1.5, H-9), 1.25 (s, H_3-10), 4.71 (d, 7.8, H-1′), 3.88 (dd, 12.0, 2.0, H-6′), 3.66 (dd, 12.0, 5.6, H-6′), 4.59 (d, 7.8, H-1″), 3.78 (dd, 12.6, 2.2, H-6″), 3.70 (dd, 12.6, 4.6, H-6″); ^{13}C-NMR (100 MHz, CD_3OD): 93.0 (C-1), 143.6 (C-3), 104.5 (C-4), 80.1 (C-5), 76.7 (C-6), 46.6 (C-7), 78.4 (C-8), 57.2 (C-9), 25.1 (C-10), 99.2 (C-1′), 74.8 (C-2′), 78.4 (C-3′), 71.7 (C-4′), 77.1 (C-5′), 62.8 (C-6′), 97.5 (C-1″), 75.2 (C-2″), 78.1 (C-3″), 70.7 (C-4″), 78.0 (C-5″), 61.9 (C-6″). *Clerodendrum chinense* (Verbenaceae).[13]

15. Genestifolioside



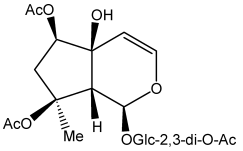
$C_{17}H_{28}O_{11}$: 408.1631; white powder; $[\alpha]_D^{25}$ −99.9° (c=0.001, MeOH); UV (MeOH): 300.0 (3.9); IR (KBr): 3400—3200, ^{1}H-NMR (500 MHz, CD_3OD): 5.43 (d, 7.3, H-1), 6.43 (d, 7.6, H-3), 4.81 (d, 7.6, H-4), 3.70 (d, 1.3, H-6), 5.40 (d, 1.3, H-7), 3.41 (d, 7.3, H-9), 2.13 (s, H_3-10), 4.10 (q, 6.8, H-11), 1.32 (t, 6.8, H_3-12), 4.71 (d, 8.0, H-1′), 3.90 (dd, 8.7, 8.0, H-2′), 3.42 (br t, 8.7, H-3′), 3.53 (dd, 8.7, 8.7, H-4′), 2.9 (m, H-5′), 3.32 (dd, 11.7, 8.7, H-6′), 3.84 (dd, 11.7, 1.9, H-6′); ^{13}C-NMR (125 MHz, CD_3OD): 93.2 (C-1), 142.3 (C-3), 104.3 (C-4), 72.2 (C-5), 83.8 (C-6), 74.9 (C-7), 78.9 (C-8), 49.2 (C-9), 20.1 (C-10), 63.3 (C-11), 14.4 (C-12), 99.2 (C-1′), 74.5 (C-2′), 77.5 (C-3′), 71.4 (C-4′), 74.2 (C-5′), 62.3 (C-6′). *Linaria genestifolia* (Scrophulariaceae).[14]

16. 6,8-Diacetylharpagide



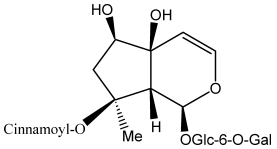
$C_{19}H_{28}O_{12}$: 448.1580; colorless amorphous powder; $[\alpha]_D^{25}$ +65.0° (c=0.5, MeOH); UV (MeOH): 203 (3.5); IR (KBr): 3500, 1734, 1650, 1030—1010; ^{1}H-NMR (500 MHz, DMSO-d_6+$CDCl_3$): 5.54 (d, 1.0, H-1), 6.53 (d, 6.6, H-3), 5.0 (dd, 6.6, 1.7, H-4), 5.23 (d, 4.5, H-6), 2.20 (d, 15.6, H-7), 2.00 (dd, 15.6, 4.0, H-7), 2.86 (m, H-9), 1.35 (s, H_3-10), 1.98 (s, AcO-8), 2.10 (s, AcO-6), 4.70 (d, 7.6, H-1′), 3.28 (m, H-2′), 3.60 (m, H-3′), 3.39 (m, H-4′), 3.52 (m, H-5′), 3.94 (dd, 13.0, 1.8, H-6′), 3.80 (dd, 13.6, 5.5, H-6′); ^{13}C-NMR (125 MHz, DMSO-d_6+$CDCl_3$): 95.1 (C-1), 144.2 (C-3), 108.0 (C-4), 74.5 (C-5), 79.1 (C-6), 47.6 (C-7), 90.7 (C-8), 55.9 (C-9), 23.5 (C-10), 98.1 (C-1′), 77.9 (C-2′), 78.8 (C-3′), 72.6 (C-4′), 77.4 (C-5′), 62.8 (C-6′), 24.8, 25.2, 170.1, 170.4 (2×Ac). *Ajuga remota* (Labiatae).[15]

17. 6,8-Diacetylharpagide-1-*O*-*β*-(2′,3′-di-*O*-acetylglucoside)



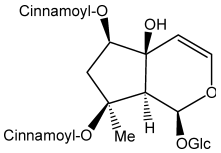
$C_{23}H_{32}O_{14}$: 532.1791; colorless crystals; mp 174—176 °C; $[\alpha]_D^{25}$ +92.0° (c=1.5, CH_2Cl_2); UV (MeOH): 210 (2.76); IR (KBr): 3500—3200, 1732, 1650, 1025—1010; ^{1}H-NMR (500 MHz, DMSO-d_6+$CDCl_3$): 5.56 (d, 1.1, H-1), 6.44 (d, 6.3, H-3), 4.94 (dd, 6.3, 1.3, H-4), 2.30 (d, 15.5, H_β-7), 2.14 (dd, 15.5, 1.2, H_α-7), 2.84 (d, 1.8, H-9), 1.36 (s, H_3-10), 2.15 (s, AcO-6), 2.04 (s, AcO-8), 4.60 (d, 7.8, H-1′), 5.02 (t, 8.8, H-2′), 5.10 (t, 9.0, H-3′), 3.50 (m, H-4′), 3.55 (m, H-5′), 4.01 (dd, 12.4, 2.2, H-6′), 3.81 (dd, 12.4, 5.4, H-6′), 2.01 (s, AcO-2′), 1.95 (s, AcO-3′); ^{13}C-NMR (125 MHz, $CDCl_3$+DMSO-d_6): 95.4 (C-1), 143.7 (C-3), 107.2 (C-4), 73.3 (C-5), 80.0 (C-6), 46.9 (C-7), 89.0 (C-8), 55.2 (C-9), 22.8 (C-10), 98.9 (C-1′), 74.0 (C-2′), 76.6 (C-3′), 71.2 (C-4′), 76.9 (C-5′), 62.4 (C-6′), 24.9, 25.0×2, 25.4, 169.8, 170.0, 170.1, 171.0 (4×Ac). *Ajuga remota* (Labiatae).[15]

18. Harprocumbide A (6′-*O*-*α*-D-Galactopyranosylharpagoside)



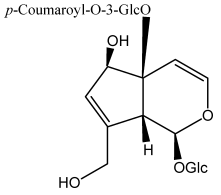
$C_{30}H_{40}O_{16}$: 656.2316; white amorphous powder; $[\alpha]_D^{22}$ +16.3° (c=0.10, MeOH); ^{1}H-NMR (400 MHz, C_5D_5N): 6.86 (s, H-1), 6.47 (d, 6.4, H-3), 5.15 (d, 6.4, H-4), 4.66 (d, 4.2, H-6), 2.10 (dd, 14.8, 4.2, H-7), 2.60 (d, 14.8, H-7), 3.60 (s, H-9), 1.70 (s, H_3-10), 5.26 (d, 8.0, H-1′), 3.99 (t, 8.4, H-2′), 4.17 (t, 8.4, H-3′), 4.08 (m, H-4′), 4.05 (m, H-5′), 4.52 (dd,10.0, 4.8, H-6′), 4.32 (d, 10.0, H-6′), 5.54 (d, H-1″), 4.57 (m, H-2″), 4.65 (d, 10.0, H-3″), 4.67 (m, H-4″), 4.75 (t, 6.0, H-5″), 4.47 (d, 5.8, H_2-6″), 7.50 (m, H-2‴, 6‴), 7.25 (m, H-3‴, 4‴,5‴), 7.82 (d, 16.0, H-7‴), 6.53 (d, 16.0, H-8‴); ^{13}C-NMR (100 MHz, C_5D_5N): 95.0 (C-1), 143.0 (C-3), 109.1 (C-4), 74.4 (C-5), 77.6 (C-6), 47.0 (C-7), 88.3 (C-8), 55.9 (C-9), 23.7 (C-10), 99.2 (C-1′), 75.6 (C-2′), 77.8 (C-3′), 72.1 (C-4′), 79.5 (C-5′), 69.1 (C-6′), 101.6 (C-1″), 71.7 (C-2″), 73.1 (C-3″), 72.6 (C-4″), 73.6 (C-5″), 63.8 (C-6″), 136.0 (C-1‴), 130.0 (C-2‴, 6‴), 129.5 (C-3‴, 5‴), 131.2 (C-4‴), 145.3 (C-7‴), 121.1 (C-8‴), 167.6 (C-9‴). *Harpagophytum procumbens* (Pedaliaceae).[11]

19. 6-*O*-*E*-Cinnamoyl-*E*-harpagoside



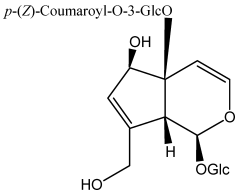
$C_{33}H_{36}O_{12}$: 624.2206; white amorphous powder; $[\alpha]_D^{25}$ +40.0° (c=0.10, MeOH); UV (MeOH): 273 (4.66), 216 (4.50), 203 (4.56); IR (KBr): 3418, 2960, 2929, 1704, 1636, 1450, 1282, 1204, 1076, 1028; ^{1}H-NMR (600 MHz, CD_3OD): 6.19 (s, H-1), 6.51 (m, H-3), 5.06 (m, H-4), 4.96 (d, 3.7, H-6), 2.45 (d, 16.0, H_a-7), 2.12 (dd, 16.0, 4.0, H_b-7), 3.09 (s, H-9), 1.60 (s, H_3-10), 4.65 (d, 7.8, H-1′), 3.23 (dd, 9.0, 7.8, H-2′), 3.41 (m, H-3′), 3.32 (m, H-4′), 3.38 (m, H-5′), 3.95 (dd, 12.6, 2.4, H_a-6′), 3.74 (dd, 12.6, 6.2, H_b-6′), 7.38 (d, 7.3, H-2″, 6″), 7.14 (t, 7.6, H-3″, 5″), 7.25 (t, 7.3, H-4″), 7.63 (d, 16.0, H-7″), 6.41 (d, 16.0, H-8″), 7.39 (d, 7.2, H-2‴, 6‴), 7.20 (t, 7.6, H-3‴, 5‴), 7.30 (t, 7.3, H-4‴), 7.74 (d, 16.0, H-7‴), 6.50 (d, 16.0, H-8‴); ^{13}C-NMR (150 MHz, CD_3OD): 93.0 (C-1), 143.4 (C-3), 104.5 (C-4), 71.7 (C-5), 78.9 (C-6), 42.6 (C-7), 87.4 (C-8), 54.7 (C-9), 20.9 (C-10), 98.9 (C-1′), 73.2 (C-2′), 76.8 (C-3′), 70.4 (C-4′), 76.2 (C-5′), 61.6 (C-6′), 133.9 (C-1″), 127.8 (C-2″, 6″), 128.4 (C-3″), 129.9 (C-4″), 128.5 (C-5″), 145.1 (C-7″), 117.6 (C-8″), 166.5 (C-9″), 134.1 (C-1‴), 127.8 (C-2‴, 6‴), 128.4 (C-3‴), 130.0 (C-4‴), 128.5 (C-5‴), 145.3 (C-7‴), 118.4 (C-8‴), 166.9 (C-9‴). *Goldfussia yunnanensis* (Acanthaceae).[16]

20. Stachysoside E (3″-*O*-*p*-Coumaroyl ester of melittoside)



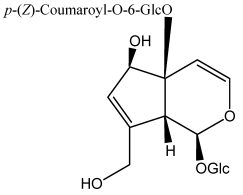
$C_{30}H_{38}O_{17}$; 670.2108; colorless amorphous powder; $[\alpha]_D^{24}$ −23.6° (c=1.06, MeOH); ^{1}H-NMR (400 MHz, CD_3OD): 5.61 (d, 3.5, H-1), 6.38 (d, 6.0, H-3), 5.13 (α, 6.0, H-4), 4.39 (m, H-6), 5.80 (m, H-7), 3.35 (overlapped, H-9), 4.20 (m, H-10), 4.62 (d, 8.0, H-1′), 3.28 (overlapped, H-2′), 3.20—3.40 (overlapped, H-3′, 4′), 3.31 (overlapped, H-5′), 3.66 (m, H-6′), 3.88 (br d, H-6′), 4.81 (d, 8.0, H-1″), 3.47 (dd, 9.5, 8.0, H-2″), 5.08 (dd, 9.5, 9.5, H-3″), 3.61 (dd, 9.5, 9.5, H-4″), 3.43 (m, H-5″), 3.75 (dd, 12.5, 5.0, H-6″), 3.83 (dd, 12.5, 2.0, H-6″), 7.47 (d, 8.5, H-2‴, 6‴), 6.89 (d, 8.5, H-3‴, 5‴), 7.66 (d, 16.0, H-7‴), 6.40 (d, 16.0, H-8‴); ^{13}C-NMR (100 MHz,CD_3OD): 94.2 (C-1), 143.5 (C-3), 105.2 (C-4), 80.2 (C-5), 80.0 (C-6), 128.2 (C-7), 147.4 (C-8), 51.7 (C-9), 61.0 (C-10), 98.3 (C-1′), 75.0 (C-2′), 78.5 (C-3′), 71.7 (C-4′), 77.3 (C-5′), 62.8 (C-6′), 99.7 (C-1″), 73.5 (C-2″), 79.3 (C-3″), 69.2 (C-4″), 78.0 (C-5″), 61.9 (C-6″), 127.4 (C-1‴), 131.1 (C-2‴, 6‴), 116.9 (C-3‴, 5‴), 161.2 (C-4‴), 146.6 (C-7‴), 115.6 (C-8‴), 169.1 (C-9‴). *Stachys lanata* (Labiatae).[17]

21. Stachysoside F



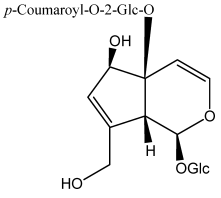
$C_{30}H_{38}O_{17}$; 670.2108; colorless amorphous powder; $[\alpha]_D^{24}$ −10.0° (c=0.30, MeOH); ^{1}H-NMR (270 MHz, CD_3OD): 5.59 (d, 4.0, H-1), 6.38 (d, 6.5, H-3), 5.14 (d, 6.5, H-4), 4.40 (m, H-6), 5.79 (m, H-7), 3.30 (overlapped, H-9), 4.19 (m, H-10), 4.61 (d, 7.6, H-1′), 3.28 (overlapped, H-2′), 3.20—3.40 (overlapped, H-3′, 4′), 3.31 (overlapped, H-5′), 3.66 (m, H-6′), 3.88 (br d, 12.0, H-6′), 4.80 (d, 8.0, H-1″), 3.42 (dd, 9.5, 8.0, H-2″), 5.07 (dd, 9.5, 9.5, H-3″), 3.55 (dd, 9.5, 9.5, H-4″), 3.40 (m, H-5″), 3.73 (dd,12.5, 5.0, H-6″), 3.82 (dd, 12.5, 2.0, H-6″), 7.66 (d, 8.5, H-2‴, 6‴), 6.73 (d, 8.5, H-3‴, 5‴), 6.86 (d, 13.0, H-7‴), 5.85 (d, 13.0, H-8‴); ^{13}C-NMR (67.5 MHz, CD_3OD): 94.4 (C-1), 143.7 (C-3), 105.3 (C-4), 80.4 (C-5), 80.1 (C-6), 128.2 (C-7), 147.3 (C-8), 51.7 (C-9), 61.0 (C-10), 98.3 (C-1′), 74.9 (C-2′), 78.5 (C-3′), 71.7 (C-4′), 77.3 (C-5′), 62.8 (C-6′), 99.7 (C-1″), 73.4 (C-2″), 78.7 (C-3″), 69.1 (C-4″), 78.0 (C-5″), 61.9 (C-6″), 127.6 (C-1‴), 133.8 (C-2‴, 6‴), 115.9 (C-3‴, 5‴), 160.2 (C-4‴), 144.8 (C-7‴), 116.9 (C-8‴), 168.1 (C-9‴). *Stachys lanata* (Labiatae).[17]

22. Stachysoside G



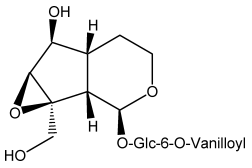
$C_{30}H_{38}O_{17}$; 670.2108; colorless amorphous powder; $[\alpha]_D^{24}$ −7.9° (c=0.51, MeOH); ^{1}H-NMR (400 MHz, CD_3OD): 5.46 (d, 5.0, H-1), 6.33 (d, 6.5, H-3), 5.10 (d, 6.5, H-4), 4.42 (m, H-6), 5.77 (m, H-7), 3.30 (overlapped, H-9), 4.12 (dd, 15.0, 1.0, H-10), 4.24 (m, H-10), 4.58 (d, 7.5, H-1′), 3.23 (overlapped, H-2′), 3.20—3.40 (overlapped, H-3′—5′), 3.61 (m, H-6′), 3.85 (dd, 11.5, 1.0, H-6′), 4.67 (d, 8.0, H-1″), 3.26 (overlapped, H-2″), 3.20—3.40 (overlapped, H-3″), 3.29 (overlapped, H-4″), 3.59 (m, H-5″), 4.23 (dd, 12.0, 5.0, H-6″), 4.53 (dd, 12.0, 2.0, H-6″), 7.47 (d, 9.0, H-2‴, 6‴), 6.82 (d, 9.0, H-3‴, 5‴), 7.65 (d, 16.0, H-7‴), 6.37 (d, 16.0, H-8‴); ^{13}C-NMR (100 MHz, CD_3OD): 95.5 (C-1), 143.8 (C-3), 105.9 (C-4), 81.1 (C-5), 81.2 (C-6), 128.0 (C-7), 147.2 (C-8), 52.2 (C-9), 61.2 (C-10), 99.2 (C-1′), 74.9 (C-2′), 78.1 (C-3′), 71.5 (C-4′), 77.6 (C-5′), 62.8 (C-6′), 99.8 (C-1″), 75.1 (C-2″), 78.5 (C-3″), 71.8 (C-4″), 75.4 (C-5″), 64.8 (C-6″), 127.2 (C-1‴), 131.3 (C-2‴, 6‴), 117.0 (C-3‴, 5‴), 161.5 (C-4‴), 146.8 (C-7‴), 115.3 (C-8‴), 169.4 (C-9‴). *Stachys lanata* (Labiatae).[17]

23. Stachysoside H



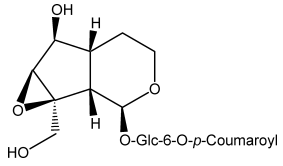
$C_{30}H_{38}O_{17}$; 670.2108; colorless amorphous powder; $[\alpha]_D^{24}$ +28.5° (c=0.40, MeOH); ^{1}H-NMR (400 MHz, CD_3OD): 5.19 (d, 7.5, H-1), 6.52 (d, 5.5, H-3), 4.83 (overlapped, H-4), 4.45 (m, H-6), 5.72 (m, H-7), 3.35 (overlapped, H-9), 4.22 (m, H-10), 4.65 (d, 7.5, H-1′), 3.23 (dd, 9.0, 7.5, H-2′), 3.37 (overlapped, H-3′), 3.20—3.40 (overlapped, H-4′), 3.26 (overlapped, H-5′), 3.62 (dd, 12.5, 5.0, H-6′), 3.84 (dd, 12.5, 2.0, H-6′), 4.82 (d, 8.0, H-1″), 4.79 (dd, 9.0, 8.0, H-2″), 3.64 (dd, 9.0, 9.0, H-3″), 3.42 (dd, 9.5, 9.0, H-4″), 3.32 (overlapped, H-5″), 3.69 (dd, 12.5, 5.0, H-6″), 3.84 (dd, 12.5, 2.0, H-6″), 7.48 (d, 9.0, H-2‴, 6‴), 6.82 (d, 9.0, H-3‴, 5‴), 7.68 (d, 16.0, H-7‴), 6.40 (d, 16.0, H-8‴); ^{13}C-NMR (100 MHz, CD_3OD): 97.7 (C-1), 145.7 (C-3), 106.3 (C-4), 83.3 (C-5), 83.9 (C-6), 129.7 (C-7), 145.5 (C-8), 52.2 (C-9), 61.5 (C-10), 99.7 (C-1′), 74.8 (C-2′), 78.5 (C-3′), 71.6 (C-4′), 77.7 (C-5′), 62.5 (C-6′), 97.9 (C-1″), 75.4 (C-2″), 76.0 (C-3″), 71.5 (C-4″), 77.9 (C-5″), 62.7 (C-6″), 127.2 (C-1‴), 131.3 (C-2‴, 6‴), 116.9 (C-3‴, 5‴), 161.4 (C-4‴), 147.4 (C-7‴), 115.1 (C-8‴), 168.9 (C-9‴). *Stachys lanata* (Labiatae).[17]

24. 6′-*O*-Vanilloyl-3,4-dihydrocatalpol (Piscroside A)



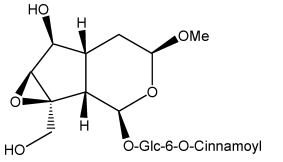
$C_{23}H_{30}O_{13}$: 514.1686; amorphous powder; $[\alpha]_D^{25}$ −59.8° (c=0.40, MeOH); IR (KBr): 3419, 2925, 1702, 1605, 1516, 1430, 1286, 1221, 1070, 763; ^{1}H-NMR (600 MHz, DMSO-d_6): 4.46 (d, 8.7, H-1), 3.74 (m, H_α-3), 3.19 (overlapped, H_β-3), 1.44 (d, 13.5, H_α-4), 1.58 (m, H_β-4), 1.80 (dd, 13.5, 8.1, H-5), 3.77 (dd, 9.0, 6.6, H-6), 3.18 (d, 9.0, H-7), 2.04 (t, 8.0, H-9), 3.41 (dd, 13.2, 7.3, H-10), 3.81 (overlapped, H-10), 4.55 (d, 7.8, H-1′), 3.02 (dd, 7.8, 5.0, H-2′), 3.21 (overlapped, H-3′), 3.20 (overlapped, H-4′), 3.47 (m, H-5′), 4.44 (br d, 12.0, H-6′), 4.32 (dd, 12.0, 6.3, H-6′), 7.44 (d, 1.8, H-2″), 6.87 (d, 8.4, H-5″), 7.46 (dd, 8.4, 1.8, H-6″), 3.81 (s, OMe); ^{13}C-NMR (150 MHz, DMSO-d_6): 96.5 (C-1), 61.7 (C-3), 23.1 (C-4), 37.2 (C-5), 71.6 (C-6), 60.9 (C-7), 65.2 (C-8), 42.4 (C-9), 59.7 (C-10), 98.3 (C-1′), 74.0 (C-2′), 76.9 (C-3′), 70.9 (C-4′), 74.6 (C-5′), 64.1 (C-6′), 121.3 (C-1″), 113.3 (C-2″), 148.0 (C-3″), 152.2 (C-4″), 115.8 (C-5″), 124.1 (C-6″), 56.3 (OMe), 166.1 (C-7″). *Picrorhiza scrophulariiflora* (Scrophulariaceae).[18]

25. 6′-*O*-*p*-Coumaroyl-3,4-dihydrocatalpol (Piscroside B)



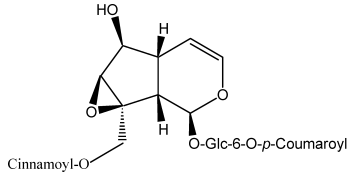
$C_{24}H_{30}O_{12}$: 510.1737; white amorphous powder; $[\alpha]_D^{25}$ −60.1° (c=0.10, MeOH); IR (KBr): 3380, 2918, 1661, 1610, 1580, 1511, 1280, 1241, 1066, 974, 772; ^{1}H-NMR (600 MHz, DMSO-d_6): 4.51 (d, 8.7, H-1), 3.75 (m, H_α-3), 3.21 (overlapped, H_β-3), 1.45 (d, 13.5, H_α-4), 1.59 (m, H_β-4), 1.83 (dd, 13.5, 8.1, H-5), 3.79 (dd, 9.0, 6.6, H-6), 3.19 (d, 9.0, H-7), 2.06 (t, 8.0, H-9), 3.46 (dd, 13.2, 7.3, H-10), 3.84 (dd, 13.2, 7.3, H-10), 4.54 (d, 7.8, H-1′), 3.03 (dd, 7.8, 5.0, H-2′), 3.22 (overlapped, H-3′), 3.23 (overlapped, H-4′), 3.40 (m, H-5′), 4.34 (br d, 12.0, H-6′), 4.25 (dd, 12.0, 6.0, H-6′), 7.57 (d, 8.5, H-2″,6″), 6.79 (d, 8.5, H-3″, 5″), 7.56 (d, 15.9, H-7″), 6.40 (d, 15.9, H-8″); ^{13}C-NMR (150 MHz, DMSO-d_6): 96.6 (C-1), 61.7 (C-3), 23.1 (C-4), 37.2 (C-5), 71.6 (C-6), 61.0 (C-7), 65.3 (C-8), 42.5 (C-9), 59.7 (C-10), 98.4 (C-1′), 73.9 (C-2′), 76.9 (C-3′), 70.7 (C-4′), 74.5 (C-5′), 65.3 (C-6′), 125.7 (C-1″), 131.0 (C-2″, 6″), 116.5 (C-3″, 5″), 160.5 (C-4″), 145.5 (C-7″), 114.7 (C-8″), 167.2 (C-9″). *Picrorhiza scrophulariiflora* (Scrophulariaceae).[18]

26. Piscroside B (6′-*O*-*E*-Cinnamoyl-3β-methoxy-3,4-dihydro-catalpol)



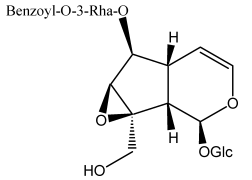
$C_{25}H_{32}O_{12}$: 524.1893; white amorphous powder; $[\alpha]_D^{20}$ −51.0° (c=0.05, MeOH); UV (MeOH): 215, 276; IR (KBr): 3433, 2921, 1712, 1635, 1449, 1388, 1263, 1175; ^{1}H-NMR (300 MHz, CD_3OD): 4.90 (d, 8.6, H-1), 4.54 (dd, 9.0, 3.0, H-3), 1.59 (m, H_a-4), 1.81 (br d, 13.9, H_b-4), 2.03 (m, H-5), 3.90 (br d, 9.1, H-6), 3.39 (br s, H-7), 2.37 (t, 8.1, H-9), 3.63 (d, 13.1, H_a-10), 4.05 (d, 13.1, H_b-10), 4.75 (d, 7.8, H-1′), 3.27 (m, H-2′), signal not observed (H-3′, 4′), 3.53 (m, H-5′), 4.44 (dd, 11.9, 5.5, H_a-6′), 4.53 (dd, 11.5, 2.4, H_b-6′), 7.62 (m, H-2″, 6″), 7.41 (m, H-3″, 5″), 7.41 (m, H-4″), 7.72 (d, 16.0, H-7″), 6.57 (d, 16.0, H-8 ″), 3.45 (s, OMe); ^{13}C-NMR (75 MHz, CD_3OD): 95.9 (C-1), 100.5 (C-3), 29.7 (C-4), 38.2 (C-5), 75.1 (C-6), 62.3 (C-7), 66.0 (C-8), 43.4 (C-9), 61.5 (C-10), 99.6 (C-1′), 74.9 (C-2′), 77.8 (C-3′), 71.7 (C-4′), 76.0 (C-5′), 64.4 (C-6′), 135.7 (C-1″),130.2 (C-2″, 6″), 129.4 (C-3″, 5″), 131.7 (C-4″), 146.7 (C-7″), 118.8 (C-8″), 168.4 (C-9″), 56.6 (OMe). *Neopicrorhiza scrophulariiflora* (Scrophulariaceae).[19]

27. Pensteminoside



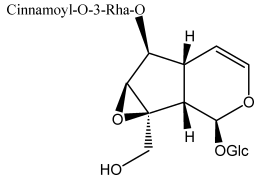
$C_{33}H_{34}O_{13}$: 638.1999; brown powder; $[\alpha]_D$ −0.06° (c=0.35, MeOH); UV (MeOH): 277, 231, 216; IR: 3263, 3207, 2935, 2561, 1725, 1457, 1024, 712, 624; ^{1}H-NMR (500 MHz, acetone-d_6): 4.95 (d, 10.0, H-1), 6.32 (dd, 6.0, 1.5, H-3), 5.02 (dd, 6.0, 5.0, H-4), 2.24 (dddd, 7.5, 5.0, 3.0, 2.0, H-5), 3.89 (d, 8.5, H-6), 3.46 (m, H-7), 2.52 (dd, 10.0, 7.5, H-9), 4.13 (d, 12.5, H-10), 5.07 (d, 12.5, H-10), 4.78 (d, 8.0, H-1′), 3.29 (t, 8.5, H-2′), 3.46 (m, H-3′, 4′), 3.58 (m, H-5′), 4.45 (dd, 8.5, 3.0, H-6′), 7.54 (d, 8.5, H-2″, 6″), 6.83 (d, 8.5, H-3″, 5″), 7.63 (d, 16.0, H-7″), 6.38 (d, 16.0, H-8″), 7.62 (dd, 6.0, 2.5, H-2‴, 6‴), 7.40 (m, H-3‴, 4‴, 5‴), 7.67 (d, 16.0, H-7‴), 6.50 (d, 16.0, H-8‴); ^{13}C-NMR (125 MHz, acetone-d_6): 95.3 (C-1), 141.5 (C-3), 103.9 (C-4), 38.9 (C-5), 79.3 (C-6), 62.0 (C-7), 62.8 (C-8), 43.3 (C-9), 63.7 (C-10), 100.0 (C-1′), 74.6 (C-2′), 77.7 (C-3′), 71.0 (C-4′), 75.3 (C-5′), 64.5 (C-6′), 127.1 (C-1″), 131.0 (C-2″, 6″), 116.8 (C-3″, 5″), 160.6 (C-4″), 145.6 (C-7″), 115.6 (C-8″), 167.6 (C-9″), 135.5 (C-1‴), 129.8 (C-2‴, 6‴), 129.1 (C-3‴, 5‴), 131.1 (C-4‴), 145.5 (C-7‴), 119.1 (C-8‴), 166.7 (C-9‴). *Penstemon gentianoides* (Plantaginaceae).[20]

28. 6-*O*-(3″-*O*-Benzoyl)-α-L-rhamnopyranosylcatalpol



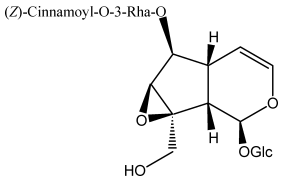
$C_{28}H_{36}O_{15}$: 612.2054; isolated as heptaacetate; viscous mass; $[\alpha]_D^{28}$ −17.7° (c=0.08, $CHCl_3$); UV: 278, 232; IR (KBr): 2956, 2925, 1759, 1654, 1637, 1560, 1544, 1510, 1422, 1375, 1080, 1066, 980; ^{1}H-NMR (300 MHz, $CDCl_3$): 4.77 (d, 9.6, H-1), 6.32 (dd, 6.0, 1.5, H-3), 5.11 (dd, 6.0, 4.8, H-4), 2.57 (m, H-5), 3.95 (dd, 8.5, 1.8, H-6), 3.59 (br s, H-7), 2.65 (dd, 9.6, 8.0, H-9), 3.98 (d, 12.6, H-10), 4.82 (d, 12.6, H-10), 4.97 (d, 8.1, H-1′), 5.27 (dd, 9.5, 8.0, H-2′), 4.95 (t, 9.6, H-3′), 5.22 (t, 9.5, H-4′), 3.69 (m, H-5′), 4.15 (dd, 12.3, 3.9, H-6′), 4.34 (dd, 12.3, 2.4, H-6′), 4.96 (br s, H-1″), 5.34 (dd, 3.5, 1.7, H-2″), 5.60 (dd, 9.6, 3.6, H-3″), 5.36 (t, 9.6, H-4″), 4.08 (dd, 9.8, 6.3, H-5″), 1.26 (d, 6.3, H_3-6″), 8.00 (dd, 8.7, 1.5, H-2‴, 6‴), 7.46 (t, 7.8, H-3‴, 5‴), 7.58 (tt, 7.5, H-4‴), 1.89, 2.04, 2.05, 2.07, 2.13, 2.15, 2.19 (each s, 7×Ac); ^{13}C-NMR (75 MHz, $CDCl_3$): 94.7 (C-1), 141.5 (C-3), 102.8 (C-4), 35.9 (C-5), 84.2 (C-6), 58.5 (C-7), 67.0 (C-8), 42.3 (C-9), 62.6 (C-10), 97.1 (C-1′), 73.0 (C-2′), 71.2 (C-3′), 68.8 (C-4′), 72.8 (C-5′), 61.6 (C-6′), 97.0 (C-1″), 70.7 (C-2″), 69.2 (C-3″), 72.1 (C-4″), 67.7 (C-5″), 17.8 (C-6″), 129.8 (C-1‴), 130.2 (C-2‴, 6‴), 128.9 (C-3‴, 5‴), 133.8 (C-4‴), 166.1 (C-7‴), 20.8×2, 20.9×2, 21.2×3, 169.3, 169.5, 170.1, 170.3, 170.5, 170.8, 170.9 (7×Ac). *Gmelina arborea* (Verbenaceae).[21]

29. 6-*O*-(3″-*O*-*trans*-Cinnamoyl)-α-L-rhamnopyranosylcatalpol



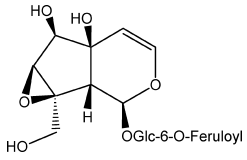
$C_{30}H_{38}O_{15}$: 638.2210; isolated as heptaacetate; viscous mass; $[\alpha]_D^{28}$ −14.2° (c=0.16, $CHCl_3$); UV: 282, 223, 218; IR (KBr): 2957, 2927, 1750, 1654, 1636, 1560, 1543, 1510, 1426, 1373, 1080, 1044, 982; ^{1}H-NMR (300 MHz, $CDCl_3$): 4.77 (d, 9.6, H-1), 6.32 (dd, 6.0, 1.5, H-3), 5.09 (dd, 6.0, 4.8, H-4), 2.50 (m, H-5), 3.93 (dd, 8.5, 1.8, H-6), 3.57 (br s, H-7), 2.61 (dd, 9.6, 8.0, H-9), 3.96 (d, 12.6, H-10), 4.80 (d, 12.6, H-10), 4.96 (d, 8.0, H-1′), 5.19 (dd, 9.5, 8.0, H-2′), 4.96 (t, 9.6, H-3′), 5.15 (t, 9.6, H-4′), 3.68 (m, H-5′), 4.15 (dd, 12.3, 3.9, H-6′), 4.32 (dd, 12.3, 2.4, H-6′), 4.96 (br s, H-1″), 5.32 (dd, 3.5, 1.7, H-2″), 5.42 (dd, 9.6, 3.6, H-3″), 5.22 (t, 9.6, H-4″), 4.00 (dd, 9.8, 6.3, H-5″), 1.24 (d, 6.3, H_3-6″), 7.53 (d, 8.2, H-2‴, 6‴), 7.40 (t, 8.2, H-3‴, 5‴), 7.34 (m, H-4‴), 7.68 (d, 16.0, H-7‴), 6.38 (d, 16.0, H-8‴), 1.93, 1.94×2, 1.97, 2.03, 2.05, 2.07 (each s, 7×Ac); ^{13}C-NMR (75 MHz, $CDCl_3$): 94.7 (C-1), 141.7 (C-3), 102.9 (C-4), 35.9 (C-5), 83.9 (C-6), 58.5 (C-7), 67.0 (C-8), 42.1 (C-9), 62.8 (C-10), 97.1 (C-1′), 72.9 (C-2′), 71.0 (C-3′), 68.7 (C-4′), 72.7 (C-5′), 61.6 (C-6′), 97.1 (C-1″), 70.4 (C-2″), 69.1 (C-3″), 71.4 (C-4″), 67.6 (C-5″), 17.8 (C-6″), 134.5 (C-1‴), 128.9 (C-2‴, 6‴), 129.5 (C-3‴, 5‴), 130.9 (C-4‴), 146.8 (C-7‴), 117.4 (C-8‴), 166.2 (C-9‴), 20.8×2, 20.9×3, 21.1×2, 169.2, 169.4, 170.1, 170.3, 170.4, 170.7, 170.8 (7×Ac). *Gmelina arborea* (Verbenaceae).[21]

30. 6-*O*-(3″-*O*-*cis*-Cinnamoyl)-α-L-rhamnopyranosylcatalpol



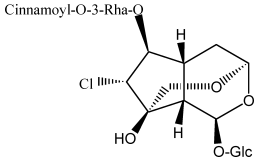
$C_{30}H_{38}O_{15}$: 638.2210; isolated as heptaacetate; viscous mass; $[\alpha]_D^{28}$ −10.4° (c=0.14, $CHCl_3$); UV: 285, 225, 215; IR (KBr): 2957, 2926, 1749, 1653, 1637, 1560, 1543, 1509, 1437, 1373, 1080, 1043, 981; ^{1}H-NMR (300 MHz, $CDCl_3$): 4.74 (d, 9.6, H-1), 6.31 (dd, 6.0, 1.5, H-3), 5.04 (dd, 6.0, 4.8, H-4), 2.51 (m, H-5), 3.95 (dd, 8.5, 1.5, H-6), 3.54 (br s, H-7), 2.61 (dd, 9.6, 8.0, H-9), 3.94 (d, 12.6, H-10), 4.86 (d, 12.6, H-10), 4.94 (d, 8.1, H-1′), 5.21 (dd, 9.5, 8.0, H-2′), 4.96 (t, 9.6, H-3′), 5.18 (t, 9.5, H-4′), 3.69 (m, H-5′), 4.21 (dd, 12.3, 3.9, H-6′), 4.30 (dd, 12.3, 2.4, H-6′), 4.92 (br s, H-1″), 5.31 (dd, 3.5, 1.7, H-2″), 5.41 (dd, 9.6, 3.6, H-3″), 5.28 (t, 9.6, H-4″), 3.98 (dd, 9.8, 6.3, H-5″), 1.27 (d, 6.3, H_3-6″), 7.58 (d, 8.2, H-2‴, 6‴), 7.38 (t, 8.2, H-3‴, 5‴), 7.35 (m, H-4‴), 7.02 (d, 12.6, H-7‴), 5.90 (d, 12.6, H-8‴), 2.01, 2.07, 2.10, 2.16, 2.18, 2.20, 2.23 (each s, 7×Ac). *Gmelina arborea* (Verbenaceae).[21]

31. Myobontioside B



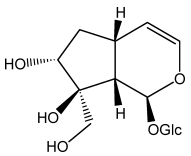
$C_{25}H_{30}O_{14}$: 554.1635; amorphous powder; $[\alpha]_D^{26}$ −54.6° (c=0.28, MeOH); UV (MeOH): 325 (3.95), 235 (3.84), 221 (3.83); IR (film): 3369, 2932, 1702, 1517, 1277, 1164, 1072, 1018; ^{1}H-NMR (400 MHz, CD_3OD): 5.22 (d, 8.0, H-1), 6.35 (d, 6.0, H-3), 4.89 (d, 6.0, H-4), 3.95 (d, 1.0, H-6), 3.53 (d, 1.0, H-7), 2.55 (d, 8.0, H-9), 4.13 (d, 13.0, H-10), 3.61 (d, 13.0, H-10), 4.73 (d, 8.0, H-1′), 3.28 (dd, 9.0, 8.0, H-2′), 3.53 (m, H-3′), 3.40 (m, H-4′, 5′), 4.50 (dd, 12.0, 2.0, H-6′), 4.43 (dd, 12.0, 6.0, H-6′), 7.20 (d, 2.0, H-2″), 6.82 (d, 8.0, H-5″), 7.09 (dd, 8.0, 2.0, H-6″), 7.63 (d, 16.0, H-7″), 6.38 (d, 16.0, H-8″), 3.90 (s, MeO-3″); ^{13}C-NMR (100 MHz, CD_3OD): 95.5 (C-1), 142.8 (C-3), 108.0 (C-4), 74.5 (C-5), 78.7 (C-6), 63.4 (C-7), 66.8 (C-8), 51.0 (C-9), 61.6 (C-10), 100.0 (C-1′), 74.7 (C-2′), 77.6 (C-3′), 71.7 (C-4′), 76.1 (C-5′), 64.1 (C-6′), 128.7 (C-1″), 112.0 (C-2″), 149.2 (C-3″), 151.1 (C-4″), 116.6 (C-5″), 124.3 (C-6″), 147.2 (C-7″), 115.4 (C-8″), 168.9 (C-9″), 56.6 (MeO-3″). *Myoporum bontioides* (Myoporaceae).[23]

32. Versibirioside



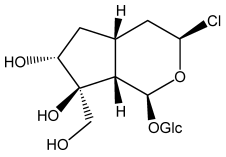
$C_{30}H_{39}ClO_{15}$: 674.1977; white amorphous powder; $[\alpha]_D^{25}$ −38.3° (c=0.014, MeOH); IR (KBr): 3423, 2931, 1702, 1635, 1451, 1355, 1266, 1073, 994, 908, 828, 770, 686; ^{1}H-NMR (300 MHz, CD_3OD): 5.66 (d, 2.0, H-1), 5.32 (d, 2.6, H-3), 2.48 (d, 10.0, H-4, 5), 1.75 (d, 10.0, H-4), 4.12 (d, 9.6, H-6), 4.26 (d, 8.2, H-7), 2.57 (d, 10.0, H-9), 3.99 (d, 12.2, H-10), 3.63 (d, 12.2, H-10), 4.70 (d, 7.9, H-1′), 3.20 (m, H-2′), 3.38 (m, H-3′, 5′), 3.35 (m, H-4′), 3.88 (d, 11.5, H-6′), 3.69 (d, 11.5, H-6′), 4.96 (d, 1.7, H-1″), 4.10 (m, H-2″), 6.06 (dd, 9.5, 3.3, H-3″), 3.71 (m, H-4″, 5″), 1.31 (s, H_3-6″), 7.62 (m, H-2‴, 6‴), 7.41 (m, H-3‴, 4‴, 5‴), 7.78 (d, 16.0, H-7‴), 6.62 (d, 16.0, H-8‴); ^{13}C-NMR (75 MHz, CD_3OD): 93.3 (C-1), 96.0 (C-3), 34.5 (C-4), 34.4 (C-5), 91.1 (C-6), 72.8 (C-7), 79.9 (C-8), 48.3 (C-9), 62.3 (C-10), 99.1 (C-1′), 74.8 (C-2′), 78.3 (C-3′), 71.7 (C-4′), 78.3 (C-5′), 62.8 (C-6′), 102.7 (C-1″), 70.1 (C-2″), 75.6 (C-3″), 71.2 (C-4″), 70.8 (C-5″), 18.2 (C-6″), 131.6 (C-1‴), 129.3 (C-2‴, 6‴), 130.1 (C-3‴, 5‴), 135.9 (C-4‴), 146.6 (C-7‴), 119.2 (C-8‴), 168.4 (C-9‴). *Veronica sibirica*.[24]

33. Kankanoside B



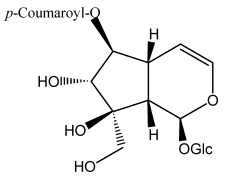
$C_{15}H_{24}O_{10}$: 364.1369; amorphous powder; $[\alpha]_D^{26}$ −118.7° (c=0.50, MeOH); IR (KBr): 3410, 1647, 1085; ^{1}H-NMR (500 MHz, CD_3OD): 5.49 (d, 6.4, H-1), 6.22 (dd, 6.1, 1.8, H-3), 4.95 (dd, 6.1, 4.0, H-4), 2.83 (m, H-5), 1.40 (ddd, 13.5, 7.3, 5.2, H_α-6), 2.52 (ddd, 13.5, 9.2, 7.0, H_β-6), 4.02 (dd, 7.0, 5.2, H-7), 2.21 (dd, 8.6, 6.4 , H-9), 3.85 (d, 11.9, H-10), 3.99 (d, 11.9, H-10), 4.72 (d, 7.9, H-1′), 3.20 (dd, 9.2, 7.9, H-2′), 3.38 (dd, 9.2, 8.9, H-3′), 3.27 (m, H-4′), 3.28 (m, H-5′), 3.65 (dd, 11.9, 5.8, H-6′), 3.88 (dd, 11.9, 1.5, H-6′), ^{13}C-NMR (125 MHz, CD_3OD): 94.1 (C-1), 139.9 (C-3), 108.9 (C-4) 30.8 (C-5), 40.6 (C-6), 80.0 (C-7), 84.1 (C-8), 50.5 (C-9), 64.6 (C-10), 99.8 (C-1′), 74.9 (C-2′), 78.0 (C-3′), 71.8 (C-4′), 78.3 (C-5′), 62.9 (C-6′). *Cistanche tubulosa* (Orobanchaceae).[25]

34. Kankanoside C



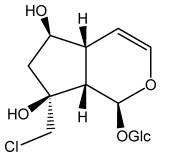
$C_{15}H_{25}ClO_{10}$: 400.1136; amorphous powder; $[\alpha]_D^{26}$ −34.0° (c=1.00, MeOH); IR (KBr): 3410, 2964, 1159, 1078; ^{1}H-NMR (500 MHz, CD_3OD): 5.48 (d, 2.5, H-1), 5.10 (br d, *ca.* 3.0, H-3), 1.70 (br dd, *ca.* 13.0, 3.0, H-4), 2.70 (br dd, *ca.* 13.0, 6.0, H-4), 2.61 (m, H-5), 1.68 (br d, *ca.* 13.0, H_α-6), 2.44 (m, H_β-6), 3.94 (br s, H-7), 2.47 (dd, 7.9, 2.5, H-9), 4.01 (d, 11.3, H-10), 4.04 (d, 11.3, H-10), 4.60 (d, 8.0, H-1′), 3.17 (dd, 9.2, 8.0, H-2′), 3.36 (dd, 9.2, 8.9, H-3′), 3.27 (m, H-4′), 3.29 (m, H-5′), 3.65 (dd, 12.2, 5.8, H-6′), 3.88 (dd, 12.2, 1.8, H-6′); ^{13}C-NMR (125 MHz, CD_3OD): 93.3 (C-1), 96.1 (C-3), 34.7 (C-4), 28.5 (C-5), 38.2 (C-6), 82.0 (C-7), 83.0 (C-8), 50.4 (C-9), 65.1 (C-10), 99.0 (C-1′), 74.8 (C-2′), 78.2 (C-3′), 71.8 (C-4′), 78.3 (C-5′), 62.9 (C-6′). *Cistanche tubulosa* (Orobanchaceae).[25]

35. Stereospermoside (6-*O*-*trans*-*p*-Coumaroyl-decinnamoyl globularimin)



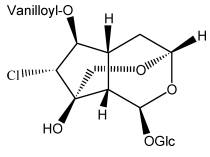
$C_{24}H_{30}O_{13}$: 526.1686; amorphous powder; $[\alpha]_D^{24}$ −90.8° (c=1.74, MeOH); IR (KBr): 3427, 2927, 1672, 1605, 832; ^{1}H-NMR (400 MHz, CD_3OD): 5.50 (d, 4.4, H-1), 6.22 (dd, 6.1, 1.8, H-3), 5.19 (dd, 6.1, 3.4, H-4), 2.71 (m, H-5), 4.71 (dd, 5.6, 5.4, H-6), 4.09 (d, 5.6, H-7), 2.45 (dd, 9.8, 4.4, H-9), 3.98 (d, 12.0, H-10), 3.78 (d, 12.0, H-10), 4.62 (d, 7.8, H-1′), 3.16 (dd, 8.8, 7.8, H-2′), 3.22 (dd, 9.0, 8.8, H-3′), 3.26 (dd, 9.0, 8.0, H-4′), 3.27 (m, H-5′), 3.83 (br d, 11.7, H-6′), 3.62 (dd, 11.7, 3.9, H-6′), 7.41 (d, 8.8, H-2″, 6″), 6.76 (d, 8.8, H-3″, 5″), 7.60 (d, 15.9, H-7″), 6.32 (d, 15.9, H-8″); ^{13}C-NMR (100 MHz, CD_3OD): 93.0 (C-1), 140.8 (C-3), 106.0 (C-4), 36.5 (C-5), 85.8 (C-6), 84.3 (C-7), 80.7 (C-8), 48.3 (C-9), 64.3 (C-10), 99.5 (C-1′), 74.7 (C-2′), 77.9 (C-3′), 71.6 (C-4′), 78.1 (C-5′), 62.8 (C-6′), 127.1 (C-1″), 131.2 (C-2″, 6″), 116.8 (C-3″, 5″), 161.3 (C-4″), 146.9 (C-7″), 115.0 (C-8″), 169.1 (C-9″). *Stereospermum cylindricum* (Bignoniaceae).[26]

36. Myobontioside A



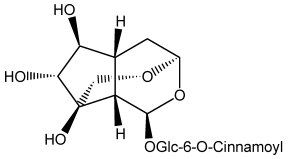
$C_{15}H_{23}{}^{35}ClO_9$: 382.1030; amorphous powder; $[\alpha]_D^{23}$ −90.7° (c=0.14, MeOH); IR (film): 3362, 2927, 1655, 1514, 1229, 1074, 1050, 1010; ^{1}H-NMR (400 MHz, CD_3OD): 5.44 (d, 4.0, H-1), 6.22 (dd, 6.0, 2.0, H-3), 4.94 (dd, 6.0, 3.0, H-4), 2.84 (dd, 9.0, 3.0, H-5), 3.96 (m, H-6), 2.34 (dd, 14.0, 6.0, H-7), 1.81 (dd, 14.0, 4.0, H-7), 2.64 (dd, 9.0, 4.0, H-9), 3.83 (d, 12.0, H-10), 3.74 (dd, 12.0, H-10), 4.65 (d, 8.0, H-1′), 3.21 (dd, 9.0, 8.0, H-2′), 3.38 (m, H-3′), 3.29 (m, H-4′, 5′), 3.90 (dd, 12.0, 2.0, H-6′), 3.65 (dd, 12.0, 6.0, H-6′); ^{13}C-NMR (100 MHz, CD_3OD): 93.3 (C-1), 140.9 (C-3), 105.7 (C-4), 42.9 (C-5), 77.7 (C-6), 46.2 (C-7), 81.8 (C-8), 52.7 (C-9), 52.9 (C-10), 99.7 (C-1′), 74.9 (C-2′), 78.1 (C-3′), 71.9 (C-4′), 78.4 (C-5′), 63.0 (C-6′). *Myoporum bontioides* (Myoporaceae).[23]

37. Piscroside A (7-Deoxy-7-α-Cl-pikuroside)



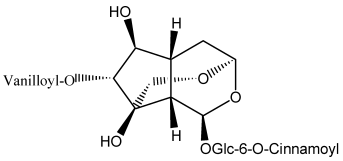
$C_{23}H_{29}O_{13}Cl$: 548.1296; white amorphous powder; $[\alpha]_D^{20}$ −83.2° (c=0.06, MeOH); UV (MeOH): 205, 218, 263, 291; IR (KBr): 3430, 1695, 1604, 1460, 1380, 1283, 1155; ^{1}H-NMR (300 MHz, CD_3OD): 5.61 (d, 2.2, H-1), 5.27 (d, 2.8, H-3), 2.07 (dd, 13.4, 3.2, H_a-4), 2.31 (dd, 13.4, 8.6, H_b-4), 2.33 (ddd, 9.5, 7.9, 2.5, H-5), 5.06 (dd, 8.2, 2.6, H-6), 4.46 (dd, 8.2,1.0, H-7), 2.59 (br d, 9.5, H-9), 3.64 (dd, 12.2, 1.3, H_a-10), 4.00 (dd, 12.2, 1.0, H_b-10), 4.63 (d, 7.9, H-1′), 3.08 (dd, 8.0, 8.9,H-2′), 3.30 (t, 8.8, H-3′), signal not observed (H-4′), 3.28 (m, H-5′), 3.60 (dd, 12.0, 2.2, H_a-6′), 3.81 (m, H_b-6′), 7.49 (d, 1.8, H-2″), 6.80 (d, 8.2, H-5″), 7.52 (dd, 8.2, 1.8, H-6″), 3.84 (s, OMe); ^{13}C-NMR (75 MHz, CD_3OD): 93.2 (C-1), 96.0 (C-3), 34.5 (C-4), 34.9 (C-5), 88.0 (C-6), 70.5 (C-7), 80.0 (C-8), signal not observed (C-9), 62.2 (C-10), 99.0 (C-1′), 74.8 (C-2′), 78.2 (C-3′), 71.7 (C-4′), 78.2 (C-5′), 62.8 (C-6′), 122.1 (C-1″), 113.8 (C-2″), 149.0 (C-3″), 153.4 (C-4″), 116.2 (C-5″), 125.4 (C-6″), 167.9 (C-7″), 56.6 (OMe). *Neopicrorhiza scrophulariiflora* (Scrophulariaceae).[19]

38. Picroroside A



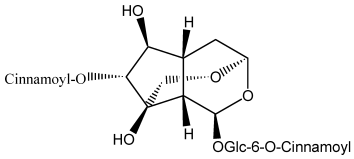
$C_{24}H_{30}O_{12}$: 510.1737; colorless amorphous powder; $[\alpha]_D^{24}$ −56.3° (c=1.12, MeOH); UV (MeOH): 277 (4.32), 217 (4.21); IR (KBr): 3434, 1701, 1636; ^{1}H-NMR (800 MHz, CD_3OD): 5.58 (d, 1.8, H-1), 5.27 (d, 3.3, H-3), 1.67 (dd, 13.8, 3.3, H_α-4), 2.43 (dd, 13.8, 8.3, H_β-4), 2.28 (ddd, 8.7, 8.3, 2.8, H-5), 4.01 (dd, 8.2, 2.8, H-6), 4.04 (dd, 8.2, 1.4, H-7), 2.56 (br d, 10.1, H-9), 3.95 (dd, 11.9, 1.4, H-10), 3.57 (dd, 11.9, 1.8, H-10), 4.72 (d, 7.8, H-1′), 3.21 (dd, 9.1, 7.8, H-2′), 3.38 (m, H-3′), 3.40 (m, H-4′), 3.55 (m, H-5′), 4.52 (dd, 11.9, 1.8, H-6′), 4.33 (dd, 11.9, 5.5, H-6′), 7.61 (overlapped, H-2″, 6″), 7.40 (overlapped, H-3″, 4″, 5″), 7.70 (d, 16.1, H-7″), 6.58 (d, 16.1, H-8″); ^{13}C-NMR (200 MHz, CD_3OD): 93.5 (C-1), 95.9 (C-3), 34.8 (C-4), 35.9 (C-5), 84.5 (C-6), 74.7 (C-7), 79.9 (C-8), 48.0 (C-9), 62.2 (C-10), 99.1 (C-1′), 74.6 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 75.6 (C-5′), 64.8 (C-6′), 135.7 (C-1″), 129.3 (C-2″, 6″), 130.0 (C-3″, 5″), 131.6 (C-4″), 146.4 (C-7″), 118.6 (C-8″), 168.5 (C-9″). *Neopicrorhiza scrophulariiflora* (Scrophulariaceae).[27]

39. Picroroside B



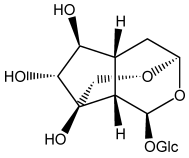
$C_{32}H_{36}O_{15}$: 660.2054; colorless amorphous powder; $[\alpha]_D^{24}$ −46.7° (c=0.15, MeOH); UV (MeOH): 269 (4.52), 217 (4.62); IR (film): 3428, 1635; ^{1}H-NMR (500 MHz, CD_3OD): 5.60 (d, 2.1, H-1), 5.33 (d, 3.3, H-3), 1.76 (dd, 13.8, 3.3, H_α-4), 2.50 (m, H_β-4), 2.33 (m, H-5), 4.13 (dd, 6.9, 2.9, H-6), 5.38 (d, 6.9, H-7), 2.74 (br d, 10.2, H-9), 3.91 (d, 12.0, H-10), 3.63 (d, 12.0, H-10), 4.74 (d, 8.0, H-1′), 3.23 (m, H-2′), 3.40 (m, H-3′), 3.41 (m, H-4′), 3.57 (m, H-5′), 4.53 (dd, 12.0, 2.1, H-6′), 4.34 (dd, 12.0, 5.5, H-6′), 7.62 (overlapped, H-2″, 6″), 7.39 (overlapped, H-3″, 5″), 7.38 (overlapped, H-4″), 7.72 (d, 16.0, H-7″), 6.59 (d, 16.0, H-8″), 7.59 (d, 2.1, H-2‴), 6.85 (d, 8.2, H-5‴), 7.63 (dd, 8.2, 2.1, H-6‴), 3.89 (s, MeO-3‴); ^{13}C-NMR (125 MHz, CD_3OD): 93.5 (C-1), 96.0 (C-3), 34.8 (C-4), 35.0 (C-5), 83.1 (C-6), 87.4 (C-7), 80.1 (C-8), 47.5 (C-9), 62.0 (C-10), 99.0 (C-1′), 74.7 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 75.5 (C-5′), 64.7 (C-6′), 135.7 (C-1″), 129.3 (C-2″, 6″), 130.0 (C-3″, 5″), 131.5 (C-4″), 146.6 (C-7″), 118.6 (C-8″), 168.5 (C-9″), 122.1 (C-1‴), 113.7 (C-2‴), 148.9 (C-3‴), 153.4 (C-4‴), 116.0 (C-5‴), 125.3 (C-6‴), 168.1 (C-7‴), 56.4 (MeO-3‴). *Neopicrorhiza scrophulariiflora* (Scrophulariaceae).[27]

40. Picroroside C



$C_{33}H_{36}O_{13}$: 640.2155; colorless amorphous powder; $[\alpha]_D^{24}$ −44.4° (c=0.09, MeOH); UV (MeOH): 278 (4.81), 217 (4.79); IR (film): 3380, 1705, 1636; ^{1}H-NMR (500 MHz, CD_3OD): 5.59 (d, 2.1, H-1), 5.31 (d, 3.5, H-3), 1.73 (dd, 13.8, 3.5, H_α-4), 2.48 (dd, 13.8, 9.0, H_β-4), 2.31 (ddd, 9.4, 9.0, 2.9, H-5), 4.09 (dd, 6.9, 2.9, H-6), 5.33 (d, 6.9, H-7), 2.71 (br d, 10.0, H-9), 3.88 (d, 12.1, H-10), 3.60 (dd, 12.1, 1.2, H-10), 4.74 (d, 8.0, H-1′), 3.23 (dd, 9.2, 8.0, H-2′), 3.39 (m, H-3′), 3.41 (m, H-4′), 3.56 (m, H-5′), 4.53 (dd, 12.0, 2.3, H-6′), 4.34 (dd, 12.0, 5.7, H-6′), 7.62 (overlapped, H-2″, 6″, 2‴, 6‴), 7.42 (overlapped, H-3″, 5″, 3‴, 5‴), 7.39 (overlapped, H-4″, 4‴), 7.72 (d, 16.0, H-7″), 6.59 (d, 16.0, H-8″), 7.76 (d, 16.0, H-7‴), 6.63 (d, 16.0, H-8‴); ^{13}C-NMR (125 MHz, CD_3OD): 93.3 (C-1), 95.9 (C-3), 34.8 (C-4, 5), 82.8 (C-6), 87.0 (C-7), 79.7 (C-8), 47.3 (C-9), 61.8 (C-10), 98.9 (C-1′), 74.6 (C-2′), 77.9 (C-3′), 71.4 (C-4′), 75.5 (C-5′), 64.6 (C-6′), 135.6 (C-1″, 1‴), 129.2 (C-2″, 6″, 2‴, 6‴), 129.9 (C-3″, 5″, 3‴, 5‴), 131.4 (C-4″, 4‴), 146.5 (C-7″), 118.5 (C-8″, 8‴), 146.7 (C-7‴) 168.5 (C-9″, 9‴). *Neopicrorhiza scrophulariiflora* (Scrophulariaceae).[27]

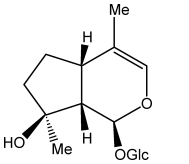
41. Scutelloside



$C_{15}H_{24}O_{11}$: 380.1318; amorphous powder; $[\alpha]_D^{20}$ −3.4° (c=0.22, MeOH); UV (MeOH): 264.0 sh (0.73); IR (film); 3352, 2914; ^{1}H-NMR (400 MHz, CD_3OD): 5.63 (d, 1.6, H-1), 5.27 (d, 2.7, H-3), 2.44 (dd, 13.4, 7.8, H-4), 1.67 (dd, 13.4, 2.7, H-4), 2.30 (ddd, 9.5, 7.8, 2.6, H-5), 4.03 (dd, 7.4, 2.6, H-6), 4.04 (dd, 7.4, 0.9, H-7), 2.53 (dd, 9.5, 1.6, H-9), 3.98 (d, 12.4, H-10), 3.60 (d, 12.4, H-10), 4.68 (d, 7.8, H-1′), 3.18 (dd, 8.6, 7.8, H-2′), 3.19—3.40 (m, H-3′, 4′, 5′), 3.87 (d, 12.4, H-6′), 3.66 (d, 12.4, H-6′); ^{13}C-NMR (100 MHz, CD_3OD): 93.6 (C-1), 96.0 (C-3), 35.3 (C-4), 35.7 (C-5), 86.0 (C-6), 74.7 (C-7), 79.9 (C-8), 48.0 (C-9), 62.0 (C-10), 99.1 (C-1′), 75.1 (C-2′), 78.3 (C-3′), 72.0 (C-4′), 78.1 (C-5′), 62.9 (C-6′). *Scutellaria albida* ssp. *albida* (Lamiaceae).[28]

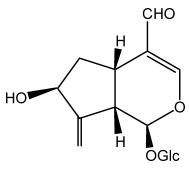
Group 3a (Iridoid glycosides with 10-carbon skeleton, sugar at C-1)

42. Kankanoside A



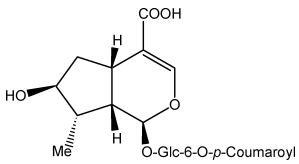
$C_{16}H_{26}O_8$: 346.1627; amorphous powder; $[\alpha]_D^{25}$ −107.4° (c=0.30, MeOH); IR (KBr): 3410, 2964, 1647, 1076; ^{1}H-NMR (500 MHz, CD_3OD): 5.33 (d, 2.7, H-1), 5.95 (br s, H-3), 2.71 (m, H-5), 1.49 (m, H_α-6), 2.02 (m, H_β-6), 1.67 (m, H_α-7), 1.64 (m, H_β-7), 2.21 (dd, 7.5, 2.7, H-9), 1.31 (s, H_3-10), 1.51 (br s, H_3-11), 4.62 (d, 7.9, H-1′), 3.18 (dd, 8.5, 7.9, H-2′), 3.36 (dd, 8.9, 8.5, H-3′), 3.26 (dd, 9.5, 8.9, H-4′), 3.28 (m, H-5′), 3.65 (dd, 11.9, 5.8, H-6′), 3.89 (dd, 11.9, 1.9, H-6′); ^{13}C-NMR (125 MHz, CD_3OD): 94.1 (C-1), 134.6 (C-3), 115.0 (C-4), 36.2 (C-5), 28.2 (C-6), 41.4 (C-7), 80.2 (C-8), 53.3 (C-9), 24.6 (C-10), 16.2 (C-11), 99.4 (C-1′), 74.9 (C-2′), 78.1 (C-3′), 71.8 (C-4′), 78.2 (C-5′), 62.9 (C-6′). *Cistanche tubulosa* (Orobanchaceae).[25]

43. Gardaloside



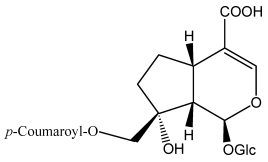
$C_{16}H_{22}O_9$: 358.1263; pale yellowish oil; $[\alpha]_D^{23}$ −69.6° (c=0.18, MeOH); UV (MeOH): 244 (3.90); IR (KBr); 3367, 2927, 1626, 1410, 1242, 1157; ^{1}H-NMR (500 MHz, CD_3OD): 5.65 (d, 3.8, H-1), 7.36 (s, H-3), 3.18 (overlapped, H-5), 2.16 (ddd, 12.6, 6.3, 4.4, H-6), 1.86 (ddd, 12.6, 7.2, 7.2, H-6), 4.31 (overlapped, H-7), 3.05 (overlapped, H-9), 5.35 (s, H_2-10) , 9.19 (s, H-11), 4.67 (d, 7.9, H-1′), 3.18 (overlapped, H-2′), 3.25 (overlapped, H-3′), 3.26 (overlapped, H-4′), 3.32 (overlapped, H-5′), 3.90 (dd, 11.7, 5.3, H-6′), 3.63 (overlapped, H-6′); ^{13}C-NMR (125 MHz, CD_3OD): 97.7 (C-1), 164.5 (C-3), 124.1 (C-4), 29.5 (C-5), 39.0 (C-6), 73.9 (C-7), 152.4 (C-8), 44.8 (C-9), 112.8 (C-10), 193.0 (C-11), 100.1 (C-1′), 74.7 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 78.5 (C-5′), 62.8 (C-6′). *Gardenia jasminoides* (Rubiaceae).[29]

44. 6′-*O*-*E*-*p*-Coumaroyl-8-*epi*-loganic acid



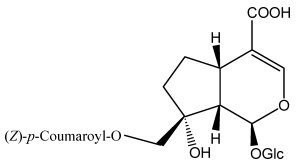
$C_{25}H_{30}O_{12}$: 522.1737; yellowish oil; $[\alpha]_D^{20}$ −50.7° (c=0.15, MeOH); UV (MeOH): 298.0 sh (3.53), 309.0 (4.03); IR (film); 3352, 2914, 1644, 1607; ^{1}H-NMR (400 MHz, CD_3OD): 5.28 (d, 5.0, H-1), 7.29 (s, H-3), 3.03 (m, H-5), 1.90 (m, H-6), 1.78 (m, H-6), 3.78 (m, H-7), 2.05 (m, H-8), 2.46 (m, H-9), 1.02 (d, 7.4, H_3-10), 4.68 (d, 8.2, H-1′), 3.24 (dd, 8.0, 7.9, H-2′), 3.40—3.34 (m, H-3′, 4′), 3.55 (m, H-5′), 4.50 (dd, 12.1, 2.7, H-6′), 4.39 (dd, 12.0, 6.2, H-6′), 7.46 (d, 8.6, H-2″, 6″), 6.80 (d, 8.5, H-3″, 5″), 7.64 (d, 16.4, H-7″), 6.36 (d, 16.4, H-8″); ^{13}C-NMR (100 MHz, CD_3OD): 95.6 (C-1), 150.4 (C-3), 115.6 (C-4), 32.2 (C-5), 41.5 (C-6), 79.2 (C-7), 45.4 (C-8), 43.2 (C-9) 14.4 (C-10), 172.7 (C-11), 99.9 (C-1′), 74.8 (C-2′), 77.9 (C-3′), 71.7 (C-4′), 75.7 (C-5′), 64.4 (C-6′), 127.1 (C-1″), 131.2 (C-2″, 6″), 116.7 (C-3″, 5″), 161.8 (C-4″), 146.9 (C-7″), 114.9 (C-8″), 169.8 (C-9″). *Scutellaria albida* ssp. *albida* (Lamiaceae).[28]

45. 10-(*E*)-*p*-Coumaroyl-6,7-dihydromonotropein



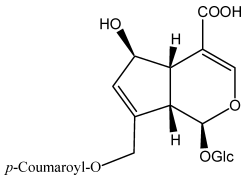
$C_{25}H_{30}O_{13}$: 538.1686; colorless solid; $[\alpha]_D^{25}$ −44.4° (c=0.20, MeOH); UV (MeOH–H_2O): 310, 230, 215; IR (Ge ATR): 3308, 1684, 1634, 1604, 1515, 1169, 1074; ^{1}H-NMR (360 MHz, CD_3OD): 5.51 (d, 5.3, H-1), 7.49 (d, 1.4, H-3), 2.93 (ddddd, 15.2, 9.2, 1.7, 1.4, 0.5, H-5), 1.70 (m, H-6), 2.17 (m, H-6), 1.84—1.71 (m, H_2-7), 2.32 (dd, 9.2, 5.3, H-9), 4.18 (d, 11.3, H-10), 4.26 (d, 11.3, H-10), 4.73 (d, 7.9, H-1′), 3.24 (dd, 9.0, 7.9, H-2′), 3.33 (overlapped, H-3′), 3.35 (t, 9.0, H-4′), 3.34 (overlapped, H-5′), 3.66 (dd, 11.8, 5.2, H-6′), 3.85 (dd, 11.8, 1.6, H-6′), 7.49 (br ddd, 8.7, 2.9, 2.0, H-2″, 6″), 6.80 (br ddd, 8.7, 2.9, 2.0, H-3″, 5″), 7.67 (d, 15.9, H-7″), 6.39 (d, 15.9, H-8″); ^{13}C-NMR (90 MHz, CD_3OD): 96.1 (C-1), 153.3 (C-3), 112.5 (C-4), 35.2 (C-5), 31.6 (C-6), 37.5 (C-7), 81.7 (C-8), 46.9 (C-9), 70.9 (C-10), 170.7 (C-11), 100.9 (C-1′), 74.6 (C-2′), 77.9 (C-3′), 71.2 (C-4′), 78.4 (C-5′), 62.5 (C-6′), 127.1 (C-1″), 131.3 (C-2″, 6″), 116.9 (C-3″, 5″), 161.4 (C-4″), 147.0 (C-7″), 114.9 (C-8″), 169.2 (C-9″). *Vaccinium macrocarpon* (Ericaceae).[30]

46. 10-(*Z*)-*p*-Coumaroyl-6,7-dihydromonotropein



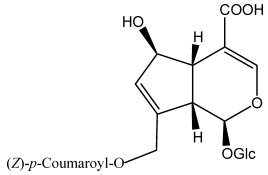
$C_{25}H_{30}O_{13}$: 538.1686; colorless amorphous solid; $[\alpha]_D^{25}$ +37.8° (c=0.10, MeOH); UV (MeOH–H_2O): 314, 231, 215; IR (Ge ATR): 3308, 1695, 1684, 1558, 1507, 1457, 1188, 1160, 1071; ^{1}H-NMR (360 MHz, CD_3OD): 5.47 (d, 5.4, H-1), 7.46 (d, 1.4, H-3), 2.84 (ddddd, 15.2, 9.4, 2.0, 1.4, 0.5, H-5), 1.63 (m, H-6), 2.11 (m, H-6), 1.75—1.65 (m, H_2-7), 2.22 (dd, 9.4, 5.4, H-9), 4.11 (d, 11.2, H-10),4.18 (d, 11.2, H-10), 4.71 (d, 7.9, H-1′), 3.24 (dd, 9.0, 7.9, H-2′), 3.33 (overlapped, H-3′, 5′), 3.35 (t, 9.0, H-4′), 3.67 (dd, 11.8, 5.1, H-6′), 3.86 (dd, 11.8, 1.4, H-6′), 7.62 (br ddd, 8.7, 3.0, 2.1, H-2″, 6″), 6.75 (br ddd, 8.7, 3.0, 2.1, H-3″, 5″), 6.91 (d, 12.6, H-7″), 5.86 (d, 12.6, H-8″); ^{13}C-NMR (90 MHz, D_2O): 95.1 (C-1), 152.5 (C-3), 111.6 (C-4), 32.4 (C-5), 29.7 (C-6), 35.6 (C-7), 80.4 (C-8), 45.7 (C-9), 69.6 (C-10), 171.3 (C-11), 98.9 (C-1′), 72.7 (C-2′), 75.7 (C-3′), 70.1 (C-4′), 76.4 (C-5′), 60.8 (C-6′), 127.3 (C-1″), 131.5 (C-2″, 6″), 115.3 (C-3″, 5″), 156.8 (C-4″), 144.3 (C-7″), 116.9 (C-8″), 169.2 (C-9″). *Vaccinium macrocarpon* (Ericaceae).[30]

47. 10-*O*-(*E*)-*p*-Coumaroylscandoside



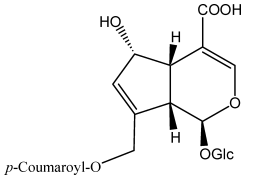
$C_{25}H_{28}O_{13}$: 536.1529; amorphous powder; $[\alpha]_D^{23}$ −65.4° (c=0.54, MeOH); UV (MeOH): 314 (4.01), 303 (3.56), 242 (3.87); IR (KBr): 3407, 2924, 1682, 1632, 1604, 1516, 1205, 1142, 1076, 839; ^{1}H-NMR (500 MHz, C_5D_5N): 5.37 (d, 8.0, H-1), 7.89 (s, H-3), 3.39 (dd, 7.0, 6.5, H-5), 4.92 (br s, H-6), 6.04 (s, H-7), 3.12 (dd, 8.0, 7.0, H-9), 5.33 (d, 14.5, H-10), 5.06 (d, 14.5, H-10), 5.40 (d, 7.5, H-1′), 4.12 (dd, 9.0, 7.5, H-2′), 4.28 (dd, 9.0, 8.5, H-3′), 4.26 (m, H-4′), 3.97 (m, H-5′), 4.48 (dd, 12.0, 2.0, H-6′), 4.33 (dd, 12.0, 5.5, H-6′), 7.58 (d, 8.5, H-2″, 6″), 7.17 (d, 8.5, H-3″, 5″), 7.91 (d, 16.0, H-7″), 6.57 (d, 16.0, H-8″); ^{13}C-NMR (125 MHz, C_5D_5N): 98.9 (C-1), 152.5 (C-3), 111.7 (C-4), 46.3 (C-5), 82.1 (C-6), 133.7 (C-7), 140.6 (C-8), 47.2 (C-9), 62.3 (C-10), 173.0 (C-11), 101.0 (C-1′), 74.8 (C-2′), 78.3 (C-3′), 71.3 (C-4′), 78.8 (C-5′), 62.6 (C-6′), 125.9 (C-1″), 130.8 (C-2″, 6″), 116.8 (C-3″, 5″), 161.5 (C-4″), 145.6 (C-7″), 114.7 (C-8″), 167.0 (C-9″). *Craibiodendron henryi* (Ericaceae).[31]

48. 10-*O*-(*Z*)-*p*-Coumaroylscandoside



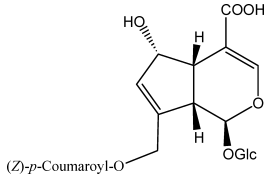
$C_{25}H_{28}O_{13}$: 536.1529; amorphous powder; $[\alpha]_D^{23}$ −27.6° (c=0.22, MeOH); UV (MeOH): 315 (4.13), 302 (3.67), 242 (3.99); IR (KBr): 3407, 2924, 1682, 1633, 1604, 1516, 1205, 1142, 1076, 839; ^{1}H-NMR (500 MHz, C_5D_5N): 5.35 (d, 8.0, H-1), 7.87 (s, H-3), 3.35 (dd, 7.0, 6.5, H-5), 4.89 (br s, H-6), 6.04 (s, H-7), 3.08 (dd, 8.0, 7.0, H-9), 5.23 (d, 14.5, H-10), 5.01 (d, 14.5, H-10), 5.39 (d, 7.5, H-1′), 4.10 (dd, 9.0, 7.5, H-2′), 4.27 (t, 9.0, H-3′), 4.21 (t, 9.0, H-4′), 3.97 (m, H-5′), 4.48 (dd, 12.0, 2.5, H-6′), 4.31 (dd, 12.0, 5.5, H-6′), 8.03 (d, 8.5, H-2″, 6″), 7.16 (d, 8.5, H-3″, 5″), 6.92 (d, 13.0, H-7″), 5.93 (d, 13.0, H-8″); ^{13}C-NMR (125 MHz, C_5D_5N): 98.8 (C-1), 152.6 (C-3), 111.8 (C-4), 46.4 (C-5), 82.1 (C-6), 132.9 (C-7), 140.3 (C-8), 47.3 (C-9), 62.7 (C-10), 173.0 (C-11), 100.9 (C-1′), 74.9 (C-2′), 78.3 (C-3′), 71.5 (C-4′), 78.9 (C-5′), 62.3 (C-6′), 126.4 (C-1″), 133.8 (C-2″, 6″), 116.0 (C-3″, 5″), 160.7 (C-4″), 144.7 (C-7″), 115.6 (C-8″), 166.2 (C-9″). *Craibiodendron henryi* (Ericaceae).[31]

49. 10-*O*-(*E*)-*p*-Coumaroyl-desacetylasperulosidic acid



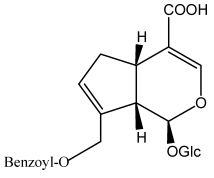
$C_{25}H_{28}O_{13}$: 536.1529; amorphous powder; $[\alpha]_D^{23}$ −19.3° (c=0.13, MeOH); UV (MeOH): 314 (3.88), 301 (3.67), 236 (3.70); IR (KBr): 3410, 2929, 1682, 1633, 1604, 1516, 1203, 1076, 839; ^{1}H-NMR (500 MHz, C_5D_5N): 5.85 (d, 8.5, H-1), 8.15 (d, 1.0, H-3), 3.47 (dd, 8.0, 5.5, H-5), 5.47 (dd, 5.5, 2.0, H-6), 6.34 (s, H-7), 2.88 (dd, 8.5, 8.0, H-9), 5.20 (d, 15.0, H-10), 5.60 (d, 15.0, H-10), 5.34 (d, 7.5, H-1′), 4.16 (dd, 8.5, 7.5, H-2′), 4.25 (dd, 9.0, 8.5, H-3′), 4.31 (m, H-4′), 3.82 (m, H-5′), 4.36 (m, H-6′), 4.30 (m, H-6′), 7.56 (d, 9.0, H-2″, 6″), 7.16 (d, 9.0, H-3″, 5″), 7.90 (d, 16.0, H-7″), 6.60 (d, 16.0, H-8″); ^{13}C-NMR (125 MHz, C_5D_5N): 101.7 (C-1), 153.8 (C-3), 109.2 (C-4), 42.7 (C-5), 74.5 (C-6), 132.3 (C-7), 144.5 (C-8), 46.1 (C-9), 63.0 (C-10), 169.8 (C-11), 101.6 (C-1′), 74.9 (C-2′), 78.3 (C-3′), 71.2 (C-4′), 78.3 (C-5′), 62.5 (C-6′), 126.0 (C-1″), 130.8 (C-2″, 6″), 116.8 (C-3″, 5″), 161.6 (C-4″), 145.6 (C-7″), 114.8 (C-8″), 167.1 (C-9″). *Craibiodendron henryi* (Ericaceae).[31]

50. 10-*O*-(*Z*)-*p*-Coumaroyl-desacetylasperulosidic acid



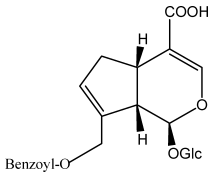
$C_{25}H_{28}O_{13}$: 536.1529; amorphous powder; $[\alpha]_D^{23}$ −55.6° (c=0.53, MeOH); UV (MeOH): 314 (4.07), 301 (3.87), 237 (4.00); IR (KBr): 3406, 2927, 1685, 1633, 1604, 1516, 1203, 1140, 839; ^{1}H-NMR (500 MHz, C_5D_5N): 5.82 (d, 8.5, H-1), 8.13 (s, H-3), 3.41 (dd, 8.0, 5.5, H-5), 5.45 (dd, 5.5, 2.0, H-6), 6.29 (s, H-7), 2.83 (dd, 8.5, 8.0, H-9), 5.42 (d, 14.0, H-10), 5.16 (d, 14.0, H-10), 5.31 (d, 7.5, H-1′), 4.13 (dd, 8.5, 7.5, H-2′), 4.26 (dd, 9.0, 8.5, H-3′), 4.29 (m, H-4′), 3.80 (m, H-5′), 4.35 (m, H-6′), 4.25 (m, H-6′), 8.04 (d, 8.5, H-2″, 6″), 7.15 (d, 8.5, H-3″, 5″), 6.92 (d, 13.0, H-7″), 5.94 (d, 13.0, H-8″); ^{13}C-NMR (125 MHz, C_5D_5N): 101.5 (C-1), 153.7 (C-3), 109.3 (C-4), 42.6 (C-5), 74.5 (C-6), 132.8 (C-7), 144.2 (C-8), 46.1 (C-9), 62.9 (C-10), 169.7 (C-11), 101.4 (C-1′), 74.9 (C-2′), 78.2 (C-3′), 71.4 (C-4′), 78.3 (C-5′), 62.5 (C-6′), 126.4 (C-1″), 133.8 (C-2″, 6″), 116.0 (C-3″, 5″), 160.7 (C-4″), 144.6 (C-7″), 115.7 (C-8″), 166.3 (C-9″). *Craibiodendron henryi* (Ericaceae).[31]

51. Hedycoryside C



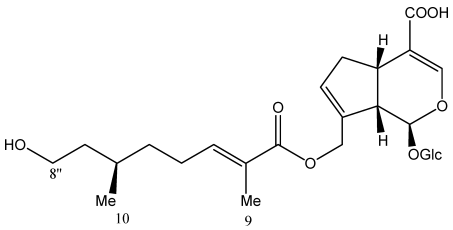
$C_{23}H_{26}O_{11}$: 478.1475; amorphous powder; $[\alpha]_D^{24}$ +11.6° (c=0.50, MeOH); UV (MeOH): 229 (4.13); IR (KBr): 3395, 2921, 2850, 1716, 1645, 1539, 1452, 1405, 1316, 1278, 1074, 903, 715; ^{1}H-NMR (500 MHz, CD_3OD): 5.17 (d, 7.6, H-1), 7.37 (br s, H-3), 3.24 (br t, 7.2, H-5), 2.15 (dd, 16.6, 7.2, H_α-6), 2.90 (dd, 16.6, 7.2, H_β-6), 5.92 (br s, H-7), 2.80 (br t, 7.6, H-9), 5.07 (br d, 13.9, H-10), 5.01 (br d, 13.9, H-10), 4.73 (d, 7.8, H-1′), 3.24 (t, 9.0, H-2′), 3.38 (t, 9.0, H-3′), overlapped (H-4′, 5′), 3.84 (dd, 12.0, 1.8, H-6′), 3.64 (dd, 12.0, 5.3, H-6′), 8.04 (dd, 7.7, 1.2, H-2″, 6″), 7.48 (t, 7.7, H-3″, 5″), 7.60 (tt, 7.2, 1.2, H-4″); ^{13}C-NMR (125 MHz, CD_3OD): 98.4 (C-1), 151.0 (C-3), 116.3 (C-4), 37.5 (C-5), 40.5 (C-6), 131.9 (C-7), 140.0 (C-8), 48.1 (C-9), 64.7 (C-10), 168.2 (C-11), 100.8 (C-1′), 75.2 (C-2′), 78.2 (C-3′), 71.8 (C-4′), 78.6 (C-5′), 63.1 (C-6′), 131.8 (C-1″), 130.9 (C-2″, 6″), 129.9 (C-3″, 5″), 134.6 (C-4″), 168.2 (C-7″). *Hedyotis corymbosa* (Rubiaceae).[32]

52. Scyphiphorin A (10-*O*-Benzoylgeniposidic acid)



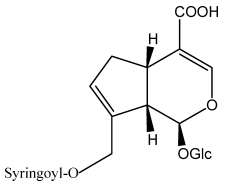
$C_{23}H_{26}O_{11}$: 478.1475; white amorphous powder; $[\alpha]_D^{20}$ +20.3° (c=7.7, MeOH); UV (MeOH): 231 (4.38); IR (KBr): 3422, 2920, 1718, 1701, 1602, 1578, 1509, 1277, 1073, 757, 714, 686; ^{1}H-NMR (500 MHz, CD_3OD): 5.24 (d, 7.5, H-1), 7.55 (s, H-3), 3.21—3.25 (m, H-5), 2.15—2.19 (m, H_α-6), 2.89—2.92 (m, H_β-6), 5.94 (s, H-7), 2.82—2.86 (m, H-9), 5.10 (d, 13.9, H-10), 5.02 (d, 13.9, H-10), 4.78 (d, 8.0, H-1′), 3.28—3.32 (m, H-2′), 3.42—3.44 (m, H-3′), 3.34—3.36 (m, H-4′, 5′), 3.87—3.89 (m, H-6′), 3.66—3.70 (m, H-6′), 8.05 (d, 7.5, H-2″, 6″), 7.50 (t, 7.5, H-3″, 5″), 7.61 (t, 7.5, H-4″); ^{13}C-NMR (125 MHz, CD_3OD): 98.4 (C-1), 153.4 (C-3), 112.6 (C-4), 36.5 (C-5), 40.0 (C-6), 131.5 (C-7), 139.5 (C-8), 47.5 (C-9), 64.3 (C-10), 170.9 (C-11), 100.5 (C-1′), 74.8 (C-2′), 77.9 (C-3′), 71.4 (C-4′), 78.3 (C-5′), 62.8 (C-6′), 131.3 (C-1″), 130.6 (C-2″, 6″), 129.6 (C-3″, 5″), 134.3 (C-4″), 167.9 (C-7″). *Scyphiphora hydrophyllacea* (Rubiaceae).[33]

53. Scyphiphorin B



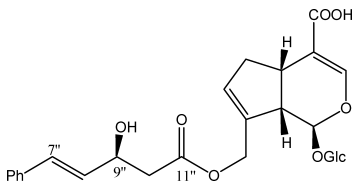
$C_{26}H_{38}O_{12}$: 542.2263; white amorphous powder; $[\alpha]_D^{20}$ +21.4° (c=5.0, MeOH); UV (MeOH): 224 (4.74); IR (KBr): 3415, 2950, 1721, 1705, 1642, 1456, 1387; ^{1}H-NMR (500 MHz, CD_3OD): 5.21 (d, 7.6, H-1), 7.54 (s, H-3), 3.21—3.23 (m, H-5), 2.14—2.19 (m, H_α-6), 2.86—2.91 (m, H_β-6), 5.86 (s, H-7), 2.76—2.80 (m, H-9), 4.92 (d, 13.8, H-10), 4.85 (d, 13.8, H-10), 4.74 (d, 7.9, H-1′), 3.23—3.27 (m, H-2′), 3.38—3.42 (m, H-3′), 3.30—3.33 (m, H-4′, 5′), 3.86—3.90 (m, H-6′), 3.64—3.69 (m, H-6′), 6.84 (t, 7.2, H-3″), 2.24—2.30 (m, H-4″), 1.49—1.53 (m, H-5″), 1.31—1.36 (m, H-5″), 1.61—1.66 (m, H-6″), 1.38—1.40 (m, H_2-7″), 3.58—3.62 (m, H_2-8″), 1.88 (s, H_3-9″), 0.95 (d, 6.5, H_{f92}-10″); ^{13}C-NMR (125 MHz, CD_3OD): 98.3 (C-1), 153.4 (C-3), 112.7 (C-4), 36.5 (C-5), 40.0 (C-6), 131.0 (C-7), 139.9 (C-8), 47.6 (C-9), 63.9 (C-10), 170.9 (C-11), 100.6 (C-1′), 74.9 (C-2′), 78.0 (C-3′), 71.5 (C-4′), 78.5 (C-5′), 62.9 (C-6′), 169.6 (C-1″), 128.6 (C-2″), 144.5 (C-3″), 27.2 (C-4″), 37.0 (C-5″), 30.5 (C-6″), 40.6 (C-7″), 61.0 (C-8″), 12.6 (C-9″), 19.8 (C-10″). *Scyphiphora hydrophyllacea* (Rubiaceae).[33]

54. Marinoid D



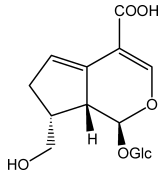
$C_{25}H_{30}O_{14}$: 554.1635; colorless oil; $[\alpha]_D^{20}$ +3.1° (c=1.5, MeOH); UV (MeOH): 278 (2.24), 218 (2.64); IR (KBr): 3422, 2925, 1704, 1629, 1514, 1462, 1425, 1336, 1225, 1111, 1078, 1041; ^{1}H-NMR (500 MHz, DMSO-d_6): 5.18 (d, 7.5, H-1), 7.41 (s, H-3), 3.15 (m, H-5), 2.13 (br dd, 6.0, 15.5, H-6), 2.78 (m, H-6), 5.91 (br s, H-7), 2.77 (m, H-9), 4.88 (d, 14.0, H-10), 4.92 (d, 14.0, H-10), 4.56 (d, 8.0, H-1′), 3.00 (dd, 8.0, 8.8, H-2′), 3.17 (dd, 8.8, 9.0, H-3′), 3.05 (dd, 9.0, 9.0, H-4′), 3.13 (dd, 6.2, 9.0, H-5′), 3.40 (dd, 11.2, 6.2, H-6′), 3.62 (d, 11.2, H-6′), 7.25 (s, H-2″, 6″), 3.82 (s, OMe); ^{13}C-NMR (125 MHz, DMSO-d_6): 96.2 (C-1), 151.1 (C-3), 112.5 (C-4), 35.1 (C-5), 38.9 (C-6), 130.2 (C-7), 138.5 (C-8), 46.7 (C-9), 63.0 (C-10), 169.1 (C-11), 99.2 (C-1′), 73.7 (C-2′), 77.0 (C-3′), 70.4 (C-4′), 77.7 (C-5′), 61.5 (C-6′), 119.7 (C-1″), 107.3 (C-2″,6″), 148.0 (C-3″,5″), 141.1 (C-4″), 166.8 (C-7″), 56.5 (OMe). *Avicennia marina* (Avicenniaceae).[34]

55. Marinoid E



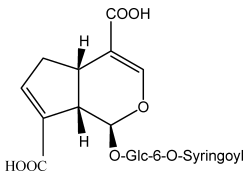
$C_{27}H_{32}O_{12}$: 548.1893; colorless oil; $[\alpha]_D^{20}$ −10.8° (c=0.6, MeOH); UV (MeOH): 246 (2.30); IR (KBr): 3412, 2924, 1721, 1642, 1606, 1512, 1451, 1421, 1252, 1158, 1077, 1039; ^{1}H-NMR (500 MHz, DMSO-d_6): 5.00 (d, 7.5, H-1), 7.31 (s, H-3), 3.06 (m, H-5), 2.03 (br dd, 16.0, 7.0, H-6), 2.73 (br dd, 10.5, 9.0, H-6), 5.83 (br s, H-7), 2.63 (m, H-9), 4.72 (br s, H_2-10), 4.55 (d, 8.0, H-1′), 3.00 (dd, 9.0, 8.0, H-2′), 3.18 (dd, 9.0, 9.0, H-3′), 3.02 (dd, 9.0, 9.0, H-4′), 3.12 (dd, 9.0, 6.0, H-5′), 3.40 (dd, 11.2, 6.0, H-6′), 3.66 (br d, 11.2, H-6′), 7.41 (d, 7.6, H-2″, 6″), 7.32 (dd, 7.6, 7.2, H-3″, 5″), 7.24 (dd, 7.2, 7.2, H-4″), 6.57 (d, 15.9, H-7″), 6.33 (dd, 15.9, 5.8, H-8″), 4.56 (ddd, 6.0, 5.8, 4.8, H-9″), 2.51 (dd, 15.4, 6.0, H-10″), 2.64 (dd, 15.4, 4.8, H-10″); ^{13}C-NMR (125 MHz, DMSO-d_6): 96.3 (C-1), 149.3 (C-3), 114.9 (C-4), 35.9 (C-5), 39.1 (C-6), 130.0 (C-7), 138.1 (C-8), 46.4 (C-9), 62.5 (C-10), 170.2 (C-11), 99.1 (C-1′), 73.7 (C-2′), 76.9 (C-3′), 70.4 (C-4′), 77.7 (C-5′), 61.5 (C-6′), 137.0 (C-1″), 126.7 (C-2″, 6″), 129.1 (C-3″, 5″), 127.9 (C-4″), 129.1 (C-7″), 133.1 (C-8″), 68.5 (C-9″), 43.0 (C-10″), 170.9 (C-11″). *Avicennia marina* (Avicenniaceae).[34]

56. 5-Dehydro-8-*epi*-adoxosidic acid



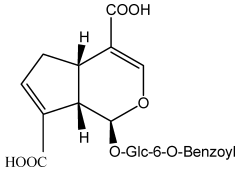
$C_{16}H_{22}O_{10}$: 374.1213; isolated as pentaacetate; white amorphous powder; UV (MeOH): 280 (3.92), 234 (4.05); IR (KBr): 2646, 1747, 1705, 1655, 1636; ^{1}H-NMR (400 MHz, $CDCl_3$): 5.11 (d, 9.5, H-1), 7.52 (d, 1.0, H-3), 5.83 (br s, H-6), 2.19 (m, H-7), 2.83 (dd, 8.0, 2.0, H-7), 3.18 (ddd, 6.0, 6.0, 6.0, H-8), 2.86 (dd, 9.5, 6.0, H-9), 4.66 (dd, 14.0, 2.0, H_2-10), 4.87 (d, 8.0, H-1′), 5.01 (dd, 8.5, 8.0, H-2′), 5.22 (dd, 9.0, 8.5, H-3′), 5.08 (dd, 9.0, 8.5, H-4′), 3.72 (m, H-5′), 4.16 (dd, 12.5, 2.5, H-6′), 4.24 (dd, 12.5, 4.5, H-6′), 1.98, 2.00, 2.02, 2.07, 2.08 (each s, 5×Ac); ^{13}C-NMR (100 MHz, $CDCl_3$): 96.2 (C-1), 152.9 (C-3), 111.3 (C-4), 136.9 (C-5), 131.2 (C-6), 38.4 (C-7), 33.5 (C-8), 46.3 (C-9), 61.8 (C-10), 172.1 (C-11), 96.9 (C-1′), 70.7 (C-2′), 72.4 (C-3′), 68.2 (C-4′), 72.1 (C-5′), 61.5 (C-6′), 20.4, 20.5×2, 20.6, 20.8, 169.1, 169.3×2, 170.2, 170.6 (5×Ac). *Wendlandia tinctoria* (Rubiaceae).[35]

57. Tarenninoside A



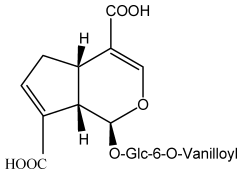
$C_{25}H_{28}O_{15}$: 568.1428; amorphous powder; $[\alpha]_D^{24}$ +42.0° (c=0.94, MeOH); UV (MeOH): 278 (3.93), 214 (4.50); IR (KBr); 3424, 1702, 1623, 1551, 1517, 1463, 1405, 1337, 1229, 1169, 1037, 764; ^{1}H-NMR (400 MHz, CD_3OD): 5.62 (d, 3.8, H-1), 7.40 (s, H-3), 3.24 (m, H-5), 2.80 (dd, 18.0, 6.5, H-6), 2.23 (d, 18.0, H-6), 6.65 (br s, H-7), 3.16 (br s, H-9), 4.69 (d, 7.8, H-1′), 3.25 (m, H-2′), 3.42 (m, H-3′), 3.37 (m, H-4′), 3.62 (m, H-5′), 4.60 (d, 11.6, H-6′), 4.39 (dd, 11.6, 6.4, H-6′), 7.29 (s, H-2″, 6″), 3.86 (s, MeO-3″, 5″); ^{13}C-NMR (100 MHz, CD_3OD): 96.0 (C-1), 152.6 (C-3), 113.8 (C-4), 35.3 (C-5), 40.0 (C-6), 144.6 (C-7), 138.6 (C-8), 47.5 (C-9), not observed (C-10), 172.0 (C-11), 99.6 (C-1′), 74.6 (C-2′), 77.6 (C-3′), 71.9 (C-4′), 75.7 (C-5′), 65.2 (C-6′), 121.2 (C-1″), 108.2 (C-2″, 6″), 148.8 (C-3″), 141.9 (C-4″), 148.8 (C-5″), 167.9 (C-7″), 56.4 (MeO-3″, 5″). *Tarenna attenuata* (Rubiaceae).[36]

58. Tarenninoside B



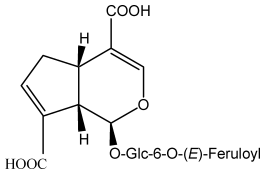
$C_{23}H_{24}O_{12}$: 492.1267; amorphous powder; $[\alpha]_D^{19}$ +24.3° (c=1.03, MeOH); UV (MeOH): 344 (2.55), 224 (4.20); IR (KBr); 3424, 1714, 1629, 1406, 1282, 1079, 962, 714; ^{1}H-NMR (400 MHz, CD_3OD): 5.58 (br s, H-1), 7.36 (s, H-3), 3.24 (m, H-5), 2.81 (m, H-6), 2.22 (m, H-6), 6.54 (br s, H-7), 3.15 (br s, H-9), 4.68 (d, 7.4, H-1′), 3.25 (m, H-2′), 3.42 (m, H-3′), 3.39 (m, H-4′), 3.60 (m, H-5′), 4.60 (d, 11.5, H-6′), 4.40 (dd, 11.5, 6.1, H-6′), 7.99 (d, 7.5, H-2″, 6″), 7.46 (dd, 7.5, 7.0, H-3″, 5″), 7.58 (t, H-4″); ^{13}C-NMR (100 MHz, CD_3OD): 96.4 (C-1), 152.2 (C-3), 114.8 (C-4), 35.4 (C-5), 40.1 (C-6), 141.5 (C-7), 138.6 (C-8), 47.8 (C-9), not observed (C-10, 11), 99.8 (C-1′), 74.6 (C-2′), 77.7 (C-3′), 72.0 (C-4′), 75.6 (C-5′), 65.3 (C-6′), 131.3 (C-1″), 130.6 (C-2″, 6″), 129.6 (C-3″, 5″), 134.3 (C-4″), 168.0 (C-7″). *Tarenna attenuata* (Rubiaceae).[36]

59. Tarenninoside C



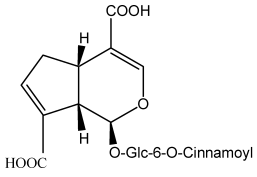
$C_{24}H_{26}O_{14}$: 538.1322; amorphous powder; $[\alpha]_D^{20}$ +37.0° (c=1.32, MeOH–C_5H_5N, 1 : 1); UV (MeOH): 362 (2.31), 292 (3.59), 251 (3.96), 220 (4.29); IR (KBr): 3420, 1705, 1631, 1595, 1517, 1405, 1285, 1181, 1078, 763; ^{1}H-NMR (500 MHz, C_5D_5N): 5.72 (br s, H-1), 7.42 (s, H-3), 3.26 (br s, H-5), 2.81 (m, H-6), 2.30 (m, H-6), 6.64 (br s, H-7), 3.20 (br s, H-9), 4.71 (d, 7.6, H-1′), 3.30 (m, H-2′), 3.46 (m, H-3′), 3.43 (m, H-4′), 3.62 (m, H-5′), 4.60 (m, H-6′), 4.37 (m, H-6′), 7.51 (s, H-2″), 6.83 (d, 7.2, H-5″), 7.54 (d, 7.2, H-6″), 3.84 (s, MeO-3″); ^{13}C-NMR (125 MHz, C_5D_5N): 96.2 (C-1), 152.6 (C-3), 111.1 (C-4), 35.5 (C-5), 40.0 (C-6), 142.0 (C-7), not observed (C-8, 10, 11), 47.9 (C-9), 100.0 (C-1′), 74.6 (C-2′), 77.8 (C-3′), 71.9 (C-4′), 75.8 (C-5′), 65.1 (C-6′), 122.4 (C-1″), 113.7 (C-2″), 148.7 (C-3″), 153.0 (C-4″), 116.1 (C-5″), 125.5 (C-6″), 167.9 (C-7″), 56.5 (MeO-3″). *Tarenna attenuata* (Rubiaceae).[36]

60. Tarenninoside D



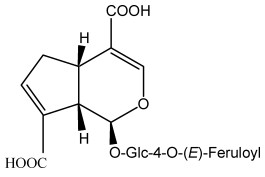
$C_{26}H_{28}O_{14}$: 564.1478; amorphous powder; $[\alpha]_D^{20}$ +23.5° (c=1.69, MeOH–C_5H_5N, 1 : 1); UV (MeOH): 325 (4.02), 263 (3.67); IR (KBr); 3424, 1698, 1631, 1596, 1516, 1441, 1402, 1356, 1282, 1162, 1082, 754; ^{1}H-NMR (500 MHz, C_5D_5N): 5.78 (br s, H-1), 7.45 (s, H-3), 3.28 (br s, H-5), 2.81 (br s, H-6), 2.38 (br s, H-6), 6.65 (br s, H-7), 3.19 (br s, H-9), 4.74 (d, 7.2, H-1′), 3.30 (m, H-2′), 3.52 (m, H-3′), 3.48 (m, H-4′), 3.59 (m, H-5′), 4.49 (m, H-6′), 4.38 (m, H-6′), 7.17 (s, H-2″), 6.81 (d, 7.7, H-5″), 7.12 (d, 7.7, H-6″), 7.59 (d, 14.9, H-7″), 6.34 (d, 14.9, H-8″), 3.82 (s, MeO-3″); ^{13}C-NMR (125 MHz, C_5D_5N): 96.2 (C-1), 152.5 (C-3), 35.5 (C-5), 40.0 (C-6), 145.6 (C-7), 47.9 (C-9), not observed (C-4, 8, 10, 11), 100.1 (C-1′), 74.6 (C-2′), 77.7 (C-3′), 71.6 (C-4′), 75.6 (C-5′), 64.6 (C-6′), 128.0 (C-1″), 111.8 (C-2″), 149.4 (C-3″), 150.7 (C-4″), 116.6 (C-5″), 124.2 (C-6″), 146.9 (C-7″), 115.4 (C-8″), 167.9 (C-9″), 56.5 (MeO-3″). *Tarenna attenuata* (Rubiaceae).[36]

61. Tarenninoside E



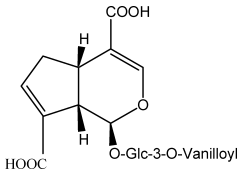
$C_{25}H_{26}O_{12}$: 518.1424; amorphous powder; $[\alpha]_D^{24}$ +36.9° (c=0.45, MeOH); UV (MeOH): 371 (2.49), 279 (4.24); IR (KBr): 3415, 1702, 1634, 1551, 1517, 1450, 1403, 1313, 1204, 1080, 1038, 769; ^{1}H-NMR (400 MHz, CD_3OD): 5.66 (br s, H-1), 7.43 (s, H-3), 3.25 (m, H-5, 2′), 2.81 (br s, H-6), 2.35 (br s, H-6), 6.65 (br s, H-7), 3.18 (br s, H-9), 4.68 (d, 6.8, H-1′), 3.40 (m, H-3′), 3.38 (m, H-4′), 3.56 (m, H-5′), 4.48 (m, H-6′), 4.35 (m, H-6′), 7.57 (d, 7.3, H-2″, 6″), 7.38 (br s, H-3″, 4″, 5″), 7.67 (d, 16.0, H-7″), 6.54 (d, 16.0, H-8″); ^{13}C-NMR (100 MHz, CD_3OD): 96.1 (C-1), 152.6 (C-3), 113.9 (C-4), 35.3 (C-5), 40.0 (C-6), 144.0 (C-7), 47.7 (C-9), not observed (C-8, 10, 11), 99.9 (C-1′), 74.5 (C-2′), 77.6 (C-3′), 71.6 (C-4′), 75.5 (C-5′), 64.8 (C-6′), 135.6 (C-1″), 129.3 (C-2″,6″), 130.0 (C-3″,5″), 131.5 (C-4″), 146.5 (C-7″), 118.6 (C-8″), 168.5 (C-9″). *Tarenna attenuata* (Rubiaceae).[36]

62. Tarenninoside F



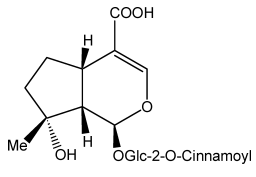
$C_{26}H_{28}O_{14}$: 564.1478; amorphous powder; $[\alpha]_D^{20}$ +7.3° (c=0.68, MeOH–C_5H_5N, 1 : 1); UV (MeOH): 325 (3.83), 216 (3.96); IR (KBr); 3431, 1605, 1517, 1364, 1282, 1159, 1087, 1033, 755; ^{1}H-NMR (400 MHz, CD_3OD): 5.66 (br s, H-1), 7.42 (s, H-3), 3.28 (br s, H-5), 2.86 (m, H-6), 2.37 (d, 16.4, H-6), 6.60 (br s, H-7), 3.20 (br s, H-9), 4.69 (d, 7.8, H-1′), 3.52 (m, H-2′), 3.32 (m, H-3′), 4.85 (m, H-4′), 3.63 (m, H-5′), 3.62 (m, H-6′), 3.51 (m, H-6′), 7.18 (d, 1.5, H-2″), 6.81 (d, 8.2, H-5″), 7.08 (d, 8.2, H-6″), 7.65 (d, 15.8, H-7″), 6.39 (d, 15.8, H-8″), 3.88 (s, MeO-3″); ^{13}C-NMR (100 MHz, CD_3OD): 96.8 (C-1), 152.5 (C-3), 35.2 (C-5), 40.1 (C-6), 142.2 (C-7), 48.0 (C-9), not observed (C-4, 8, 10, 11), 100.3 (C-1′), 74.7 (C-2′), 76.3 (C-3′), 72.3 (C-4′), 75.6 (C-5′), 62.3 (C-6′), 127.7 (C-1″), 111.8 (C-2″), 149.4 (C-3″), 150.8 (C-4″), 116.5 (C-5″), 124.2 (C-6″), 147.6 (C-7″), 115.1 (C-8″), 168.6 (C-9″), 56.5 (MeO-3″). *Tarenna attenuata* (Rubiaceae).[36]

63. Tarenninoside G



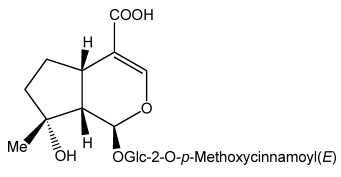
$C_{24}H_{26}O_{14}$: 538.1322; amorphous powder; $[\alpha]_D^{24}$ +26.4° (c=0.42, MeOH); UV (MeOH): 391 (2.49), 292 (3.69), 260 (3.98), 217 (4.36); IR (KBr); 3430, 1698, 1633, 1602, 1553, 1519, 1403, 1285, 1107, 1081, 762; ^{1}H-NMR (400 MHz, CD_3OD): 5.67 (br s, H-1), 7.42 (s, H-3), 3.28 (br s, H-5), 2.86 (d, 17.4, H-6), 2.36 (d, 17.4, H-6), 6.59 (br s, H-7), 3.18 (br s, H-9), 4.76 (d, 7.7, H-1′), 3.49 (m, H-2′), 5.15 (t, 9.4, H-3′), 3.63 (m, H-4′), 3.41 (m, H-5′), 3.85 (br s, H-6′), 3.71 (m, H-6′), 7.60 (s, H-2″), 6.84 (d, 8.0, H-5″), 7.61 (d, 8.0, H-6″), 3.89 (s, MeO-3″); ^{13}C-NMR (100 MHz, CD_3OD): 96.7 (C-1), 152.6 (C-3), 35.3 (C-5), 40.1 (C-6), 142.0 (C-7), 48.0 (C-9), not observed (C-4, 8, 10, 11), 100.2 (C-1′), 73.1 (C-2′), 79.0 (C-3′), 69.6 (C-4′), 78.1 (C-5′), 62.3 (C-6′), 122.8 (C-1″), 113.9 (C-2″), 148.6 (C-3″), 152.8 (C-4″), 115.8 (C-5″), 125.3 (C-6″), 168.1 (C-7″), 54.6 (MeO-3″). *Tarenna attenuata* (Rubiaceae).[36]

64. Marinoid A



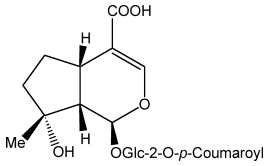
$C_{25}H_{30}O_{11}$: 506.1788; colorless oil; $[\alpha]_D^{20}$ −72.9° (c=0.7, MeOH); UV (MeOH): 282 (2.98), 221 (2.79); IR (KBr): 3394, 2930, 1711, 1649, 1550, 1420, 1182, 1074, 1027; ^{1}H-NMR (500 MHz, DMSO-d_6): 5.18 (br s, H-1), 7.09 (s, H-3), 2.87 (m, H-5), 1.29 (m, H-6), 2.09 (m, H-6), 1.52 (m, H_2-7), 1.90 (m, H-9), 1.18 (s, H_3-10), 4.81 (d, 8.6, H-1′), 4.66 (dd, 9.1, 8.6, H-2′), 3.49 (dd, 9.1, 9.0, H-3′), 3.18 (dd, 9.0, 9.0, H-4′), 3.27 (br dd, 9.0, 5.5, H-5′), 3.47 (dd, 11.0, 5.5, H-6′), 3.72 (br d, 11.0, H-6′), 7.69 (m, H-2″, 6″), 7.42 (m, H-3″, 4″, 5″), 7.59 (d, 16.0, H-7″), 6.53 (d, 16.0, H-8″); ^{13}C-NMR (125 MHz, DMSO-d_6): 94.2 (C-1), 147.5 (C-3), 115.2 (C-4), 31.6 (C-5), 30.0 (C-6), 39.9 (C-7), 78.7 (C-8), 51.2 (C-9), 27.1 (C-10), 171.5 (C-11), 96.5 (C-1′), 74.0 (C-2′), 74.4 (C-3′), 70.6 (C-4′), 76.5 (C-5′), 61.3 (C-6′), 134.6 (C-1″), 128.8 (C-2″, 6″), 129.4 (C-3″, 5″), 130.7 (C-4″), 144.7 (C-7″), 118.7 (C-8″), 165.6 (C-9″). *Avicennia marina* (Avicenniaceae).[34]

65. Marinoid B



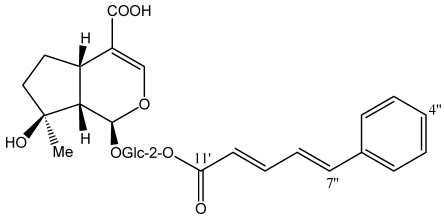
$C_{26}H_{32}O_{12}$: 536.1893; colorless oil; $[\alpha]_D^{20}$ −53.5° (c=1.9, MeOH); UV (MeOH): 312 (2.69), 229 (2.61); IR (KBr): 3416, 2926, 1709, 1641, 1604, 1513, 1422, 1254, 1173, 1071, 1024; ^{1}H-NMR (500 MHz, DMSO-d_6): 5.19 (br s, H-1), 7.11 (s, H-3), 2.86 (m, H-5), 1.29 (m, H-6), 2.09 (m, H-6), 1.52 (m, H_2-7), 1.91 (m, H-9), 1.18 (s, H_3-10), 4.79 (d, 8.1, H-1′), 4.65 (dd, 9.1, 8.1, H-2′), 3.46 (dd, 9.1, 9.0, H-3′), 3.19 (dd, 9.0, 9.0, H-4′), 3.28 (br dd, 9.0, 6.0, H-5′), 3.49 (dd, 11.0, 6.0, H-6′), 3.72 (br d, 11.1, H-6′), 7.64 (d, 8.5, H-2″, 6″), 6.97 (d, 8.5, H-3″, 5″), 7.54 (d, 15.9, H-7″), 6.37 (d, 15.9, H-8″), 3.80 (s, MeO-4″); ^{13}C-NMR (125 MHz, DMSO-d_6): 94.1 (C-1), 147.8 (C-3), 116.4 (C-4), 31.5 (C-5), 29.9 (C-6), 40.5 (C-7), 78.7 (C-8), 51.2 (C-9), 27.7 (C-10), 171.9 (C-11), 96.5 (C-1′), 73.8 (C-2′), 74.5 (C-3′), 70.6 (C-4′), 77.9 (C-5′), 61.3 (C-6′), 127.3 (C-1″), 130.6 (C-2″, 6″), 114.8 (C-3″, 5″), 161.4 (C-4″), 144.5 (C-7″), 116.0 (C-8″), 165.9 (C-9″), 55.7 (MeO-4″). *Avicennia marina* (Avicenniaceae).[34]

66. Marinoid C



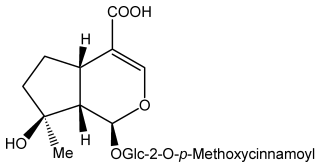
$C_{25}H_{30}O_{12}$: 522.1737; colorless oil; $[\alpha]_D^{20}$ −75.0° (c=0.2, MeOH); UV (MeOH): 313 (2.22), 230 (2.14); IR (KBr): 3418, 2925, 1701, 1648, 1605, 1514, 1419, 1260, 1172, 1074, 1025; ^{1}H-NMR (500 MHz, DMSO-d_6): 5.17 (br s, H-1), 7.07 (s, H-3), 2.88 (m, H-5), 1.30 (m, H-6), 2.09 (m, H-6), 1.52 (m, H_2-7), 1.87 (m, H-9), 1.18 (s, H_3-10), 4.80 (d, 8.0, H-1′), 4.65 (dd, 9.0, 8.0, H-2′), 3.47 (dd, 9.0, 9.0, H-3′), 3.18 (dd, 9.0, 9.0, H-4′), 3.26 (br dd, 6.0, 9.0, H-5′), 3.47 (dd, 11.0, 6.0, H-6′), 3.72 (br d, 11.0, H-6′), 7.53 (d, 8.5, H-2″, 6″), 6.80 (d, 8.5, H-3″, 5″), 7.51 (d, 16.0, H-7″), 6.31 (d, 16.0, H-8″); ^{13}C-NMR (125 MHz, DMSO-d_6): 94.1 (C-1), 147.6 (C-3), 116.2 (C-4), 31.4 (C-5), 29.8 (C-6), 40.6 (C-7), 78.6 (C-8), 51.1 (C-9), 27.3 (C-10), 171.6 (C-11), 96.4 (C-1′), 73.6 (C-2′), 74.5 (C-3′), 70.7 (C-4′), 77.8 (C-5′), 61.3 (C-6′), 125.7 (C-1″), 130.7 (C-2″, 6″), 116.2 (C-3″, 5″), 160.4 (C-4″), 144.9 (C-7″), 116.2 (C-8″), 166.0 (C-9″). *Avicennia marina* (Avicenniaceae).[34]

67. 2′-*O*[(2*E*,4*E*)-5-Phenylpenta-2,4-dienoyl] mussaenosidic acid



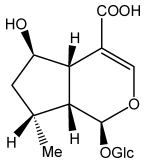
$C_{27}H_{32}O_{11}$: 532.1944; colorless amorphous powder; $[\alpha]_D^{22}$ −122.1° (c=0.21, MeOH); UV (MeOH): 311 (4.42), 232 (4.18); IR (KBr): 3396, 2962, 1701, 1625, 1073; ^{1}H-NMR (500 MHz, CD_3OD): 5.49 (d, 2.4, H-1), 7.29 (s, H-3), 2.97—3.02 (m, H-5), 2.18—2.22 (m, H_α-6), 1.45—1.51 (m, H_β-6), 1.65—1.73 (m, H_α-7), 1.60—1.64 (m, H_β-7), 2.25 (dd, 9.5, 2.2, H-9), 1.28 (s, H_3-10), 4.87 (overlapped, H-1′), 4.79 (dd, 9.3, 8.3, H-2′), 3.62 (dd, 8.9, 8.5, H-3′), 3.36—3.38 (m, H-4′), 3.38—3.40 (m, H-5′), 3.93 (d, 11.5, H-6′), 3.71 (dd, 11.5, 5.1, H-6′), 7.56 (d, 7.4, H-2″, 6″), 7.36 (t, 7.4, H-3″, 5″), 7.31 (t, 7.4, H-4″), 7.00—7.01 (m, H-7″), 6.99—7.00 (m, H-8″), 7.42—7.47 (m, H-9″), 5.99 (d,15.3, H-10″); ^{13}C-NMR (125 MHz, CD_3OD): 95.0 (C-1), 151.1 (C-3), 114.4 (C-4), 31.4 (C-5), 30.3 (C-6), 41.5 (C-7), 79.8 (C-8), 52.6 (C-9), 24.4 (C-10), not observed (C-11), 97.6 (C-1′), 74.8 (C-2′), 76.0 (C-3′), 71.8 (C-4′), 78.6 (C-5′), 62.8 (C-6′), 137.7 (C-1″), 128.4 (C-2″, 6″), 129.8 (C-3″, 5″), 130.0 (C-4″), 142.6 (C-7″), 127.6 (C-8″), 146.8 (C-9″), 121.6 (C-10″), 167.8 (C-11″). *Avicennia marina* (Verbenaceae).[37]

68. 2′-*O*-(4-Methoxycinnamoyl) mussaenosidic acid



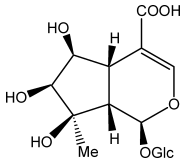
$C_{26}H_{32}O_{12}$: 536.1893; colorless amorphous powder; $[\alpha]_D^{22}$ −129.5° (c=0.27, MeOH); UV (MeOH): 309 (4.27), 221 sh (4.34), 207 (4.47); IR (KBr): 3403, 2963, 1700, 1635, 1603, 1513, 1253, 1173, 1072, 1028; ^{1}H-NMR (500 MHz, CD_3OD): 5.49 (d, 2.5, H-1), 7.28 (s, H-3), 2.99—3.02 (m, H-5), 2.22—2.24 (m, H_α-6), 1.43—1.49 (m, H_β-6), 1.68—1.72 (m, H_α-7), 1.62—1.66 (m, H_β-7), 2.25 (dd, 9.5, 2.5, H-9), 1.28 (s, H_3-10), 4.90 (d, 8.2, H-1′), 4.81 (dd, 9.4, 8.2, H-2′), 3.62—3.65 (m, H-3′), 3.37—3.39 (m, H-4′), 3.39—3.40 (m, H-5′), 3.94 (d, 12.0, H-6′), 3.71 (dd, 12.0, 5.5, H-6′), 7.54 (d, 8.7, H-2″, 6″), 6.96 (d, 8.7, H-3″, 5″), 7.62 (d, 15.9, H-7″), 6.32 (d, 15.9, H-8″), 3.84 (s, MeO-4″); ^{13}C-NMR (125 MHz, CD_3OD): 95.1 (C-1), 151.2 (C-3), 114.2 (C-4), 31.5 (C-5), 30.3 (C-6), 41.4 (C-7), 79.9 (C-8), 52.6 (C-9), 24.4 (C-10), 170.2 (C-11), 97.8 (C-1′), 74.8 (C-2′), 76.0 (C-3′), 71.7 (C-4′), 78.6 (C-5′), 62.8 (C-6′), 128.6 (C-1″), 131.1 (C-2″, 6″), 115.4 (C-3″, 5″), 163.1 (C-4″), 146.4 (C-7″), 116.0 (C-8″), 168.0 (C-9″), 55.9 (OMe). *Avicennia marina* (Avicenniaceae).[37]

69. 8-Deoxyshanzhiside



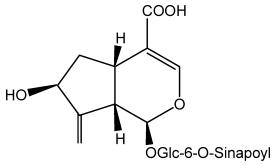
$C_{16}H_{24}O_{10}$: 376.1369; crystals; mp 213—214 °C; $[\alpha]_D^{25}$ −155.7° (c=0.18, H_2O); UV (MeOH): 237 (6.33); IR (KBr): 3613, 3467, 3382, 2943, 2884, 1676, 1641; ^{1}H-NMR (400 MHz, D_2O): 5.44 (d, 2.0, H-1), 7.34 (s, H-3), 2.70 (d, 9.0, H-5), 4.11 (t, 2.0, H-6), 1.38 (ddd, 13.0, 10.0, 4.0, H-7), 1.65 (dd, 13.0, 8.0, H-7), 2.43 (m, H-8), 2.56 (dt, 9.2, 2.0, H-9), 0.87 (d, 7.0, H_3-10), 4.63 (d, 8.0, H-1′), 3.10 (t, 9.0, H-2′), 3.33 (t, 9.0, H-3′), 3.23 (t, 9.0, H-4′), 3.33 (t, 9.0, H-5′), 3.62 (dd, 12.0, 6.0, H-6′), 3.77 (d, 12.0, H-6′); ^{13}C-NMR (100 MHz, D_2O): 96.0 (C-1), 153.3 (C-3), 110.3 (C-4), 412.1 (C-5), 77.1 (C-6), 40.8 (C-7), 32.5 (C-8), 40.5 (C-9), 15.7 (C-10), 171.1 (C-11), 98.6 (C-1′), 72.9 (C-2′), 75.9 (C-3′), 69.9 (C-4′), 76.5 (C-5′), 61.0 (C-6′). *Lamiophlomis rotata* (Labiatae).[38]

70. Lamalbidic acid



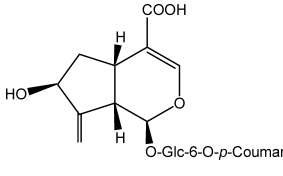
$C_{16}H_{24}O_{12}$: 408.1267; amorphous powder; $[\alpha]_D^{33}$ −122.0° (c=0.1, MeOH); UV (MeOH): 232 (3.94); IR (KBr): 3420, 2921, 1684, 1646; ^{1}H-NMR (400 MHz, D_2O): 5.66 (d, 0.8, H-1), 7.47 (s, H-3), 2.94 (dd, 11.0, 3.4, H-5), 4.08 (dd, 4.4, 3.4, H-6), 3.70 (d, 4.4, H-7), 2.84 (s, H-9), 1.23 (s, H_3-10), 4.78 (d, 8.1, H-1′), 3.27 (dd, 9.3, 8.1, H-2′), 3.50 (t, 9.3, H-3′), 3.40 (t, 9.5, H-4′), 3.52 (overlapped, H-5′), 3.93 (dd, 12.4, 2.1, H-6′), 3.72 (dd, 12.4, 6.1, H-6′); ^{13}C-NMR (100 MHz, D_2O): 94.5 (C-1), 152.4 (C-3), 111.4 (C-4), 36.1 (C-5), 76.6 (C-6), 78.8 (C-7), 78.5 (C-8), 47.9 (C-9), 21.3 (C-10), 171.7 (C-11), 98.8 (C-1′), 73.3 (C-2′), 76.7 (C-3′), 70.2 (C-4′), 77.1 (C-5′), 61.5 (C-6′). *Eremostachys moluccelloides* (Lamiaceae).[39]

71. 6′-*O*-[(*E*)-Sinapoyl] gardoside



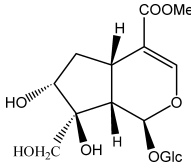
$C_{27}H_{32}O_{14}$: 580.1791; pale yellow powder; $[\alpha]_D^{22}$ −5.8° (c=0.25, MeOH); UV (MeOH): 326 (4.64), 234 (4.14); IR (KBr): 3438, 2923, 1635, 1558, 1516, 1456, 1404, 1258, 1157, 577; ^{1}H-NMR (500 MHz, CD_3OD): 5.11 (d, 7.6, H-1), 7.14 (br s, H-3), 3.04 (d, 8.4, H-5), 1.83—1.84 (m, H-6), 4.27—4.30 (m, H-7), 2.83—2.84 (m, H-9), 5.15 (br d, 7.7, H_2-10), 4.57 (d, 7.8, H-1′), 3.14—3.18 (m, H-2′), 3.31—3.35 (m, H-3′), 3.25—3.28 (m H-4′), 3.46—3.49 (m, H-5′), 4.41 (dd, 12.3, 1.9, H-6′), 4.38 (dd, 12.3, 5.1, H-6′), 6.81 (br d, H-2″, 6″), 7.53 (d, 15.8, H-7″), 6.37 (d, 15.8, H-8″), 3.77 (s, MeO-3″, 5″); ^{13}C-NMR (125 MHz, CD_3OD): 97.0 (C-1), 153.9 (C-3), 112.4 (C-4), 31.6 (C-5), 41.0 (C-6), 73.9 (C-7), 152.2 (C-8), 44.9 (C-9), 112.7 (C-10), 169.5 (C-11), 101.1 (C-1′), 74.9 (C-2′), 78.5 (C-3′), 71.5 (C-4′), 75.9 (C-5′), 64.4 (C-6′), 125.3 (C-1″), 107.0 (C-2″, 6″), 149.7 (C-3″, 5″), 140.8 (C-4″), 146.2 (C-7″), 115.5 (C-8″), 167.6 (C-9″), 56.6 (MeO-3″, 5″). *Gardenia jasminoides* (Rubiaceae).[40]

72. 6′-*O*-*E*-*p*-Coumaroylgardoside



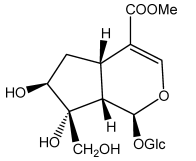
$C_{25}H_{28}O_{12}$: 520.1580; yellowish oil; $[\alpha]_D^{20}$ −4.29° (c=0.12, MeOH); UV (MeOH): 300.5 sh (4.42), 312 (4.89); IR (film); 3352, 2914, 1644, 1607; ^{1}H-NMR (400 MHz, CD_3OD): 5.25 (d, 4.2, H-1), 7.13 (s, H-3), 3.19 (d, 8.0, H-5), 1.90—2.10 (m, H_2-6), 4.39 (m, H-7), 2.9 (m, H-9), 5.19 (br d, 7.5, H_2-10), 4.65 (d, 8.0, H-1′), 3.25 (dd, 9.5, 8.0, H-2′), 3.40 (t, 9.5, H-3′), 3.33 (t, 9.5, H-4′), 3.50 (m, H-5′), 4.47 (dd, 12.0, 2.2, H-6′), 4.38 (dd, 12.0, 6.2, H-6′), 7.57 (d, 8.5, H-2″, 6″), 6.80 (d, 8.5, H-3″, 5″), 7.63 (d, 16.0, H-7″), 6.36 (d, 15.7, H-8″); ^{13}C-NMR (100 MHz, CD_3OD): 96.5 (C-1), 147.2 (C-3), 113.5 (C-4), 31.0 (C-5), 40.9 (C-6), 72.8 (C-7), 150.9 (C-8), 45.9 (C-9) 112.0 (C-10), 171.2 (C-11), 99.5 (C-1′), 73.5 (C-2′), 77.0 (C-3′), 70.9 (C-4′), 74.8 (C-5′), 63.8 (C-6′), 127.9 (C-1″), 130.2 (C-2″, 6″), 115.7 (C-3″, 5″), 160.1 (C-4″), 147.0 (C-7″), 114.9 (C-8″), 168.7 (C-9″). *Scutellaria albida* ssp. *albida* (Lamiaceae).[28]

73. Genameside A



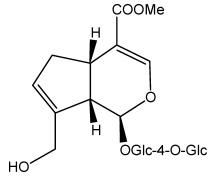
$C_{17}H_{26}O_{12}$: 422.1423; colourless syrup; $[\alpha]_D^{26}$ −91.9° (*c*=2.4, MeOH); ^{1}H-NMR (500 MHz, CD_3OD): 5.68 (d, 8.0, H-1), 7.45 (d, 1.0, H-3), 3.29 (m, H-5), 2.80 (ddd, 14.5, 10.0, 7.0, H_a-6), 1.37 (ddd, 14.5, 8.0, 4.0, H_b-6), 4.03 (dd, 7.0, 4.0, H-7), 2.19 (dd, 8.0, 8.0, H-9), 3.98 (d,12.0, H_a-10), 3.83 (d, 12.0, H_b-10), 3.71 (s, OMe), 4.73 (d, 8.0, H-1′), 3.23 (dd, 9.0, 8.0, H-2′), 3.39 (deformed, H-3′), 3.30 (H-4′, 5′), 3.86 (d, 11.5, H_a-6′), 3.67 (deformed, H_b-6′); ^{13}C-NMR (125 MHz, CD_3OD): 95.4 (C-1), 152.5 (C-3), 112.8 (C-4), 31.9 (C-5), 41.5 (C-6), 79.0 (C-7), 84.7 (C-8), 49.4 (C-9), 64.4 (C-10), 169.4 (C-11), 51.7 (OMe), 100.2 (C-1′), 74.8 (C-2′), 77.9 (C-3′), 71.7 (C-4′), 78.3 (C-5′), 62.9 (C-6′). *Genipa americana* (Rubiaceae).[41]

74. Genameside B



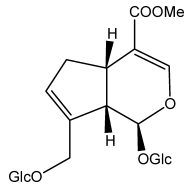
$C_{17}H_{26}O_{12}$: 422.1423; colorless syrup: $[\alpha]_D^{26}$ −63.8° (*c*=1.9, MeOH); ^{1}H-NMR (500 MHz, CD_3OD): 5.53 (d, 3.5, H-1), 7.41 (s, H-3), 3.15 (ddd, 8.0, 8.0, 8.0, H-5), 2.18 (ddd, 13.5, 7.5, 3.0, H_a-6), 1.82 (ddd, 13.5, 8.0, 5.0, H_b-6), 3.94 (dd, 5.0, 3.0, H-7), 2.44 (dd, 8.0, 3.5, H-9), 3.78 (d, 11.5, H_a-10), 3.72 (d, 11.5, H_b-10), 3.70 (s, OMe), 4.67 (d, 8.0, H-1′), 3.20 (dd, 9.0, 8.0, H-2′), 3.37 (deformed, H-3′), 3.31 (*ca.* H-4′, 5′), 3.86 (d, 11.5, H_a-6′), 3.68 (*ca.* H_b-6′); ^{13}C-NMR (125 MHz, CD_3OD): 96.3 (C-1), 152.6 (C-3), 113.7 (C-4), 31.4 (C-5), 40.5 (C-6), 79.3 (C-7), 84.5 (C-8), 45.4 (C-9), 66.4 (C-10), 169.4 (C-11), 51.7 (OMe), 100.6 (C-1′), 74.7 (C-2′), 78.0 (C-3′), 71.4 (C-4′), 78.9 (C-5′), 62.6 (C-6′). *Genipa americana* (Rubiaceae).[41]

75. Genameside C



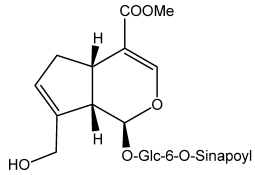
$C_{23}H_{34}O_{15}$: 550.1897; white powder; $[\alpha]_D^{26}$ −0.4° (*c*=3.3, MeOH); ^{1}H-NMR (500 MHz, CD_3OD): 5.13 (d, 8.0, H-1), 7.51 (d, 2.0, H-3), 3.19 (ddd, 8.0, 8.0, 8.0, H-5), 2.82 (dd, 16.5, 8.0, H_a-6), 2.08 (dddd, 16.5, 8.0, 2.0, 2.0, H_b-6), 5.80 (br s, H-7), 2.72 (dd, 8.0, 8.0, H-9), 4.31 (br d, 14.0, H_a-10), 4.18 (dd,14.0, 2.0, H_b-10), 3.71 (s, OMe), 4.74 (d, 8.0, H-1′), 3.30 (*ca.* H-2′), 3.55 (dd, 9.0, 9.0, H-3′), 3.58 (dd, 9.0, 9.0, H-4′), 3.43 (ddd, 9.0, 4.0, 2.5, H-5′), 3.89 (dd, 11.5, 2.5, H_a-6′), 3.83 (dd, 11.5, 4.0, H_b-6′), 4.41 (d, 8.0, H-1″), 3.23 (dd, 9.0, 8.0, H-2″), 3.38 (dd, 9.0, 9.0, H-3″), 3.30 (*ca.* H-4″), 3.35 (*ca.* H-5″), 3.88 (dd, 11.5, 2.5, H_a-6″), 3.66 (dd, 11.5, 5.5, H_b-6″); ^{13}C-NMR (125 MHz, CD_3OD): 98.4 (C-1), 153.3 (C-3), 112.6 (C-4), 36.6 (C-5), 39.7 (C-6), 128.4 (C-7), 144.8 (C-8), 47.0 (C-9), 61.4 (C-10), 169.5 (C-11), 51.7 (OMe), 100.3 (C-1′), 74.9 (C-2′), 76.9 (C-3′), 80.6 (C-4′), 76.2 (C-5′), 61.8 (C-6′),104.6 (C-1″), 74.6 (C-2″), 77.9 (C-3″), 74.1 (C-4″), 78.1 (C-5″), 62.5 (C-6″). *Genipa americana* (Rubiaceae).[41]

76. Genameside D



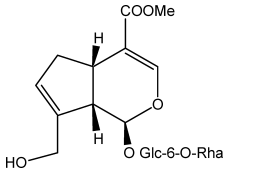
$C_{23}H_{34}O_{15}$: 550.1897; colorless syrup; $[\alpha]_D^{26}$ +3.3° (*c*=6.0, MeOH); ^{1}H-NMR (500 MHz, CD_3OD): 5.25 (d, 6.5, H-1), 7.50 (d,1.0, H-3), 3.21 (*ca.*, H-5), 2.83 (dd, 16.5, 8.5, H_a-6), 2.11 (br ddq, 16.5, 5.5, H_b-6), 6.88 (br s, H-7), 2.95 (dd, 7.5, 7.5, H-9), 4.61 (d, 13.0, H_a-10), 4.27 (d, 13.0, H_b-10), 3.71 (s, OMe), 4.72 (d, 8.0, H-1′), 3.26 (*ca.* H-2′), 3.39 (*ca.* H-3′), 3.31 (*ca.* H-4′), 3.30 (*ca.* H-5′), 3.87 (dd, 11.5, 1.0, H_a-6′), 3.66 (*ca.* H_b-6′), 4.35 (d, 8.0, H-1″), 3.26 (*ca.* H-2″), 3.39 (*ca.* H-3″), 3.31 (*ca.* H-4″), 3.30 (*ca.* H-5″), 3.87 (dd, 11.5, 1.0, H_a-6″), 3.68 (*ca.* H_b-6″); ^{13}C-NMR (125 MHz, CD_3OD): 97.9 (C-1), 153.4 (C-3), 112.8 (C-4), 36.0 (C-5), 39.8 (C-6), 130.6 (C-7), 141.5 (C-8), 47.1 (C-9), 69.1 (C-10), 169.7 (C-11), 51.9 (OMe), 100.3 (C-1′), 74.9 (C-2′), 77.9 (C-3′), 71.7 (C-4′), 78.1 (C-5′), 62.8 (C-6′), 104.6 (C-1″), 75.3 (C-2″), 78.0 (C-3″), 71.4 (C-4″), 78.4 (C-5″), 62.9 (C-6″). *Genipa americana* (Rubiaceae).[41]

77. 6′-*O*-Sinapoylgeniposide



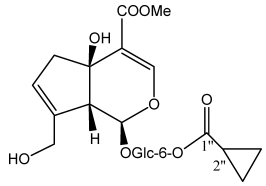
$C_{28}H_{34}O_{14}$: 594.1948; pale yellow powder; $[\alpha]_D^{20}$ −6.7° (*c*=0.05, MeOH); UV (MeOH): 325, 235; ^{1}H-NMR (500 MHz, CD_3OD): 4.97 (d, 8.1, H-1), 7.46 (s, H-3), 3.11 (m, H-5), 2.73 (m, H-6), 1.95 (m, H-6), 5.76 (br s, H-7), 2.68 (m, H-9), 4.24 (d, 14.0, H-10), 4.17 (d, 14.0, H-10), 4.70 (d, 7.9, H-1′), 3.28 (m, H-2′), 3.39 (m, H-3′), 3.42 (m, H-4′), 3.53 (m, H-5′), 4.46 (m, H-6′), 4.39 (m, H-6′), 6.88 (s, H-2″, 6″), 7.58 (d, 15.8, H-7″), 6.36 (d, 15.8, H-8″), 3.64 (s, MeO-11), 3.87 (MeO-3″, 5″); ^{13}C-NMR (125 MHz, CD_3OD): 98.8 (C-1), 153.2 (C-3), 112.5 (C-4), 36.9 (C-5), 39.9 (C-6), 128.8 (C-7), 145.0 (C-8), 46.6 (C-9), 61.6 (C-10), 169.4 (C-11), 100.6 (C-1′), 74.9 (C-2′), 77.8 (C-3′), 71.9 (C-4′), 75.8 (C-5′), 64.4 (C-6′), 126.6 (C-1″), 107.1 (C-2″, 6″), 149.5 (C-3″, 5″), 139.5 (C-4″), 147.3 (C-7″), 115.8 (C-8″), 168.9 (C-9″), 51.7 (MeO-11), 56.9 (MeO-3″, 5″). *Gardenia jasminoides* (Rubiaceae).[42]

78. Genipin-1-*O*-α-L-rhamnopyranosyl(1→6)-β-D-glucopyranoside



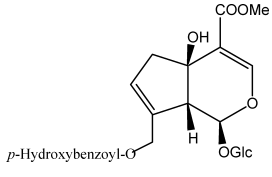
$C_{23}H_{34}O_{14}$: 534.1948; colorless gum; $[\alpha]_D^{20}$ +25.7° (*c*=0.04, MeOH); UV (MeOH): 234 (3.45); IR (KBr); 3358, 2951, 1704, 1629, 1589, 1408, 1282, 1248, 1157, 1074, 985, 942, 896, 842; ^{1}H-NMR (500 MHz, D_2O): 5.22 (d, 7.6, H-1), 7.60 (s, H-3), 3.25 (q, 7.6, H-5), 2.16 (dd, 16.4, 7.6, H-6), 2.84 (dd, 16.4, 7.6, H-6), 5.91 (br s, H-7), 2.87 (t, 7.6, H-9), 4.28 (d, 14.0, H-10), 4.32 (d, 14.0, H-10), 3.77 (s, OMe), 4.84 (d, 8.4, H-1′), 3.38 (dd, 9.2, 8.4, H-2′), 3.54 (dd, 9.2, 9.2, H-3′), 3.44 (dd, 9.2, 9.2, H-4′), 3.60 (dd, 9.2, 5.6, H-5′), 3.70 (dd, 10.8, 5.6, H-6′), 4.01 (br d, 10.8, H-6′), 4.83 (br s, H-1″), 3.95 (br s, H-2″), 3.73 (m, H-3″), 3.42 (br d, 8.8, H-4″), 3.67 (dq, 8.8, 6.0, H-5″), 1.30 (d, 6.0, H_3-6″); ^{13}C-NMR (125 MHz, D_2O): 100.6 (C-1), 155.8 (C-3), 114.8 (C-4), 37.6 (C-5), 41.2 (C-6), 132.7 (C-7), 144.5 (C-8), 48.7 (C-9), 63.0 (C-10), 173.5 (C-11), 55.0 (OMe), 102.1 (C-1′), 75.9 (C-2′), 78.8 (C-3′), 72.8 (C-4′), 78.2 (C-5′), 70.0 (C-6′), 103.8 (C-1″), 73.2 (C-2″), 73.4 (C-3″), 75.2 (C-4″), 71.9 (C-5″), 19.8 (C-6″). *Adina polycephala* (Rubiaceae).[43]

79. 6′-*O*-Cyclopropanoyltheviridoside



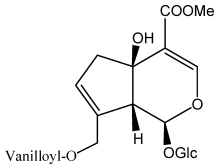
$C_{21}H_{28}O_{12}$: 472.1580; pale yellow amorphous powder; $[\alpha]_D^{25}$ −27.3° (*c*=1.0, MeOH); UV (MeOH): 324 (3.01), 282 (3.13), 231 (3.79), 200 (4.04); ^{1}H-NMR (500 MHz, CD_3OD): 5.36 (d, 5.9, H-1), 7.49 (s, H-3), 2.82 (dd, 17.6, 9.8, H_2-6), 5.72 (d, 1.5, H-7), 3.03 (d, 4.9, H-9), 4.18 (dd, 25.4, 16.7, H_2-10), 3.73 (s, MeO),4.64 (d, 7.8, H-1′), 3.22 (m, H-2′), 3.36 (t, 9.0, H-3′), 3.31 (m, H-4′), 3.47 (m, H-5′), 4.36 (dd, 12.0, 2.2, H-6′), 4.22 (dd, 11.7, 5.9, H-6′), 1.65 (m, H-2″), 0.91 (m, H_4-3″, 4″); ^{13}C-NMR (125 MHz, CD_3OD): 97.6 (C-1), 153.9 (C-3), 114.7 (C-4), 76.6 (C-5), 47.1 (C-6), 126.9 (C-7), 142.1 (C-8), 56.7 (C-9), 61.1 (C-10), 168.2 (C-11), 51.7 (OMe), 100.2 (C-1′), 74.5 (C-2′), 77.4 (C-3′), 71.5 (C-4′), 75.7 (C-5′), 64.5 (C-6′), 176.5 (C-1″), 13.6 (C-2″), 8.9 (C-3″), 8.8 (C-4″). *Pithecoctenium crucigerum* (Bignoniaceae).[44]

80. 10-*O*-*p*-Hydroxybenzoyltheviridoside



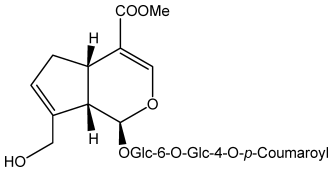
$C_{24}H_{28}O_{13}$: 524.1529; pale yellow amorphous solid; $[\alpha]_D^{25}$ −31.8° (*c*=1.0, MeOH); UV (MeOH): 325 (3.32), 253 (3.91), 201 (4.22); ^{1}H-NMR (500 MHz, CD_3OD): 5.58 (d, 5.9, H-1), 7.51 (s, H-3), 2.88 (br s, H_2-6), 5.86 (d, 1.5, H-7), 3.09 (dd, 5.9, 1.0, H-9), 4.93 (d, 2.4, H_2-10), 3.73 (s, OMe), 4.64 (d, 8.3, H-1′), 3.23 (dd, 9.3, 7.8, H-2′), 3.37 (t, 9.3, H-3′), 3.28 (m, H-4′), 3.27 (m, H-5′), 3.83 (dd, 12.0, 1.2, H-6′), 3.63 (dd, 11.7, 5.3, H-6′), 7.91 (d, 8.8, H-2″, 6″), 6.83 (d, 8.8, H-3″, 5″); ^{13}C-NMR (125 MHz, CD_3OD): 97.6 (C-1), 154.0 (C-3), 114.6 (C-4), 76.5 (C-5), 47.3 (C-6), 130.1 (C-7), 137.3 (C-8), 57.4 (C-9), 63.3 (C-10), 167.9 (C-11), 51.6 (OMe), 100.3 (C-1′), 74.6 (C-2′), 77.7 (C-3′), 71.5 (C-4′), 78.4 (C-5′), 62.8 (C-6′), 120.7 (C-1″), 132.9 (C-2″, 6″), 116.2 (C-3″, 5″), 162.0 (C-4″), 167.9 (C-7″). *Pithecoctenium crucigerum* (Bignoniaceae).[44]

81. 10-*O*-Vanilloyltheviridoside



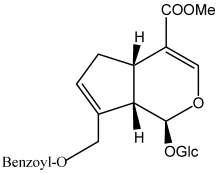
$C_{25}H_{30}O_{14}$: 554.1635; pale yellow amorphous solid; $[\alpha]_D^{25}$ −26.6° (c=2.0, MeOH); UV (MeOH): 327 (3.46), 292 (3.68), 254 (3.85), 220 (4.16), 202 (4.31); ^{1}H-NMR (500 MHz, CD_3OD): 5.62 (d, 5.9, H-1), 7.51 (s, H-3), 2.89 (br s, H_2-6), 5.87 (d, 1.5, H-7), 3.10 (d, 5.9, H-9), 4.94 (s, H_2-10), 3.73 (s, OMe), 4.64 (d, 8.3, H-1′), 3.23 (m, H-2′), 3.36 (t, 9.3, H-3′), 3.28 (m, H-4′), 3.27 (m, H-5′), 3.82 (m, H-6′), 3.63 (dd, 12.0, 5.1, H-6′), 7.58 (d, 1.9, H-2″), 6.86 (d, 8.3, H-5″), 7.60 (dd, 8.3, 1.9, H-6″), 3.90 (s, MeO-3″); ^{13}C-NMR (125 MHz, CD_3OD): 97.5 (C-1), 154.0 (C-3), 114.6 (C-4), 76.5 (C-5), 47.3 (C-6), 130.4 (C-7), 137.2 (C-8), 57.5 (C-9), 63.5 (C-10), 167.9 (C-11), 51.7 (OMe), 100.3 (C-1′), 74.6 (C-2′), 77.7 (C-3′), 71.5 (C-4′), 78.2 (C-5′), 62.8 (C-6′), 122.5 (C-1″), 113.8 (C-2″), 148.9 (C-3″), 152.8 (C-4″), 116.1 (C-5″), 125.3 (C-6″), 168.2 (C-7″), 56.5 (MeO-3″). *Pithecoctenium crucigerum* (Bignoniaceae).[44]

82. 4″-*O*-[(*E*)-*p*-Coumaroyl]-gentiobiosylgenipin



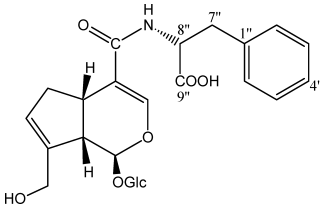
$C_{32}H_{40}O_{17}$: 696.2265; pale yellow powder; $[\alpha]_D^{22}$ −7.1° (c=0.25, MeOH); UV (MeOH): 311 (4.02), 232 (4.24); IR (KBr): 3411, 2923, 1697, 1631, 1604, 1514, 1439, 1375, 1282, 1163, 1075, 896, 833, 768, 532; ^{1}H-NMR (500 MHz, C_5D_5N): 5.87 (d, 7.4, H-1), 7.75 (s, H-3), 3.45—3.40 (m, H-5), 3.05 (dd, 16.8, 8.2, H-6), 2.61 (br d, 16.8, H-6), 6.31 (s, H-7), 3.11 (dd, 7.5, 7.5, H-9), 4.95 (d, 14.8, H-10), 4.77 (d, 14.8, H-10), 3.68 (s, OMe), 5.39 (d, 7.9, H-1′), 4.25—4.27 (m, H-2′), 4.08—4.11 (m, H-3′), 4.23—4.25 (m, H-4′), 3.95—3.99 (m, H-5′), 4.85 (dd, 11.0, 1.9, H-6′), 4.32 (dd, 11.0, 6.0, H-6′), 5.27 (d, 7.8, H-1″) 4.14—4.17 (m, H-2″), 4.47—4.51 (m, H-3″), 5.84 (dd, 9.4, 9.4, H-4″), 4.24—4.25 (m, H-5″), 4.32 (dd, 12.4, 4.9, H-6″), 4.27 (dd, 11.3, 2.0, H-6″), 7.61 (dd, 8.6, 1.3, H-2‴, 6‴), 7.24 (dd, 8.6, 1.3, H-3‴, 5‴), 8.02 (d, 15.8, H-7‴), 6.64 (d, 15.8, H-8‴); ^{13}C-NMR (125 MHz, C_5D_5N): 98.3 (C-1), 152.5 (C-3), 111.7 (C-4), 35.9 (C-5), 39.3 (C-6), 127.3 (C-7), 145.6 (C-8), 47.0 (C-9), 61.0 (C-10), 167.8 (C-11), 51.1 (OMe), 101.2 (C-1′), 78.4 (C-2′), 74.8 (C-3′), 78.3 (C-4′), 71.8 (C-5′), 70.0 (C-6′), 105.2 (C-1″), 75.6 (C-2″), 75.9 (C-3″), 72.9 (C-4″), 76.4 (C-5″), 62.4 (C-6″), 126.2 (C-1‴), 130.9 (C-2‴, 6‴), 116.9 (C-3‴, 5‴), 161.6 (C-4‴), 145.8 (C-7‴), 115.2 (C-8‴), 167.3 (C-9‴). *Gardenia jasminoides* (Rubiaceae).[40]

83. Hedycoryside A



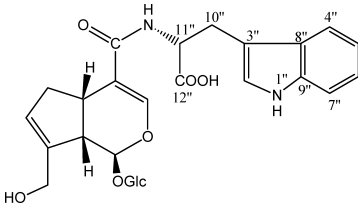
$C_{24}H_{28}O_{11}$: 492.1631; amorphous powder; $[\alpha]_D^{24}$ +13.2° (c=0.25, MeOH); UV (MeOH): 231 (4.26); IR (KBr): 3371, 2921, 2851, 1713, 1633, 1452, 1385, 1273, 1158, 1073, 716; ^{1}H-NMR (500 MHz, CD_3OD): 5.24 (d, 7.8, H-1), 7.52 (br s, H-3), 3.24 (br t, 8.0, H-5), 2.15 (dd, 16.6, 8.0, H-6), 2.89 (dd, 16.6, 8.0, H-6), 5.94 (br s, H-7), 2.84 (br t, 7.8, H-9), 5.07 (br d, 13.6, H-10), 5.01 (br d, 13.6, H-10), 3.71 (s,OMe), 4.72 (d, 7.8, H-1′), 3.24 (t, 9.0, H-2′), 3.38—3.35 (m, H-3′), overlapped (H-4′, 5′), 3.84 (br d, 11.5, H-6′), 3.63 (dd, 11.5, 5.3, H-6′), 8.04 (dd, 7.8, 1.3, H-2″, 6″), 7.48 (t, 7.8, H-3″, 5″), 7.60 (br t, 7.8, H-4″); ^{13}C-NMR (125 MHz, CD_3OD): 98.7 (C-1), 153.7 (C-3), 112.7 (C-4), 36.8 (C-5), 40.3 (C-6), 131.8 (C-7), 139.9 (C-8), 47.9 (C-9), 64.6 (C-10), 169.7 (C-11), 52.0 (OMe), 100.9 (C-1′), 75.2 (C-2′), 78.3 (C-3′), 71.8 (C-4′), 78.7 (C-5′), 63.1 (C-6′), 131.8 (C-1″), 130.9 (C-2″, 6″), 129.9 (C-3″, 5″), 134.6 (C-4″), 168.2 (C-7″). *Hedyotis corymbosa* (Rubiaceae).[32]

84. Eucomoside B



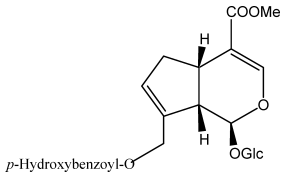
$C_{25}H_{31}NO_{11}$: 521.1897; white powder; $[\alpha]_D$ −10.6° (c=0.1, MeCN); ^{1}H-NMR (500 MHz, CD_3OD): 5.10 (d, 7.3, H-1), 7.14 (d, 1.2, H-3), 3.20 (m, H-5), 1.88 (dd, 15.9, 7.9, H-6), 2.50 (dd, 15.3, 7.9, H-6), 5.69 (s, H-7), 2.72 (d, 9.2, 9.2, H-9), 4.16 (d, 14.0, H-10), 4.29 (d, 14.0, H-10), 4.69 (d, 7.3, H-1′), 3.27 (m, H-2′), 3.39 (dd, 9.2, 9.2, H-3′), 3.27 (m, H-4′, 5′), 3.65 (dd, 12.2, 1.8, H-6′), 3.85 (dd, 12.2, 1.8, H-6′), 7.20 (s, H-2″, 6″), 7.21 (s, H-3″, 5″), 7.17 (s, H-4″), 3.09 (dd, 14.0, 7.3, H-7″), 3.27 (m, H-7″), 4.60 (m, H-8″); ^{13}C-NMR (125 MHz, CD_3OD): 97.8 (C-1), 148.6 (C-3), 115.8 (C-4), 36.2 (C-5), 39.2 (C-6), 127.9 (C-7), 144.8 (C-8), 47.4 (C-9), 61.4 (C-10), 168.9 (C-11), 100.3 (C-1′), 74.9 (C-2′), 77.8 (C-3′), 71.6 (C-4′), 78.3 (C-5′), 62.7 (C-6′), 139.8 (C-1″), 130.7 (C-2″, 6″), 129.2 (C-3″, 5″), 127.4 (C-4″), 38.7 (C-7″), 56.7 (C-8″), 177.0 (C-9″). *Eucommia ulmoides* (Eucommiaceae).[45]

85. Eucomoside C



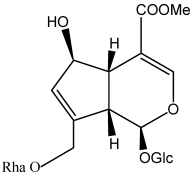
$C_{27}H_{32}N_2O_{11}$: 560.2006; white powder; $[\alpha]_D$ −13.1° (c=0.5, H_2O); ^{1}H-NMR (500 MHz, CD_3OD): 5.06 (d, 7.3, H-1), 7.11 (s, H-3), 3.13 (m, H-5), 1.63 (dd, 15.9, 7.9, H-6), 2.24 (dd, 15.3, 7.9, H-6), 5.58 (s, H-7), 2.67 (dd, 9.2, 9.2, H-9), 4.12 (d, 14.7, H-10), 4.29 (d, 14.7, H-10), 4.65 (d, 7.9, H-1′), 3.20 (m, H-2′), 3.37 (m, H-3′), 3.27 (m, H-4′, 5′), 3.63 (dd, 11.6, 5.5, H-6′), 3.84 (dd, 12.2, 1.8, H-6′), 7.09 (s, H-2″), 7.57 (d, 7.9, H-4″), 6.98 (dd, 7.9, 7.3, H-5″, 6″), 7.30 (d, 8.6, H-7″), 3.20 (m, H-10″), 3.43 (dd, 14.7, 4.3, H-10″), 4.61 (d, 6.7, H-11″); ^{13}C-NMR (125 MHz, CD_3OD): 97.7 (C-1), 150.2 (C-3), 115.5 (C-4), 36.0 (C-5), 38.8 (C-6), 127.9 (C-7), 144.7 (C-8), 47.4 (C-9), 61.3 (C-10), 169.9 (C-11), 100.3 (C-1′), 74.9 (C-2′), 77.9 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.7 (C-6′), 124.4 (C-2″), 111.8 (C-3″), 119.6 (C-4″), 119.8 (C-5″), 122.4 (C-6″), 112.2 (C-7″), 129.0 (C-8″), 138.1 (C-9″), 28.3 (C-10″), 57.5 (C-11″), 180.0 (C-12″). *Eucommia ulmoides* (Eucommiaceae).[45]

86. Hedycoryside B



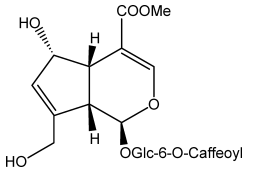
$C_{24}H_{28}O_{12}$: 508.1580; amorphous powder; $[\alpha]_D^{24}$ +7.5° (c=0.65, MeOH); UV (MeOH): 252 (4.20); IR (KBr): 3420, 2923, 1699, 1633, 1609, 1441, 1385, 1275, 1166, 1100, 1043, 758; ^{1}H-NMR (500 MHz, acetone-d_6): 5.25 (d, 7.5, H-1), 7.49 (br s, H-3), overlapped (H-5), 2.14 (dd, 16.5, 7.8, H-6), 2.87 (dd, 16.5, 7.8, H-6), 5.91 (br s, H-7), 2.83 (br t, 7.5, H-9), 5.08 (br d, 14.0, H-10), 4.93 (br d, 14.0, H-10), 3.69 (s, OMe), 4.77 (d, 7.8, H-1′), 3.29 (t, 8.6, H-2′), 3.47 (t, 8.6, H-3′), 3.40 (t, 8.6, H-4′), 3.38—3.36 (m, H-5′), 3.82 (dd, 11.9, 2.5, H-6′), 3.66 (dd, 11.9, 5.8, H-6′), 7.94 (d, 8.8, H-2″, 6″), 6.93 (d, 8.8, H-3″, 5″); ^{13}C-NMR (125 MHz, acetone-d_6): 97.9 (C-1), 152.5 (C-3), 112.1 (C-4), 35.9 (C-5), 39.5 (C-6), 130.2 (C-7), 139.7 (C-8), 47.3 (C-9), 63.2 (C-10), 168.0 (C-11), 51.4 (OMe), 100.5 (C-1′), 74.5 (C-2′), 77.6 (C-3′), 71.1 (C-4′), 77.8 (C-5′), 62.6 (C-6′), 122.1 (C-1″), 132.6 (C-2″, 6″), 116.1 (C-3″, 5″), 163.0 (C-4″), 166.7 (C-7″). *Hedyotis corymbosa* (Rubiaceae).[32]

87. Teneoside B



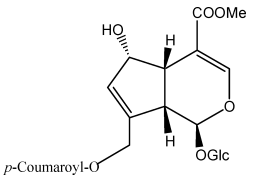
$C_{23}H_{34}O_{15}$: 550.1897; amorphous powder; $[\alpha]_D^{25}$ −132.5° (c=0.068, MeOH); UV (MeOH): 233 (4.48); IR (KBr): 3430, 1685, 1630, 1307, 1020; ^{1}H-NMR (500 MHz, D_2O): 5.38 (d, 5.1, H-1), 7.48 (d, 0.86, H-3), 3.21 (t, 6.3, H-5), 4.58 (t, 1.9, H-6), 5.81 (t, 1.8, H-7), 3.05 (m, H-9), 4.88 (s, H_2-10), 3.75 (s, OMe), 4.80 (d, 8.0, H-1′), 3.27 (dd, 9.1, 7.9, H-2′), 3.36 (t, 9.1, H-3′), 3.23 (t, 9.1, H-4′), 3.33 (m, H-5′), 3.65 (dd, 12.0, 6.7, H-6′), 3.94 (dd, 12.4, 2.2, H-6′), 5.10 (d, 1.7, H-1″), 3.86 (dd, 3.7, 2.0, H-2″), 3.81 (dd, 9.3, 3.7, H-3″), 3.52 (t, 9.5, H-4″), 3.91 (dd, 10.0, 6.2, H-5″), 1.21 (d, 6.2, H_3-6″); ^{13}C-NMR (125 MHz, D_2O): 98.7 (C-1), 153.8 (C-3), 112.5 (C-4), 43.5 (C-5), 81.8 (C-6), 133.5 (C-7), 147.8 (C-8), 48.5 (C-9), 71.8 (C-10), 172.1 (C-11), 54.4 (OMe), 102.2 (C-1′), 75.4 (C-2′), 79.6 (C-3′), 72.4 (C-4′), 78.8 (C-5′), 63.5 (C-6′), 102.1 (C-1″), 72.3 (C-2″, 3″), 73.8 (C-4″), 70.2 (C-5″), 18.0 (C-6″). *Hedyotis tenelliflora* (Rubiaceae).[46]

88. 6′-*O*-[(*E*)-Caffeoyl]-deacetylasperulosidic acid methyl ester



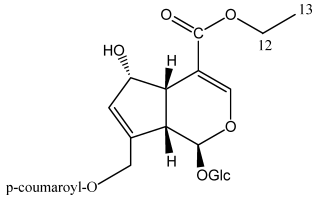
$C_{26}H_{30}O_{14}$: 566.1762; pale yellow powder; $[\alpha]_D$ −7.4° (c=0.25, MeOH); UV (MeOH): 324 (4.46), 234 (4.26); IR (KBr): 3426, 2924, 1693, 1632, 1522, 1441, 1384, 1279, 1162, 1077, 896, 787, 555; ^{1}H-NMR (500 MHz, CD_3OD): 5.00 (d, 8.9, H-1), 7.55 (s, H-3), 2.95—2.96 (m, H-5), 4.70 (d, 15.6, H-6), 2.61 (br d, 16.8, H-6), 5.95 (s, H-7), 2.56 (dd, 8.1, 8.1, H-9), 4.99 (dd, 9.0, 4.4, H-10), 4.77 (dd, 9.0, 4.4, H-10), 3.64 (s, OMe), 4.64 (d, 7.8, H-1′), 3.14—3.18 (m, H-2′, 3′, 4′), 3.30—3.31 (m, H-5′), 3.77 (dd, 12.3, 1.9, H-6′), 3.56 (dd, 12.3, 5.1, H-6′), 6.96 (d, 1.3, H-2″), 6.70 (d, 8.2, H-5″), 6.87 (dd, 8.2, 1.3, H-6″), 7.49 (d, 15.8, H-7″), 6.21 (d, 15.8, H-8″); ^{13}C-NMR (125 MHz, CD_3OD): 101.7 (C-1), 155.6 (C-3), 108.3 (C-4), 42.6 (C-5), 75.6 (C-6), 132.0 (C-7), 146.4 (C-8), 46.6 (C-9), 63.9 (C-10), 169.6 (C-11), 51.2 (OMe), 101.0 (C-1′), 75.2 (C-2′), 78.7 (C-3′), 71.7 (C-4′), 78.1 (C-5′), 63.2 (C-6′), 127.9 (C-1″), 115.5 (C-2″), 147.0 (C-3″), 149.9 (C-4″), 116.8 (C-5″), 123.3 (C-6″), 147.6 (C-7″), 115.1 (C-8″), 169.1 (C-9″). *Gardenia jasminoides* (Rubiaceae).[40]

89. 10-*O*-*p*-Coumaroyl-10-*O*-deacetyldaphylloside



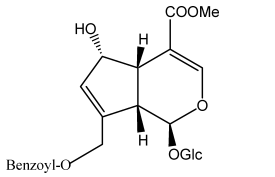
$C_{26}H_{30}O_{13}$: 550.1686; white powder; $[\alpha]_D^{20}$ +5.0° (c=0.23, MeOH); UV (MeOH): 316.5 (0.75), 225.8 (0.71); IR (KBr): 3427, 2922, 1695, 1633, 1604, 1516, 1440, 1275, 1169, 1076, 833, 519; ^{1}H-NMR (300 MHz, DMSO-d_6): 4.99 (d, 9.0, H-1), 7.63 (s, H-3), 2.91 (t, 6.6, H-5), 4.64 (br d, 6.0, H-6), 6.00 (br s, H-7), 2.55 (t, 7.8, H-9), 4.80 (br d, 15.3, H-10), 4.90 (br d, 15.3, H-10), 3.20 (OMe), 4.59 (d, 8.1, H-1′), 3.02—3.22 (m, H-2′, 3′, 4′, 5′), 3.43 (dd, 11.9, 4.8, H-6′), 3.64—3.66 (m, H-6′), 7.54—7.58 (m, H-2″, 6″), 6.79 (d, 9.0, H-3″, 5″), 7.58—7.62 (m, H-7″), 6.44 (d, 15.9, H-8″); ^{13}C-NMR (75 MHz, DMSO-d_6): 99.6 (C-1), 153.2 (C-3), 107.2 (C-4), 40.8 (C-5), 73.2 (C-6), 131.8 (C-7), 143.0 (C-8), 44.8 (C-9), 61.0 (C-10), 166.9 (C-11), 51.2 (OMe), 99.1 (C-1′), 73.4 (C-2′), 76.6 (C-3′), 69.9 (C-4′), 77.2 (C-5′), 62.0 (C-6′), 125.1 (C-1″), 130.5 (C-2″, 6″), 115.9 (C-3″, 5″), 160.1 (C-4″), 145.1 (C-7″), 113.9 (C-8″), 166.3 (C-9″). *Daphniphyllum angustifolium* (Daphniphyllaceae).[47]

90. 10-*O*-*p*-Coumaroyl-10-*O*-deacetyl-11-demethoxy-11-ethoxydaphylloside



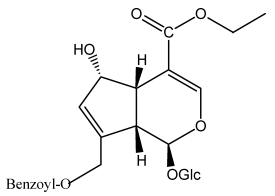
$C_{27}H_{32}O_{13}$: 564.1842; white powder; $[\alpha]_D^{20}$ −7.0° (c=0.24, MeOH); UV (MeOH): 316.2 (0.74), 225.0 (0.70); ^{1}H-NMR (300 MHz, CD_3OD): 5.09 (d, 9.0, H-1), 7.63 (s, H-3), 3.02 (t, 6.6, H-5), 4.78 (br d, 6.0, H-6), 6.03 (br s, H-7), 2.65 (t, 8.1, H-9), 4.78—4.82 (m, H-10), 5.08 (d, 15.3, H-10), 4.17 (q, 7.2, H_2-12), 1.27 (t, 7.2, H_3-13), 4.72 (d, 7.2, H-1′), 3.23—3.39 (m, H-2′, 3′, 4′, 5′), 3.57 (dd, 6.9, 2.0, H-6′), 3.84 (d, 12.0, H-6′), 7.45 (d, 9.0, H-2″, 6″), 6.78 (d, 9.0, H-3″, 5″), 7.63 (d, 16.2, H-7″), 6.35 (d, 16.2, H-8″); ^{13}C-NMR (75 MHz, CD_3OD): 101.5 (C-1), 155.4 (C-3), 108.5 (C-4), 42.6 (C-5), 75.0 (C-6), 131.8 (C-7), 146.3 (C-8), 48.3 (C-9), 61.4 (C-10), 169.0 (C-11), 63.8 (C-12), 14.7 (C-13), 100.8 (C-1′), 75.6 (C-2′), 77.9 (C-3′), 71.6 (C-4′), 78.7 (C-5′), 63.1 (C-6′), 127.1 (C-1″), 131.4 (C-2″, 6″), 117.1 (C-3″, 5″), 161.7 (C-4″), 147.2 (C-7″), 114.9 (C-8″), 168.9 (C-9″). *Daphniphyllum angustifolium* (Daphniphyllaceae).[47]

91. 10-*O*-Benzoyl-10-*O*-deacetyldaphylloside



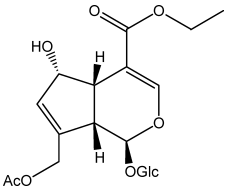
$C_{24}H_{28}O_{12}$: 508.1580; white powder; $[\alpha]_D^{20}$ +3.0° (c=0.09, MeOH); UV (MeOH): 232 (1.36), 202 (0.63); ^{1}H-NMR (300 MHz, DMSO-d_6): 5.14 (d, 5.1, H-1), 7.66 (s, H-3), 2.94 (t, 6.6, H-5), 4.74 (d, 6.0, H-6), 6.08 (s, H-7), 2.61 (t, 8.1, H-9), 4.99 (d, 15.3, H-10), 5.04 (d, 15.3, H-10), 3.35 (s, OMe), 4.59 (d, 7.5, H-1′), 2.98—3.19 (m, H-2′, 3′, 4′, 5′), 3.39—3.42 (m, H-6′), 3.60—3.64 (m, H-6′), 8.03 (d, 7.2, H-2″, 6″), 7.55 (t, 7.2, H-3″, 5″), 7.66 (t, 7.2, H-4″); ^{13}C-NMR (75 MHz, DMSO-d_6): 99.6 (C-1), 153.2 (C-3), 107.2 (C-4), 40.7 (C-5), 73.4 (C-6), 131.9 (C-7), 142.7 (C-8), 44.8 (C-9), 61.0 (C-10), 166.9 (C-11), 51.1 (OMe), 99.1 (C-1′), 73.4 (C-2′), 76.5 (C-3′), 69.9 (C-4′), 77.2 (C-5′), 62.8 (C-6′), 129.6 (C-1″), 129.4 (C-2″, 6″), 128.9 (C-3″, 5″), 133.5 (C-4″), 165.4 (C-7″). *Daphniphyllum angustifolium* (Daphniphyllaceae).[47]

92. 10-*O*-Benzoyl-10-*O*-deacetyl-11-demethoxy-11-ethoxydaphylloside



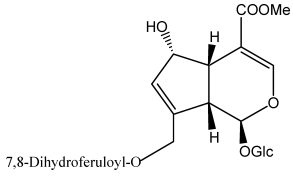
$C_{25}H_{30}O_{12}$: 522.1737; white powder; $[\alpha]_D^{20}$ −9.0° (c=0.16, MeOH); UV (MeOH): 231.8 (1.18), 204.0 (0.73); ^{1}H-NMR (300 MHz, CD_3OD): 5.10 (d, 9.0, H-1), 7.64 (d, 1.2, H-3), 3.07 (t, 6.6, H-5), 4.78—4.82 (m, H-6), 6.09 (br s, H-7), 2.68 (t, 8.1, H-9), 5.01 (br d, 15.3, H-10), 5.22 (br d, 15.3, H-10), 4.17 (q, H_2-12), 1.27 (t, 7.2, H_3-13), 4.73 (d, 7.2, H-1′), 3.23—3.40 (m, H-2′), 3.02—3.22 (m, H-3′, 4′, 5′), 3.60 (dd, 12.0, 5.4, H-6′), 3.86 (d, 12.0, H-6′), 8.04 (d, 7.2, H-2″, 6″), 7.48 (t, 7.2, H-3″, 5″), 7.60 (t, 7.2, H-4″); ^{13}C-NMR (75 MHz, CD_3OD): 101.5 (C-1), 155.4 (C-3), 108.5 (C-4), 42.6 (C-5), 75.0 (C-6), 131.4 (C-7), 146.1 (C-8), 46.6 (C-9), 61.4 (C-10), 169.1 (C-11), 64.4 (C-12), 14.7 (C-13), 100.8 (C-1′), 75.6 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 78.7 (C-5′), 63.1 (C-6′), 131.4 (C-1″), 130.8 (C-2″, 6″), 129.8 (C-3″, 5″), 134.6 (C-4″), 167.8 (C-7″). *Daphniphyllum angustifolium* (Daphniphyllaceae).[47]

93. 11-Demethoxy-11-ethoxydaphylloside



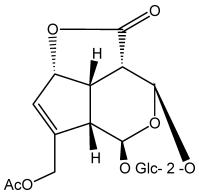
$C_{20}H_{28}O_{12}$: 460.1580; white powder; $[\alpha]_D^{20}$ −10.0° (c=0.20, MeOH); UV: 233 (0.53), 203 (0.46); ^{1}H-NMR (300 MHz, CD_3OD): 5.06 (d, 9.0, H-1), 7.65 (d, 1.2, H-3), 3.05 (t, 8.1, H-5), 4.77—4.87 (m, H-6), 6.02 (br s, H-7), 2.63 (t, 8.1, H-9), 4.77—4.87 (m, H-10), 4.94 (d, 15.3, H-10), 4.17 (q, 7.2, H_2-12), 1.27 (t, 7.2, H_3-13), 4.72 (d, 7.5, H-1′), 3.23—3.39 (m, H-2′, 3′, 4′, 5′), 3.61 (dd, 11.7, 5.7, H-6′), 3.84 (d, 11.7, H-6′), 2.08 (s, Ac); ^{13}C-NMR (75 MHz, CD_3OD): 101.4 (C-1), 155.3 (C-3), 108.5 (C-4), 42.5 (C-5), 75.0 (C-6), 131.9 (C-7), 146.0 (C-8), 46.3 (C-9), 61.4 (C-10), 172.6 (C-11), 63.9 (C-12), 14.7 (C-13), 100.7 (C-1′), 75.6 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 78.7 (C-5′), 63.1 (C-6′), 20.9, 169.0 (Ac). *Daphniphyllum angustifolium* (Daphniphyllaceae).[47]

94. 10-*O*-Dihydroferuloyl-10-*O*-deacetyldaphylloside



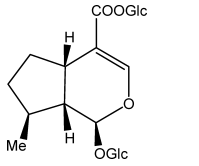
$C_{27}H_{34}O_{14}$: 582.1948; isolated as hexaacetate; white amorphous powder; UV (MeOH): 324 (3.20), 302 (3.04), 280 (3.32), 236 (3.96); IR (KBr): 1750, 1640, 1605, 1503, 1040, 908; ^{1}H-NMR (400 MHz, $CDCl_3$): 4.82 (d, 8.0, H-1), 7.52 (d, 1.0, H-3), 3.28 (dd, 8.0, 8.0, H-5), 5.56 (dd, 8.0, 2.0, H-6), 6.05 (d, 2.0, H-7), 2.85 (dd, 8.0, 8.0, H-9), 4.92 (br s, H_2-10), 3.73 (s, OMe), 4.97 (d, 8.0, H-1′), 4.98 (dd, 8.5, 8.0, H-2′), 5.24 (dd, 9.0, 8.5, H-3′), 5.08 (dd, 9.0, 9.0, H-4′), 3.76 (m, H-5′), 4.14 (dd, 12.5, 2.5, H-6′), 4.32 (dd, 12.5, 4.5, H-6′), 7.50 (d, 2.0, H-2″), 7.02 (d, 8.0, H-5″), 7.56 (dd, 8.0, 2.0, H-6″), 2.84 (t, 7.0, H-7″), 2.34 (t, 7.0, H-8″), 3.82 (s, MeO-3″), 1.96, 1.99, 2.06, 2.07, 2.08, 2.26 (each s, 6×Ac); ^{13}C-NMR (100 MHz, $CDCl_3$): 95.8 (C-1), 154.0 (C-3), 106.9 (C-4), 42.5 (C-5), 75.7 (C-6), 131.5 (C-7), 150.0 (C-8), 46.7 (C-9), 62.3 (C-10), 169.3 (C-11), 52.0 (OMe), 97.5 (C-1′), 70.6 (C-2′), 72.5 (C-3′), 68.2 (C-4′), 72.1 (C-5′), 61.7 (C-6′), 136.9 (C-1″), 112.2 (C-2″), 149.8 (C-3″), 147.7 (C-4″), 116.3 (C-5″), 122.2 (C-6″), 29.6 (C-7″), 38.5 (C-8″), 168.6 (C-9″), 56.2 (MeO-3″), 20.6×2, 20.7, 20.8, 20.9, 21.1, 169.4, 169.5, 169.6, 170.7, 171.3, 171.6 (6×Ac). *Wendlandia tinctoria* (Rubiaceae).[35]

95. Eucomoside A



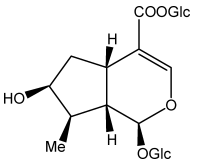
$C_{18}H_{22}O_{11}$: 414.1162; white powder; $[\alpha]_D$ +99.1° (c=0.1, MeOH); ^{1}H-NMR (500 MHz, C_5D_5N): 5.67 (d, 1.2, H-1), 5.87 (d, 2.4, H-3), 3.54 (dd, 12.8, 2.5, H-4), 3.72 (m, H-5), 5.90 (s, H-7), 3.30 (d, 8.5, H-9), 4.78 (d, 14.7, H-10), 4.85 (d, 14.7, H-10), 2.07 (s, OAc), 5.32 (d, 7.3, H-1′), 4.03 (m, H-2′), 4.29 (dd, 9.2, 8.6, H-3′), 4.23 (dd, 9.2, 9.2, H-4′), 4.03 (m, H-5′), 4.39 (dd, 11.6, 5.5, H-6′), 4.60 (dd, 12.2, 2.1, H-6′); ^{13}C-NMR (125 MHz, C_5D_5N): 91.9 (C-1), 95.8 (C-3), 38.3 (C-4), 35.3 (C-5), 86.9 (C-6), 129.3 (C-7), 143.7 (C-8), 45.5 (C-9), 61.0 (C-10), 178.5 (C-11), 20.5, 170.3 (OAc), 99.0 (C-1′), 80.3 (C-2′), 75.8 (C-3′), 71.2 (C-4′), 79.9 (C-5′), 62.6 (C-6′). *Eucommia ulmoides* (Eucommiaceae).[45]

96. 7-Deoxyloganic acid-β-D-glucopyranosyl ester



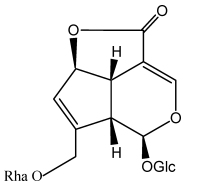
$C_{22}H_{34}O_{14}$: 522.1948; amorphous powder; $[\alpha]_D^{25}$ −37.8° (c=0.138, MeOH); UV (MeOH): 238 (4.0); ^{1}H-NMR (400 MHz, CD_3OD): 5.26 (d, 5.5, H-1), 7.51 (d, 1.1, H-3), 2.90 (m, H-5), 1.44 (m, H_α-6), 2.22 (m, H_β-6), 1.87 (m, H_α-7), 1.20 (m, H_β-7), 1.98 (m, H-8), 1.76 (m, H-9), 1.10 (d, 7.0, H_3-10), 4.67 (d, 8.0, H-1′), 3.20 (dd, 9.2, 8.0, H-2′), 3.65—3.70 (m, H_a-6′, 6″), 3.84 (dd, 11.7, 2.2, H_b-6′), 5.51 (d, 8.1, H-1″), 3.89 (dd, 11.7, 2.0, H_b-6″); ^{13}C-NMR (100 MHz, CD_3OD): 98.0 (C-1), 154.2 (C-3),112.3 (C-4), 35.1 (C-5), 33.2 (C-6), 34.2 (C-7), 36.5 (C-8), 49.6 (C-9), 20.8 (C-10), 167.7 (C-11), 100.2 (C-1′), 74.8 (C-2′), 78.1 (C-3′), 71.6 (C-4′), 78.8 (C-5′, 5″), 62.8 (C-6′), 95.4 (C-1″), 74.0 (C-2″), 78.4 (C-3″), 71.1 (C-4″), 62.3 (C-6″). *Hydrangea macrophylla* (Saxifragaceae).[48]

97. Loganic acid 11-O-β-glucopyranosyl ester



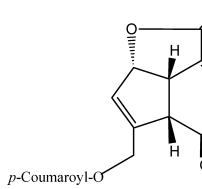
$C_{22}H_{34}O_{15}$: 538.1897; white amorphous powder; $[\alpha]_D^{28}$ −50.0° (c=0.1, MeOH); IR (KBr): 3427, 1719, 1640, 1288, 1076; ^{1}H-NMR (400 MHz, CD_3OD): 5.36 (d, 4.0, H-1), 7.60 (s, H-3), 3.09 (m, H-5), 1.88 (ddd, 14.0, 4.8, 2.4, H-6), 2.21 (ddd, 14.0, 8.0, 6.0, H-6), 4.16 (m, H-7), 1.75 (ddq, 13.6, 9.6, 6.8, H-8), 2.14 (ddd, 9.6, 4.0, 3.6, H-9), 1.10 (d, 6.8, H_3-10), 4.89 (d, 7.9, H-1′), 3.24 (m, H-2′), 3.49 (m, H-3′), 3.36—3.42 (m, H-4′, 5′), 3.93 (dd, 14.4, 6.0, H-6′), 3.73 (dd, 14.4, 4.4, H-6′), 5.51 (d, 8.0, H-1″), 3.36—3.42 (m, H-2″), 3.49 (m, H-3″), 3.36—3.42 (m, H-4″, 5″), 3.83 (dd, 12.0, 6.0, H-6″), 3.90 (dd, 12.0, 2.0, H-6″); ^{13}C-NMR (100 MHz, CD_3OD): 97.8 (C-1), 154.0 (C-3), 113.3 (C-4), 31.4 (C-5), 42.1 (C-6), 75.1 (C-7), 44.8 (C-8), 46.3 (C-9), 13.2 (C-10), 168.0 (C-11), 99.8 (C-1′), 75.1 (C-2′), 78.4 (C-3′), 71.2 (C-4′), 78.0 (C-5′), 62.3 (C-6′), 95.2 (C-1″), 74.3 (C-2″), 78.4 (C-3″), 70.7 (C-4″), 77.2 (C-5″), 62.0 (C-6″). *Gentiana rhodantha* (Gentianaceae).[49]

98. Teneoside A (10-O-(α-L-Rhamnopyranosyl) deacetylasperuloside)



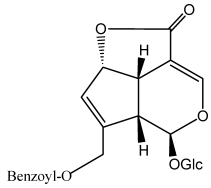
$C_{22}H_{30}O_{14}$: 518.1635; amorphous powder; $[\alpha]_D^{25}$ −156.5° (c=0.023, MeOH); UV (MeOH): 233 (4.23); IR (KBr): 3430, 2930, 1755, 1650, 1070; ^{1}H-NMR (500 MHz, D_2O): 5.82 (d, 1.8, H-1), 7.31 (d, 2.8, H-3), 3.55 (d, 3.6, H-5), 5.60 (m, H-6), 5.68 (m, H-7), 3.33 (m, H-9), 4.56 (s, H_2-10), 4.76 (d, 8.2, H-1′), 3.27 (dd, 9.3,7.9, H-2′), 3.40 (t, 9.1, H-3′), 3.25 (t, 9.1, H-4′), 3.34 (m, H-5′), 3.67 (dd, 11.9, 6.7, H-6′), 3.94 (dd, 11.9, 2.1, H-6′), 5.10 (d, 1.8, H-1″), 3.93 (dd, 3.5, 1.8, H-2″), 3.67 (dd, 9.5, 3.3, H-3″), 3.64 (t, 9.8, H-4″), 3.81 (dd, 10.5, 6.2, H-5″), 1.21 (d, 6.2, H_3-6″); ^{13}C-NMR (125 MHz, D_2O): 95.7 (C-1), 152.3 (C-3), 107.4 (C-4), 38.6 (C-5), 88.5 (C-6), 127.0 (C-7), 149.1 (C-8), 45.1 (C-9), 70.9 (C-10), 174.5 (C-11), 102.5 (C-1′), 75.8 (C-2′), 79.5 (C-3′), 71.9 (C-4′), 78.5 (C-5′), 63.6 (C-6′), 102.0 (C-1″), 72.1 (C-2″, 3″), 73.9 (C-4″), 70.3 (C-5″), 18.0 (C-6″). *Hedyotis tenelliflora* (Rubiaceae).[46]

99. 10-O-Coumaroyl-10-O-deacetylasperuloside



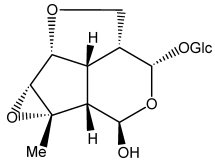
$C_{25}H_{26}O_{12}$: 518.1424; white powder; $[\alpha]_D^{20}$ −96.1° (c=0.60, MeOH); UV (MeOH): 312.5 (3.08), 222.8 (3.25); IR (KBr): 3411, 2923, 1739, 1656, 1604, 1516, 1261, 1168, 1074, 1020, 982, 833; ^{1}H-NMR (300 MHz, CD_3OD): 6.04 (br s, H-1), 7.29 (s, H-3), 3.33—3.40 (m, H-5), 5.55 (br d, 6.0, H-6), 5.77 (s, H-7), 3.22—3.27 (m, H-9), 4.76 (br d, 14.3, H-10), 4.89 (br d, 14.3, H-10), 4.72 (d, 7.8, H-1′), 3.30—3.47 (m, H-2′, 3′, 4′, 5′), 3.64 (dd, 12.0, 6.3, H-6′), 3.86 (d, 12.0, H-6′), 7.54 (d, 8.4, H-2″, 6″), 6.87 (d, 8.4, H-3″, 5″), 7.65 (d, 15.9, H-7″), 6.37 (d, 15.9, H-8″); ^{13}C-NMR (75 MHz, CD_3OD): 93.5 (C-1), 150.5 (C-3), 106.2 (C-4), 37.4 (C-5), 86.4 (C-6), 129.1 (C-7), 144.5 (C-8), 45.9 (C-9), 61.8 (C-10), 173.0 (C-11), 100.1 (C-1′), 74.7 (C-2′), 77.9 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.8 (C-6′), 127.1 (C-1″), 131.5 (C-2″, 6″), 117.0 (C-3″, 5″), 161.5 (C-4″), 147.4 (C-7″), 114.6 (C-8″), 168.6 (C-9″). *Daphniphyllum angustifolium* (Daphniphyllaceae).[47]

100. 10-O-Benzoyl-10-O-deacetylasperuloside



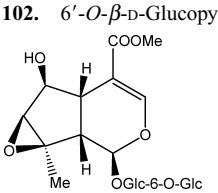
$C_{23}H_{24}O_{11}$: 476.1318; white powder; $[\alpha]_D^{20}$ −88.0° (c=0.07, MeOH); UV (MeOH): 231.0 (1.80), 202.5 (1.25); ^{1}H-NMR (300 MHz, CD_3OD): 6.06 (br s, H-1), 7.31 (d, 1.8, H-3), 3.29—3.32 (m, H-5), 5.58 (br d, 6.0, H-6), 5.82 (s, H-7), 3.17—3.21 (m, H-9), 4.90 (d, 13.8, H-10), 5.03 (d, 13.8, H-10), 4.68 (d, 8.1, H-1′), 3.18—3.40 (m, H-2′, 3′, 4′, 5′), 3.71 (d, 12.0, H-6′), 3.86 (d, 12.0, H-6′), 8.03 (d, 7.2, H-2″, 6″), 7.49 (t, 7.2, H-3″, 5″), 7.61 (t, 7.2, H-4″); ^{13}C-NMR (75 MHz, CD_3OD): 93.6 (C-1), 150.4 (C-3), 106.4 (C-4), 37.6 (C-5), 86.4 (C-6), 129.5 (C-7), 144.4 (C-8), 45.6 (C-9), 62.7 (C-10), 172.7 (C-11), 100.2 (C-1′), 74.7 (C-2′), 77.9 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.8 (C-6′), 131.0 (C-1″), 130.8 (C-2″, 6″), 129.8 (C-3″, 5″), 134.7 (C-4″), 167.5 (C-7″). *Daphniphyllum angustifolium* (Daphniphyllaceae).[47]

101. Wendoside



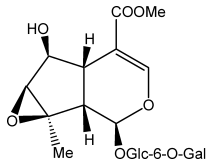
$C_{16}H_{24}O_{10}$: 376.1369; isolated as pentaacetate; white amorphous powder; IR (KBr): 1755, 2856, 1128; ^{1}H-NMR (400 MHz, $CDCl_3$): 5.30 (d, 2.5, H-1), 6.54 (br s, H-3), 2.32 (m, H-4), 3.06 (m, H-5), 5.04 (dd, 7.5, 1.2, H-6), 3.82 (br s, H-7), 2.62 (m, H-9), 1.23 (s, H_3-10), 3.84 (dd, 11.5, 4.5, H-11), 3.92 (dd, 11.5, 2.5, H-11), 4.73 (d, 7.5, H-1′), 5.22 (dd, 8.5, 7.5, H-2′), 5.24 (dd, 9.0, 8.5, H-3′), 5.08 (dd, 9.0, 9.0, H-4′), 3.76 (m, H-5′), 4.12 (dd, 12.5, 2.5, H-6′), 4.24 (dd, 12.5, 4.5, H-6′), 2.02, 2.03, 2.04, 2.05, 2.07 (each s, 5×Ac); ^{13}C-NMR (100 MHz, $CDCl_3$): 101.3 (C-1), 103.1 (C-3), 31.8 (C-4), 54.3 (C-5), 85.7 (C-6), 56.4 (C-7), 77.5 (C-8), 53.8 (C-9), 29.2 (C-10), 72.0 (C-11), 103.1 (C-1′), 71.8 (C-2′), 73.0 (C-3′), 68.5 (C-4′), 72.0 (C-5′), 62.3 (C-6′), 20.6×2, 20.7×3, 169.3, 169.4×2, 170.4, 170.6 (5×Ac). *Wendlandia tinctoria* (Rubiaceae).[35]

102. 6′-O-β-D-Glucopyranosylphlorigidoside C



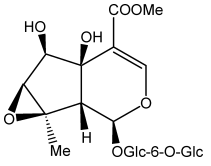
$C_{23}H_{34}O_{16}$: 566.1846; amorphous powder; $[\alpha]_D^{23}$ −53.9° (c=0.28, H_2O); UV: 239, 205; IR (KBr): 3415, 2897, 1668, 1637, 1443, 1313, 1078, 960, 657; ^{1}H-NMR (400 MHz, CD_3OD): 5.26 (d, 9.7, H-1), 7.53 (s, H-3), 2.66 (t-like, 7.8, H-5), 4.09 (dd, 7.8, 1.2, H-6), 3.39 (d, 1.2, H-7), 2.39 (dd, 9.7, 7.5, H-9), 1.54 (s, H_3-10), 3.73 (s, OMe), 4.78 (d, 8.0, H-1′), 3.23 (H-2′, 3″, 4″), 3.39 (H-3′), 3.20 (H-4′), 3.51—3.55 (m, H-5′), 3.68 (dd, 12.0, 4.2, H-6′), 4.18 (dd, 12.0, 1.8, H-6′), 4.34 (d, 7.7, H-1″), 3.64 (dd, 11.8, 5.7, H-6″), 3.86 (dd, 11.8, 2.3, H-6″); ^{13}C-NMR (100 MHz, CD_3OD): 97.4 (C-1), 154.7 (C-3), 109.0 (C-4), 38.9 (C-5), 79.7 (C-6), 65.5 (C-7), 63.5 (C-8), 45.6 (C-9), 18.5 (C-10), 171.4 (C-11), 52.7 (OMe), 100.8 (C-1′), 75.3 (C-2′), 78.4 (C-3′), 72.6 (C-4′), 78.3 (C-5′), 71.2 (C-6′), 106.2 (C-1″), 75.6 (C-2″), 78.7 (C-3″), 72.2 (C-4″), 78.6 (C-5″), 63.3 (C-6″). *Lamiophlomis rotata* (Labiatae).[50]

103. 6′-*O*-α-D-Galactopyranosylphlorigidoside C



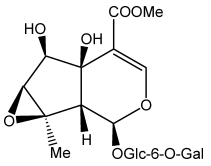
$C_{23}H_{34}O_{16}$: 566.1846; amorphous powder; $[\alpha]_D^{23}$ −1.8° (c=0.17, H_2O); UV: 239, 205; IR (KBr): 3421, 2920, 1637, 1443, 1313, 1078, 960, 557; ^{1}H-NMR (400 MHz, CD_3OD): 5.19 (d, 9.7, H-1), 7.54 (s, H-3), 2.66 (t-like, 7.4, H-5), 3.97 (dd, 7.4, 1.1, H-6), 3.36 (d, 1.1, H-7), 2.39 (dd, 9.7, 7.4, H-9), 1.55 (s, H_3-10), 3.73 (s, OMe), 4.77 (d, 7.9, H-1′), 3.26 (H-2′, 4′), 3.40 (H-3′), 3.51—3.55 (m, H-5′), 3.83 (H-6′), 3.80 (H-6′), 4.87 (d, 3.7, H-1″), 3.75 (H-2″), 3.70 (H-3″), 3.86 (H-4″), 3.82 (H-5″), 3.67 (H_2-6″); ^{13}C-NMR (100 MHz, CD_3OD): 97.6 (C-1), 154.7 (C-3), 109.1 (C-4), 39.0 (C-5), 80.0 (C-6), 65.1 (C-7), 63.5 (C-8), 45.6 (C-9), 18.5 (C-10), 171.3 (C-11), 52.8 (OMe), 101.0 (C-1′), 75.3 (C-2′), 78.5 (C-3′), 72.7 (C-4′), 77.3 (C-5′), 69.2 (C-6′), 100.8 (C-1″), 70.7 (C-2″), 72.1 (C-3″), 71.4 (C-4″), 73.0 (C-5″), 63.0 (C-6″). *Lamiophlomis rotata* (Labiatae).[50]

104. 6′-*O*-β-D-Glucopyranosylsesamoside



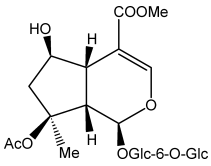
$C_{23}H_{34}O_{17}$: 582.1795; amorphous powder; $[\alpha]_D^{20}$ −62.0° (c=0.18, H_2O); UV: 234, 203; IR (KBr): 3415, 2918, 1720, 1635, 1387, 1313, 1082, 1034, 606; ^{1}H-NMR (400 MHz, CD_3OD): 5.43 (d, 9.3, H-1), 7.55 (s, H-3), 4.39 (d, 1.3, H-6), 3.51 (br s, H-7), 2.50 (d, 9.3, H-9), 1.52 (s, H_3-10), 3.73 (s, OMe), 4.73 (d, 7.9, H-1′), 3.34—3.20 (H-2′, 4′, 3″, 4″, 5″), 3.37 (t-like, 9.0, H-3′), 3.50—3.55 (m, H-5′), 4.19 (dd, 12.1, 1.7, H-6′), 3.69 (dd, 12.1, 5.2, H-6′), 4.33 (d, 7.6, H-1″), 3.16 (dd, 8.6, 7.6, H-2″), 3.64 (dd, 11.8, 5.7, H-6″), 3.86 (dd, 11.8, 1.9, H-6″); ^{13}C-NMR (100 MHz, CD_3OD): 97.8 (C-1), 155.7 (C-3), 113.3 (C-4), 75.1 (C-5), 78.0 (C-6), 66.3 (C-7), 63.9 (C-8), 54.7 (C-9), 18.3 (C-10), 169.5 (C-11), 52.5 (OMe), 100.6 (C-1′), 74.9 (C-2′), 78.1 (C-3′), 72.3 (C-4′), 78.0 (C-5′), 71.0 (C-6′), 106.0 (C-1″), 75.4 (C-2″), 78.5 (C-3″), 72.0 (C-4″), 78.4 (C-5″), 63.1 (C-6″). *Lamiophlomis rotata* (Labiatae).[50]

105. 6′-*O*-α-D-Galactopyranosylsesamoside



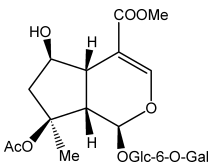
$C_{23}H_{34}O_{17}$: 582.1795; amorphous powder; $[\alpha]_D^{20}$ −9.0° (c=0.235, H_2O); UV: 233, 203; IR (KBr): 3415, 2926, 1686, 1635, 1406, 1313, 1209, 1151, 1082,1030; ^{1}H-NMR (400 MHz, CD_3OD): 5.39 (d, 8.8, H-1), 7.56 (s, H-3), 4.31 (d, 1.5, H-6), 3.48 (br s, H-7), 2.50 (d, 8.8, H-9), 1.51 (s, H_3-10), 3.73 (s, OMe), 4.72 (d, 7.9, H-1′), 3.25 (dd, 9.0, 7.9, H-2′), 3.37 (t-like, 9.0, H-3′), 3.29 (H-4′), 3.50—3.55 (m, H-5′), 3.83 (H-6′, 5″), 4.87 (d, 3.6, H-1″), 3.76 (H-2″), 3.70 (H-3″), 3.87 (H-4″), 3.67 (H_2-6″); ^{13}C-NMR (100 MHz, CD_3OD): 97.7 (C-1), 155.7 (C-3), 113.4 (C-4), 75.3 (C-5), 78.0 (C-6), 66.1 (C-7), 64.0 (C-8), 54.6 (C-9), 18.1 (C-10), 169.4 (C-11), 52.5 (OMe), 100.7 (C-1′), 74.9 (C-2′), 78.1 (C-3′), 72.3 (C-4′), 77.1 (C-5′), 68.8 (C-6′), 100.6 (C-1″), 70.6 (C-2″), 71.9 (C-3″), 71.2 (C-4″), 72.8 (C-5″), 62.9 (C-6″). *Lamiophlomis rotata* (Labiatae).[50]

106. 6′-*O*-β-D-Glucopyranosylbarlerin



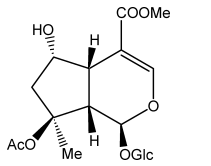
$C_{25}H_{38}O_{17}$: 610.2108; amorphous powder; $[\alpha]_D^{23}$ −74.0° (c=0.145, H_2O); UV: 236, 203; IR (KBr): 3412, 2924, 1707, 1639, 1441, 1383, 1292, 1188, 1082, 864, 611; ^{1}H-NMR (400 MHz, CD_3OD): 5.89 (d, 2.7, H-1), 7.43 (d, 1.2, H-3), 3.06 (br d, 8.8, H-5), 4.31 (m, H-6), 2.19 (br d, 14.9, H-7), 2.04 (dd, 14.9, 5.5, H-7), 2.96 (dd, 8.8, 2.7, H-9), 1.52 (s, H_3-10), 3.70 (s, OMe), 2.01 (s, Ac), 4.63 (d, 8.0, H-1′), 3.16 (dd, 9.0, 8.0, H-2′), 3.40 (t-like, 9.0, H-3′), 3.28 (H-4′, 4″), 3.49—3.53 (m, H-5′), 3.77 (dd, 11.8, 6.6, H-6′), 4.18 (dd, 11.8, 1.5, H-6′), 4.46 (d, 7.5, H-1″), 3.33 (H-3″, 5″), 3.87 (dd, 11.9, 2.1, H-6″), 3.66 (dd, 11.9, 5.5, H-6″); ^{13}C-NMR (100 MHz, CD_3OD): 95.9 (C-1), 154.1 (C-3), 110.4 (C-4), 43.0 (C-5), 76.6 (C-6), 48.1 (C-7), 90.2 (C-8), 50.1 (C-9), 22.9 (C-10), 169.6 (C-11), 52.3 (OMe), 22.7, 173.4 (Ac), 100.3 (C-1′), 75.1 (C-2′), 78.3 (C-3′), 72.2 (C-4′), 78.1 (C-5′), 70.5 (C-6′), 105.4 (C-1″), 75.8 (C-2″), 78.3 (C-3″), 72.2 (C-4″), 78.4 (C-5″), 63.3 (C-6″). *Lamiophlomis rotata* (Labiatae).[50]

107. 6′-*O*-α-D-Galactopyranosylbarlerin



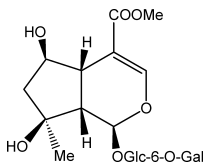
$C_{25}H_{38}O_{17}$: 610.2108; amorphous powder; $[\alpha]_D^{23}$ −26.0° (c=0.115, H_2O); UV: 236, 203; IR (KBr): 3412, 2929, 1707, 1639, 1439, 1377, 1292, 1188, 1086, 1024, 866, 615; ^{1}H-NMR (400 MHz, CD_3OD): 5.95 (d, 2.0, H-1), 7.43 (d, 1.1, H-3), 3.07 (br d, 8.8, H-5), 4.34 (m, H-6), 2.17 (br d, 15.0, H-7), 1.95 (dd, 15.0, 5.5, H-7), 2.99 (dd, 8.8, 2.0, H-9), 1.50 (s, H_3-10), 3.71 (s, OMe), 2.01 (s, Ac), 4.63 (d, 7.7, H-1′), 3.17 (dd, 9.0, 7.7, H-2′), 3.36 (t-like, 9.0, H-3′), 3.28 (t-like, 9.0, H-4′), 3.54—3.58 (m, H-5′), 3.89 (H-6′), 3.79 (H-6′), 4.91 (d, 3.5, H-1″), 3.76 (H-2″), 3.82 (H-3″), 3.93 (H-4″), 3.98 (H-5″), 3.73 (H_2-6″); ^{13}C-NMR (100 MHz, CD_3OD): 95.8 (C-1), 154.1 (C-3), 110.4 (C-4), 43.0 (C-5), 76.3 (C-6), 48.3 (C-7), 89.9 (C-8), 50.1 (C-9), 22.9 (C-10), 169.4 (C-11), 52.3 (OMe), 22.7, 173.1 (Ac), 100.2 (C-1′), 75.1 (C-2′), 78.7 (C-3′), 72.3 (C-4′), 77.2 (C-5′), 68.4 (C-6′), 100.7 (C-1″), 71.0 (C-2″), 72.1 (C-3″), 71.7 (C-4″), 72.8 (C-5″), 63.4 (C-6″). *Lamiophlomis rotata* (Labiatae).[50]

108. 6-*epi*-Barlerin



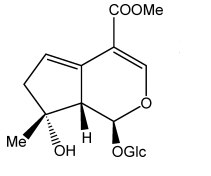
$C_{19}H_{28}O_{12}$: 448.1580; amorphous powder; ^{1}H-NMR (400 MHz, CD_3OD): 5.90 (d, 2.0, H-1), 7.40 (br s, H-3), 4.38 (dt, 4.5, 1.0, H-6), 1.48 (s, H_3-10), 3.67 (s, OMe), 4.64 (d, 8.0, H-1′), 3.66 (br d, 12.0, H-6′), 3.89 (br d, 12.0, H-6′), other protons (not assigned); ^{13}C-NMR (100 MHz, CD_3OD): 93.1 (C-1), 152.9 (C-3), 108.0 (C-4), 42.2 (C-5), 76.7 (C-6), 47.5 (C-7), 86.4 (C-8), 48.5 (C-9), 20.5 (C-10), 169.3 (C-11), 51.5 (OMe), 98.2 (C-1′), 72.8 (C-2′), 76.2 (C-3′), 69.9 (C-4′), 76.6 (C-5′), 60.8 (C-6′). *Mussaenda macrophylla* (Rubiaceae).[51]

109. 6′-*O*-α-D-Galactopyranosylshanzhiside methyl ester



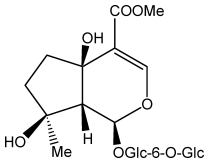
$C_{23}H_{36}O_{16}$: 568.2003; amorphous soild; $[\alpha]_D^{20}$ −29.0° (c=0.14, H_2O); UV: 237, 203; IR (KBr): 3408, 2929, 1691, 1641, 1439, 1383, 1309, 1084, 1057, 1020, 868, 579; ^{1}H-NMR (400 MHz, CD_3OD): 5.49 (d, 2.9, H-1), 7.39 (d, 1.0, H-3), 3.00 (dd, 10.0, 3.0, H-5), 4.03 (m, H-6), 1.98 (dd, 13.3, 6.4, H-7), 1.81 (dd, 13.3, 5.8, H-7), 2.60 (dd, 10.0, 2.9, H-9), 1.25 (s, H_3-10), 3.72 (s, OMe), 4.64 (d, 8.0, H-1′), 3.18 (dd, 8.8, 8.0, H-2′), 3.37 (t-like, 8.8, H-3′), 3.34 (H-4′), 3.50—3.55 (m, H-5′), 3.89 (H-6′, 5″), 3.79 (H-6′), 4.87 (d, 2.8, H-1″), 3.75 (H-2″, 3″), 3.91 (H-4″), 3.69 (H-6″); ^{13}C-NMR (100 MHz, CD_3OD): 95.5 (C-1), 153.1 (C-3), 111.8 (C-4), 41.9 (C-5), 77.8 (C-6), 49.5 (C-7), 79.4 (C-8), 52.1 (C-9), 25.0 (C-10), 170.0 (C-11), 52.2 (OMe), 100.3 (C-1′), 74.9 (C-2′), 78.4 (C-3′), 72.1 (C-4′), 77.0 (C-5′), 68.3 (C-6′), 100.5 (C-1″), 70.7 (C-2″), 71.9 (C-3″), 71.3 (C-4″), 72.7 (C-5″), 63.0 (C-6″). *Lamiophlomis rotata* (Labiatae).[50]

110. 5-Dehydro-8-*epi*-mussaenoside



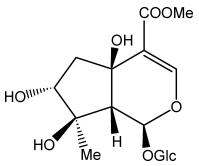
$C_{17}H_{24}O_{10}$: 388.1369; isolated as tetraacetate; amorphous powder; UV (MeOH): 280.6 (3.81), 235 (4.04); IR (KBr): 3475, 1751, 1640; ^{1}H-NMR (400 MHz, $CDCl_3$): 4.93 (d, 9.5, H-1), 7.43 (d, 1.0, H-3), 5.84 (br s, H-6), 1.95 (d, 18.0, H-7), 2.64 (d, 18.0, H-7), 3.42 (dd, 9.5, 3.0, H-9), 1.31 (s, H_3-10), 3.74 (s, OMe), 4.82 (d, 8.0, H-1′), 4.98 (dd, 8.5, 8.0, H-2′), 5.23 (dd, 9.5, 8.5, H-3′), 5.09 (dd, 8.5, 9.0, H-4′), 3.75 (ddd, 9.5, 4.5, 2.5, H-5′), 4.13 (dd, 12.5, 2.5, H-6′), 4.33 (dd, 12.5, 4.5 H-6′), 1.95, 2.01, 2.03, 2.40 (each s, 4×Ac); ^{13}C-NMR (100 MHz, $CDCl_3$): 93.0 (C-1), 153.3 (C-3), 111.1 (C-4), 137.1 (C-5), 132.2 (C-6), 38.3 (C-7), 78.3 (C-8), 46.2 (C-9), 24.7 (C-10), 168.6 (C-11), 52.5 (OMe), 96.3 (C-1′), 70.6 (C-2′), 72.5 (C-3′), 68.6 (C-4′), 74.3 (C-5′), 61.8 (C-6′), 20.5, 20.6, 20.7, 20.8, 169.1, 169.4, 170.1, 170.6 (4×Ac). *Wendlandia tinctoria* (Rubiaceae).[35]

111. Eriobioside (Ipolamiide 6′-*O*-*β*-glucopyranoside)



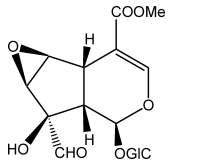
$C_{23}H_{36}O_{16}$: 568.2003; amorphous powder; $[\alpha]_D^{20}$ −70.0° (c=0.1, MeOH); UV (MeOH): 229 (3.30); ^{1}H-NMR (400 MHz, CD_3OD): 5.80 (s, H-1), 7.43 (s, H-3), 2.26 (ddd, 13.5, 8.2, 5.2, H-6), 2.09 (ddd, 14.3, 9.5, 7.9, H-6), 1.97 (dd, 12.2, 8.6, H-7), 1.56 (ddd, 12.2, 6.9, 5.2, H-7), 2.50 (s, H-9), 1.15 (s, H_3-10), 3.73 (s, OMe), 4.61 (d, 7.9, H-1′), 3.19 (t, 8.0, H-2′), 3.38 (overlapped, H-3′), 3.31 (overlapped, H-4′), 3.51 (overlapped, H-5′), 4.20 (dd, 11.8, 1.8, H-6′), 3.80 (dd, 11.8, 6.2, H-6′), 4.42 (d, 7.8, H-1″), 3.21 (t, 8.0, H-2″), 3.36 (overlapped, H-3″), 3.31 (overlapped, H-4″), 3.28 (overlapped, H-5″), 3.88 (d, 11.8, H-6″), 3.67 (dd, 11.8, 4.1, H-6″); ^{13}C-NMR (100 MHz, CD_3OD): 94.5 (C-1), 152.7 (C-3), 115.3 (C-4), 71.7 (C-5), 38.9 (C-6), 40.5 (C-7), 79.0 (C-8), 61.8 (C-9), 23.4 (C-10), 168.1 (C-11), 51.7 (OMe), 99.7 (C-1′), 74.4 (C-2′), 77.9 (C-3′), 71.8 (C-4′), 77.4 (C-5′), 69.9 (C-6′), 105.1 (C-1″), 74.4 (C-2″), 77.5 (C-3″), 71.9 (C-4″), 78.0 (C-5″), 62.8 (C-6″). *Lamium eriocephalum* ssp. *eriocephalum* (Lamiaceae).[52]

112. Lamerioside



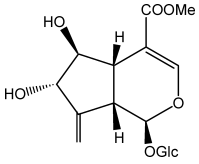
$C_{17}H_{26}O_{12}$: 422.1424; amorphous powder; $[\alpha]_D^{20}$ −170.0° (c=0.1, MeOH); UV (MeOH): 229 (3.50); ^{1}H-NMR (400 MHz, CD_3OD): 5.83 (s, H-1), 7.43 (s, H-3), 2.54 (dd, 14.8, 8.2, H-6), 1.81 (dd, 14.8, 11.2, H-6), 4.18 (dd, 11.1, 8.2, H-7), 2.50 (s, H-9), 1.03 (s, H_3-10), 3.75 (s, OMe), 4.61 (d, 7.9, H-1′), 3.19 (t, 9.1, H-2′), 3.38 (t, 8.9, H-3′), 3.33 (t, 8.9, H-4′), 3.36 (ddd, 8.9, 5.8, 2.0, H-5′), 3.90 (dd, 11.9, 2.0, H-6′), 3.67 (dd, 11.9, 5.8, H-6′); ^{13}C-NMR (100 MHz, CD_3OD): 93.5 (C-1), 152.1 (C-3), 116.0 (C-4), 66.3 (C-5), 47.0 (C-6), 78.4 (C-7), 79.8 (C-8), 59.0 (C-9), 15.9 (C-10), 168.0 (C-11), 51.7 (OMe), 99.6 (C-1′), 74.5 (C-2′), 77.5 (C-3′), 71.8 (C-4′), 77.9 (C-5′), 62.9 (C-6′). *Lamium eriocephalum* ssp. *eriocephalum* (Lamiaceae).[52]

113. Tudoside



$C_{18}H_{23}O_{13}$: 450.1373; viscous oil; $[\alpha]_D^{20}$ −172.5° (c=0.030, MeOH); ^{1}H-NMR (400 MHz, acetone-d_6): 5.73 (s, H-1), 7.31 (d, 1.9, H-3), 3.30 (m, H-5), 3.39 (d, 3.0, H-6), 3.95 (d, 2.6, H-7), 2.43 (dd, 8.2, 1.3, H-9), 9.59 (s, H-10), 3.71 (s, OMe), 4.58 (d, 7.7, H-1′), 3.15 (dd, 8.0, 8.0, H-2′), 3.34 (dd, 8.0, 8.0, H-4′), 3.59 (m, H-5′), 3.85 (dd, 12.1, 2.0, H-6′), 3.59 (m, H-6′); ^{13}C-NMR (100 MHz, CD_3OD): (exists as hemiacetal mixture in CD_3OD) 94.6 (C-1), 154.7 (C-3), 107.4 (C-4), 33.7 (C-5), 60.8 (C-6), 58.7 (C-7), 82.1 (C-8), 46.8 (C-9), 98.4 (C-10), 168.7 (C-11), 100.1 (C-1′), 74.6 (C-2′), 77.9 (C-3′), 71.6 (C-4′), 78.3 (C-5′), 62.8 (C-6′), 51.8 (OMe), 54.2 (OCD_3). *Pentas lanceolata* (Rubiaceae).[53]

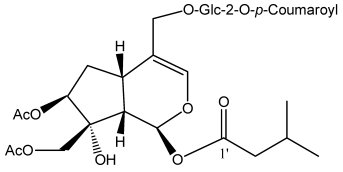
114. 6*β*-Hydroxy-7-epigardoside methyl ester



$C_{17}H_{24}O_{11}$: 404.1318; amorphous powder; $[\alpha]_D^{28}$ −17.5° (c=0.032, MeOH); UV (MeOH): 236 (3.01); IR (KBr); 3400, 2925, 1692, 1638, 1235, 1156, 947, 840; ^{1}H-NMR (500 MHz, DMSO-d_6): 5.61 (d, 2.0, H-1), 7.34 (d, 1.0, H-3), 2.81 (br d, 8.0, H-5), 4.08 (br s, H-6), 4.02 (br s, H-7), 3.12—3.15 (m, H-9), 5.21 (d, 2.5, H_2-10) , 3.64 (s, MeO), 4.41 (d, 8.5, H-1′), 2.94 (t, 8.5, H-2′), 3.12—3.15 (m, H-3′), 3.03 (t, 8.5, H-4′), 3.13—3.16 (m, H-5′), 3.44 (dd, 11.5, 6.0, H-6′), 3.68 (dd, 11.5, 5.0, H-6′); ^{13}C-NMR (125 MHz, DMSO-d_6): 95.0 (C-1), 152.2 (C-3), 107.9 (C-4), 35.5 (C-5), 73.7 (C-6), 73.5 (C-7), 150.4 (C-8), 41.8 (C-9) 110.0 (C-10), 166.3 (C-11), 50.9 (OMe), 98.4 (C-1′), 72.9 (C-2′), 76.6 (C-3′), 70.0 (C-4′), 77.2 (C-5′), 61.0 (C-6′). *Alibertia edulis* (Rubiaceae).[54]

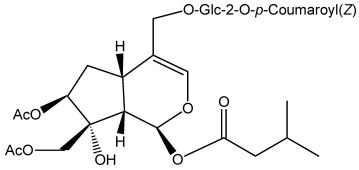
Group 3b (Iridoid glycosides with 10-carbon skeleton, valeriana type)

115. Viburtinoside A (7-*O*-Acetylviburtinoside II)



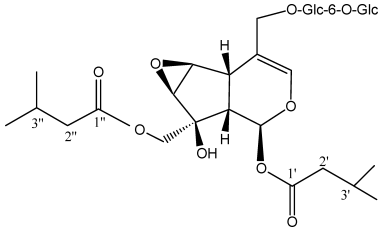
$C_{34}H_{44}O_{16}$: 708.2629; creamy white amorphous powder; $[\alpha]_D$ −59.0° (c=0.26, MeOH); UV (MeOH): 309 (4.00), 297 (3.90), 225 (3.70); IR (KBr): 3405, 1733, 1700, 1630, 1600, 1515, 1240, 830; ^{1}H-NMR (300 MHz, acetone-d_6): 6.17 (d, 5.4, H-1), 6.37 (br s, H-3), 2.95 (br q, H-5), 2.06 (m, H-6), 5.07 (t like, 3.6, H-7), 2.42 (dd, 9.9, 5.4, H-9), 4.16 (br d, 11.3, H_2-10), 4.07 (dd, 12.5, 1.3, H_2-11), 2.23 (d, 7.0, H_2-2′), 2.10 (m, H-3′), 0.95 (d, 6.0, H_3-4′, 5′), 4.62 (d, 8.1, H-1″), 4.87 (dd, 9.3, 8.1, H-2″), 3.53 (t-like, 9.3, H-3″), 3.42—3.29 (m, H-4″, 5″), 3.85 (br d, 12.9, H-6″), 3.70 (br dd, 12.5, 5.1, H-6″), 7.55 (d, 8.7, H-2‴, 6‴), 6.90 (d, 8.7, H-3‴, 5‴), 7.63 (d, 15.9, H-7‴), 6.40 (d, 15.9, H-8‴), 1.95, 1.89 (each s, 2×Ac); ^{13}C-NMR (75 MHz, acetone-d_6): 90.3 (C-1), 139.8 (C-3), 115.4 (C-4), 32.7 (C-5), 35.6 (C-6), 80.3 (C-7), 81.6 (C-8), 45.1 (C-9), 67.2 (C-10), 68.7 (C-11), 171.2 (C-1′), 43.6 (C-2′), 26.0 (C-3′), 22.4 (C-4′, 5′), 100.5 (C-1″), 74.7 (C-2″), 76.0 (C-3″), 71.8 (C-4″), 77.2 (C-5″), 62.8 (C-6″), 126.8 (C-1‴), 130.8 (C-2‴, 6‴), 116.5 (C-3‴, 5‴), 160.4 (C-4‴), 145.5 (C-7‴), 115.6 (C-8‴), 166.4 (C-9‴), 20.6, 20.5, 170.7, 170.1 (2×Ac). *Viburnum tinus* (Adoxaceae).[55]

116. Viburtinoside B



$C_{34}H_{44}O_{16}$: 708.2629; creamy-white amorphous powder; $[\alpha]_D$ −61.0° (c=0.23, MeOH); UV (MeOH): 311 (4.10), 299 (3.90), 226 (3.70); IR (KBr): 3400, 1735, 1705, 1625, 1600, 1510, 1235, 835; ^{1}H-NMR (300 MHz, acetone-d_6): 6.15 (d, 5.4, H-1), 6.35 (br s, H-3), 2.92 (br q, H-5), 2.03 (m, H-6), 5.01 (t-like, 3.6, H-7), 2.35 (dd, 9.9, 5.4, H-9), 4.14 (br d, 11.5, H_2-10), 4.07 (dd, 12.5, 1.2, H_2-11), 2.19 (d, 7.0, H-2′), 2.12 (m, H-3′), 0.93 (d, 6.0, H_3-4′, 5′), 4.56 (d, 8.1, H-1″), 4.85 (dd, 9.3, 8.1, H-2″), 3.50 (t-like, 9.1, H-3″), 3.40—3.27 (m, H-4″, 5″), 3.83 (br d,12.5, H-6″), 3.69 (br dd, 12.5, 5.1, H-6″), 7.76 (d, 8.7, H-2‴, 6‴), 6.82 (d, 8.7, H-3‴, 5‴), 6.88 (d, 12.9, H-7‴), 5.78 (d, 12.9, H-8‴), 1.98, 1.95 (each s, 2×Ac); ^{13}C-NMR (75 MHz, acetone-d_6): 90.3 (C-1), 139.7 (C-3), 115.3 (C-4), 32.9 (C-5), 35.8 (C-6), 80.2 (C-7), 81.6 (C-8), 45.1 (C-9), 67.2 (C-10), 68.7 (C-11), 171.3 (C-1′), 43.6 (C-2′), 26.0 (C-3′), 22.4 (C-4′, 5′), 100.5 (C-1″),74.7 (C-2″), 75.9 (C-3″), 71.8 (C-4″), 77.2 (C-5″), 62.8 (C-6″), 126.9 (C-1‴), 133.6 (C-2‴, 6‴), 115.2 (C-3‴, 5‴), 159.6 (C-4‴), 144.2 (C-7‴), 114.7 (C-8‴), 166.4 (C-9‴), 20.5, 20.2, 170.2, 170.1 (2×Ac). *Viburnum tinus* (Adoxaceae).[55]

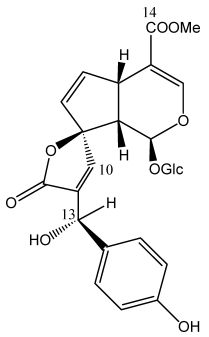
117. 10-Isovalerylkanokoside C



$C_{32}H_{60}O_{18}$: 722.2996; amorphous; $[\alpha]_D^{26}$ −68.5° (c=0.5, MeOH); UV (MeOH): 208.0; IR (film): 3421, 2959, 1738, 1675, 1635, 1372; ^{1}H-NMR (500 MHz, CD_3OD): 6.53 (s, H-1), 6.47 (d, 1.8, H-3), 3.13 (d, 7.8, H-5), 4.11 (d, 2.4, H-6), 3.37 (m, H-7), 2.14 (d, 7.8, H-9), 4.33 (d, 11.4, H_a-10), 4.27 (d, 11.4, H_b-10), 4.37 (d, 12.0, H_a-11), 4.26 (d,12.0, H_b-11), 4.42 (d, 7.8, H-1‴), 3.26 (dd, 9.0, 7.8, H-2‴), 3.31 (m, H-3‴), 3.34 (m, H-4‴), 3.50 (m, H-5‴), 3.81 (m, H_a-6‴), 4.19 (dd, 11.4, 6.6, H_b-6‴), 2.21 (dd, 7.2, 2.4, H-2′), 2.07 (m, H-3′), 0.97 (d, 6.6, H_3-4′, 5′), 2.31 (d, 7.2, H-2″), 2.12 (m, H-3″), 0.99 (d, 6.6, H_3-4″,5″), 4.40 (d, 7.8, H-1⁗), 3.26 (dd, 9.0, 7.8, H-2⁗), 3.39 (m, H-3⁗), 3.37 (m, H-4⁗),3.40 (m, H-5⁗), 3.71 (dd, 12.0, 5.4, H_a-6⁗), 3.90 (dd, 12.0, 6.0, H_b-6⁗); ^{13}C-NMR (125 MHz, CD_3OD): 90.1 (C-1), 142.8 (C-3), 108.8 (C-4), 35.4 (C-5), 59.8 (C-6), 60.3 (C-7), 78.4 (C-8), 43.9 (C-9), 69.4 (C-10), 69.5 (C-11), 172.8 (C-1′), 44.0 (C-2′), 26.7 (C-3′), 22.6 (C-4′, 4″), 22.7 (C-5′, 5″), 174.5 (C-1″), 44.0 (C-2″), 26.8 (C-3″), 101.9 (C-1‴), 75.0 (C-2‴), 77.9 (C-3‴), 71.6 (C-4‴), 77.0 (C-5‴), 70.0 (C-6‴), 105.0 (C-1⁗), 75.1 (C-2⁗), 78.0 (C-3⁗), 71.7 (C-4⁗), 78.0 (C-5⁗), 62.7 (C-6⁗). *Valeriana fauriei* (Valerianaceae).[22]

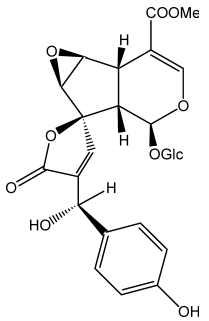
Group 3c (Iridoid glycosides with 10-carbon skeleton, plumeria type)

118. 13(*R*)-*epi*-Gaertneroside



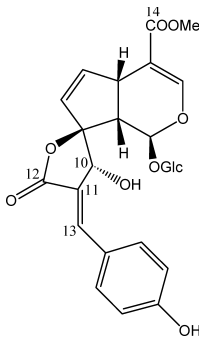
$C_{26}H_{28}O_{13}$: 548.1529; viscous oil; $[\alpha]_D^{20}$ −153.1° (c=0.095, MeOH); ^{1}H-NMR (400 MHz, CD_3OD): 5.34 (d, 3.7, H-1), 7.47 (d, 1.5, H-3), 3.88 (m, H-5), 6.45 (dd, 5.8, 2.6, H-6), 5.46 (dd, 5.5, 1.8, H-7), 2.99 (dd, 8.1, 3.6, H-9), 7.24 (d, 1.5, H-10), 5.39 (d, 1.1, H-13), 4.64 (d, 8.0, H-1′), 3.21 (dd, 9.2, 8.0, H-2′), 3.34 (m, H-3′), 3.27 (m, H-4′), 3.63 (H-6′), 3.73 (s, OMe), 7.20 (d, 8.4, H-2″, 6″), 6.76 (d, 8.8, H-3″, 5″); ^{13}C-NMR (100 MHz, CD_3OD): 93.8 (C-1), 152.2 (C-3), 111.4 (C-4), 39.9 (C-5), 141.0 (C-6), 130.2 (C-7), 97.9 (C-8), 50.6 (C-9), 150.6 (C-10), 137.9 (C-11), 172.5 (C-12), 69.5 (C-13), 168.4 (C-14), 99.8 (C-1′), 74.5 (C-2′), 77.8 (C-3′), 71.4 (C-4′), 78.5 (C-5′), 62.6 (C-6′), 51.9 (OMe), 133.3 (C-1″), 129.2 (C-2″, 6″), 116.2 (C-3″, 5″), 158.4 (C-4″). *Pentas lanceolata* (Rubiaceae).[53]

119. 13(*R*)-*epi*-Epoxygaertneroside



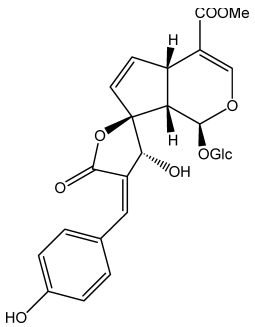
$C_{26}H_{28}O_{14}$: 564.1478; viscous oil; $[\alpha]_D^{20}$ −228.8° (c=0.032, MeOH); ^{1}H-NMR (400 MHz, CD_3OD): 5.33 (d, 1.4, H-1), 7.55 (d, 1.6, H-3), 3.45 (d, 8.1, H-5), 3.42 (m, H-6), 4.02 (d, 2.4, H-7), 2.77 (dd, 8.4, 1.1, H-9), 7.03 (d, 1.6, H-10), 5.39 (d, 1.4, H-13), 4.53 (d, 7.8, H-1′), 3.12 (dd, 8.9, 8.0, H-2′), 3.35 (m, H-3′), 3.30 (m, H-4′), 3.21 (m, H-5′), 3.85 (dd, 12.0, 2.0, H-6′), 3.70 (m, H-6′), 7.21 (d, 8.3, H-2″, 6″), 6.76 (d, 8.6, H-3″, 5″), 3.76 (s, OMe); ^{13}C-NMR (100 MHz, CD_3OD): 92.8 (C-1), 153.9 (C-3), 108.0 (C-4), 33.0 (C-5), 59.2 (C-6), 57.8 (C-7), 92.6 (C-8), 43.6 (C-9), 148.1 (C-10), 140.5 (C-11), 171.7 (C-12), 69.6 (C-13), 168.0 (C-14), 51.9 (OMe), 99.6 (C-1′), 74.4 (C-2′), 77.8 (C-3′), 71.3 (C-4′), 78.4 (C-5′), 62.5 (C-6′), 132.4 (C-1″), 129.3 (C-2″, 6″), 116.3 (C-3″, 5″), 158.6 (C-4″). *Pentas lanceolata* (Rubiaceae).[53]

120. (*E*)-Uenfoside



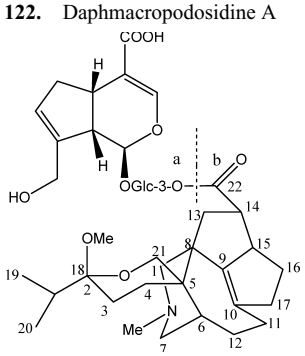
$C_{26}H_{28}O_{13}$: 548.1529; viscous oil (isolated as mixture with *Z*-isomer); $[\alpha]_D^{20}$ −185.4° (c=0.034, MeOH); ^{1}H-NMR (400 MHz, CD_3OD): 5.20 (d, 6.2, H-1), 7.46 (d, 1.9, H-3), 3.90 (m, H-5), 6.09 (dd, 5.8, 2.5, H-6), 6.45 (dd, 5.8, 2.3, H-7), 2.55 (dd, 7.0, 6.2, H-9), 5.57 (d, 1.1, H-10), 7.59 (s, H-13), 4.61 (d, 8.1, H-1′), 2.71 (dd, 8.9, 8.0, H-2′), 3.34 (m, H-3′), 3.30 (m, H-4′, 5′), 3.85 (m, H-6′), 3.70 (m, H-6′), 7.65 (d, 8.6, H-2″, 6″), 6.84 (d, 8.9, H-3″, 5″), 3.74 (s, OMe); ^{13}C-NMR (100 MHz, CD_3OD): 94.3 (C-1), 152.6 (C-3), 110.4 (C-4), 41.0 (C-5), 129.5 (C-6), 141.9 (C-7), 101.0 (C-8), 51.0 (C-9), 69.5 (C-10), 124.0 (C-11), 173.6 (C-12), 143.9 (C-13), 168.6 (C-14), 99.7 (C-1′), 74.2 (C-2′), 77.7 (C-3′), 71.3 (C-4′), 78.5 (C-5′), 62.6 (C-6′), 125.6 (C-1″), 134.9 (C-2″, 6″), 117.9 (C-3″, 5″), 164.1 (C-4″), 52.0 (OMe). *Pentas lanceolata* (Rubiaceae).[53]

121. (*Z*)-Uenfoside



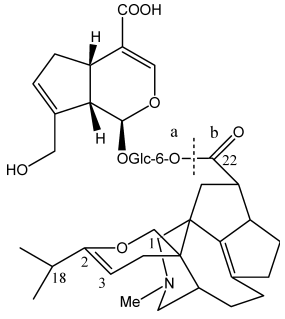
$C_{26}H_{28}O_{13}$: 548.1529; viscous oil (isolated as mixture with *E*-isomer); ^{1}H-NMR (400 MHz, CD_3OD): 5.45 (d, 5.6, H-1), 7.49 (d, 1.6, H-3), 3.85 (m, H-5), 5.87 (dd, 5.6, 2.4, H-6), 6.38 (dd, 5.8, 2.3, H-7), 2.77 (dd, 7.4, 5.8, H-9), 5.29 (d, 1.9, H-10), 7.06 (d, 1.9, H-13), 4.74 (d, 7.8, H-1′), 3.14 (dd, 9.6, 8.2, H-2′), 3.30 (H-3′-5′), 3.85 (H-6′), 3.70 (H-6′), 7.97 (d, 8.9, H-2″, 6″), 6.78 (d, 8.9, H-3″, 5″), 3.73 (s, OMe); ^{13}C-NMR (100 MHz,CD_3OD): 94.8 (C-1), 152.8 (C-3), 110.4 (C-4), 40.5 (C-5), 129.9 (C-6), 141.3 (C-7), 99.0 (C-8), 49.9 (C-9), 73.4 (C-10), 124.9 (C-11), 169.3 (C-12), 143.3 (C-13), 169.3 (C-14), 52.0 (OMe), 100.3 (C-1′), 74.6 (C-2′), 77.8 (C-3′), 71.4 (C-4′), 78.4 (C-5′), 62.5 (C-6′), 126.6 (C-1″), 135.0 (C-2″, 6″), 116.4 (C-3″, 5″), 161.8 (C-4″). *Pentas lanceolata* (Rubiaceae).[53]

122. Daphmacropodosidine A



$C_{40}H_{57}NO_{13}$: 759.3829; colorless crystals; mp 176—178 °C; $[\alpha]_D^{29.3}$ −43.5° (c=0.84, MeOH); UV (MeOH): 374.4 (2.42), 307.2 (2.73); IR (KBr): 3422, 2930, 1729, 1643, 1549, 1458, 1400, 1158, 1082, 1042; ^{1}H-NMR (500 MHz, CD_3OD): unit a: 5.05 (d, 7.5, H-1), 7.22 (s, H-3), 3.21 (m, H-5), 2.83 (m, H-6), 2.06 (m, H-6), 5.76 (s, H-7), 2.63 (m, H-9), 4.27 (d, 13.2, H-10), 4.16 (d, 13.2, H-10), 4.77 (d, 7.6, H-1′), 3.35 (m, H-2′), 4.95 (t, 7.0, H-3′), 3.46 (m, H-4′), 3.32 (m, H-5′), 3.84 (d, 12.0, H-6′), 3.66 (dd, 12.0, 5.1, H-6′); unit b: 2.55 (d, 10.8, H-1), 2.43 (d, 10.8, H-1), 1.73 (m, H-3), 1.35 (m, H-3), 1.96 (m, H-4), 1.58 (m, H-4), 2.31 (m, H-6), 2.90 (d, 12.4, H-7), 2.77 (overlapped, H-7), 2.11 (m, H-11), 1.65 (m, H-11), 2.45 (m, H-12), 2.27 (m, H-12), 2.76 (m, H-13), 1.68 (m, H-13), 3.00 (m, H-14), 3.55 (m, H-15), 1.83 (m, H-16), 1.73 (m, H-16), 2.57 (m, H-17), 2.33 (m, H-17), 2.04 (m, H-18), 0.84 (d, 6.9, H_3-19), 0.93 (d, 6.7, H_3-20), 4.06 (d, 12.4, H-21), 3.88 (d, 12.4, H-21), 3.17 (s, OMe), 2.34 (s, NMe); ^{13}C-NMR (125 MHz, CD_3OD): unit a: 97.8 (C-1), 148.7 (C-3), 118.5 (C- 4), 37.7 (C-5), 40.0 (C-6), 128.4 (C-7), 145.0 (C-8), 47.5 (C-9), 61.6 (C-10), 175.7 (C-11), 100.2 (C-1′), 73.2 (C-2′), 78.4 (C-3′), 69.7 (C-4′), 78.3 (C-5′), 62.2 (C-6′); unit b: 61.2 (C-1), 102.3 (C-2), 22.8 (C- 3), 23.2 (C-4), 37.7 (C-5), 34.1 (C-6), 56.7 (C-7), 47.3 (C-8), 146.5 (C-9), 135.4 (C-10), 27.8 (C-11, 12), 40.5 (C-13), 44.2 (C-14), 56.0 (C-15), 29.0 (C-16), 43.6 (C-17), 32.5 (C-18), 16.7 (C-19), 17.7 (C-20), 64.3 (C-21), 175.9 (C-22), 47.2 (OMe), 46.8 (NMe). *Daphniphyllum macropodum* (Daphniphyllaceae).[56]

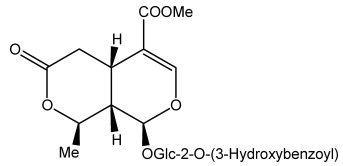
123. Daphmacropodosidine B



$C_{39}H_{53}NO_{12}$: 727.3567; white amorphous powder; $[\alpha]_D^{29.3}$ ±0° (*c*=0.26, MeOH); UV (MeOH): 377.8 (2.26), 308.6 (2.52); IR (KBr): 3425, 2927, 1735, 1641, 1549, 1452, 1397, 1169, 1146, 1086, 1044; ^{1}H-NMR (500 MHz, C_5D_5N): unit a: 5.68 (d, 7.3, H-1), 7.94 (s, H-3), 3.57 (m, H-5), 3.15 (m, H-6), 2.44 (m, H-6), 6.02 (s, H-7), 3.13 (m, H-9), 4.77 (d, 14.2, H-10), 4.65 (d, 14.2, H-10), 5.39 (d, 7.8, H-1′), 4.06 (m, H-2′), 4.25 (t, 8.9, H-3′), 3.99 (t, 8.9, H-4′), 4.09 (m, H-4′), 5.01 (d, 11.3, H-6′), 4.55 (dd, 11.3, 6.7, H-6′); unit b: 2.32 (d, 10.4, H-1), 2.01 (d, 10.4, H-1), 4.45 (br d, 4.2, H_2-3), 2.26 (dd, 16.8, 4.2, H-4), 1.88 (d, 16.8, H-4), 2.09 (m, H-6), 2.63 (d, 11.6, H-7), 2.46 (m, H-7), 2.64 (m, H-11), 2.40 (m, H-11), 1.97 (m, H-12), 1.62 (m, H-12), 2.47 (m, H-13), 1.54 (m, H-13), 2.95 (m, H-14), 3.53 (m, H-15), 1.96 (m, H-16), 1.56 (m, H-16), 2.48 (m, H-17), 2.36 (m, H-17), 2.33 (m, H-18), 1.08 (d, 6.8, H_3-19, 20), 4.72 (d, 11.6, H-21), 4.38 (d, 11.6, H-21), 2.11 (s, NMe); ^{13}C-NMR (125 MHz, C_5D_5N): unit a: 97.7 (C-1), 151.9 (C-3), 113.2 (C- 4), 36.2 (C-5), 39.6 (C-6), 127.2 (C-7), 145.6 (C-8), 47.0 (C-9), 61.0 (C-10), 169.8 (C-11), 100.7 (C-1′), 74.9 (C-2′), 78.2 (C-3′), 71.6 (C-4′), 75.8 (C-5′), 64.6 (C-6′); unit b: 64.4 (C-1), 159.6 (C-2), 91.2 (C- 3), 27.6 (C-4), 37.2 (C-5), 34.8 (C-6), 55.5 (C-7), 46.8 (C-8), 147.3 (C-9), 133.5 (C-10), 27.6 (C-11), 27.7 (C-12), 40.0 (C-13), 49.9 (C-14), 55.5 (C-15), 28.9 (C-16), 43.0 (C-17), 32.6 (C-18), 20.7 (C-19), 20.8 (C-20), 70.1 (C-21), 175.3 (C-22), 46.6 (NMe). *Daphniphyllum macropodum* (Daphniphyllaceae).[56)]

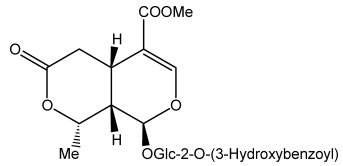
Group 3d (Rearranged iridoid glycosides: with 10-carbon skeleton)

124. 2′-*O*-(3″-Hydroxybenzoyl)-8-epikingiside



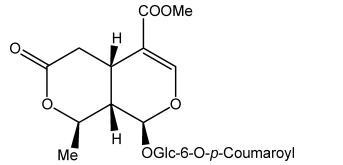
$C_{24}H_{28}O_{13}$: 524.1529; white amorphous powder; $[\alpha]_D^{26}$ −67.4° (*c*=0.7, MeOH); IR (KBr): 3429, 1716, 1636, 1453, 1287, 1104, 981, 754; ^{1}H-NMR (400 MHz, CD_3OD): 5.54 (d, 5.0, H-1), 7.25 (d, 1.2, H-3), 2.97 (br q, 6.9, H-5), 2.57 (dd, 16.9, 8.4, H-6), 2.83 (dd, 16.9, 6.3, H-6), 4.36 (dq, 8.2, 6.4, H-8), 2.09 (td, 7.9, 5.0, H-9), 1.46 (d, 6.4, H_3-10), 3.45 (s, OMe), 4.98 (d, 8.1, H-1′), 4.95 (dd, 8.1, 9.2, H-2′), 3.70 (dd, 9.2, 8.7, H-3′), 3.41 (dd, 8.7, 9.0, H-4′), 3.47 (m, H-5′), 3.97 (dd, 12.0, 1.9, H-6′), 3.72 (dd, 12.0, 4.5, H-6′), 7.39 (t, 2.4, H-2″), 7.03 (dd, 7.9, 2.4, H-4″), 7.27 (t, 7.9, H-5″), 7.48 (dd, 7.9, 2.4, H-6″); ^{13}C-NMR (100 MHz, CD_3OD): 95.4 (C-1), 153.2 (C-3), 110.6 (C-4), 26.5 (C-5), 33.8 (C-6), 174.4 (C-7), 75.8 (C-8), 42.4 (C-9), 20.8 (C-10), 167.7 (C-11), 51.8 (OMe), 98.3 (C-1′), 75.1 (C-2′), 75.8 (C-3′), 71.8 (C-4′), 78.7 (C-5′), 62.7 (C-6′), 134.4 (C-1″), 117.4 (C-2″), 158.6 (C-3″), 121.3 (C-4″), 130.5 (C-5″), 121.9 (C-6″), 167.1 (C-7″). *Gentiana rhodantha* (Gentianaceae).[49)]

125. 2′-*O*-(3″-Hydroxybenzoyl)-kingiside



$C_{24}H_{28}O_{13}$: 524.1529; white amorphous powder; $[\alpha]_D^{26}$ −86.6° (*c*=0.7,MeOH); IR (KBr): 3427, 1719, 1640, 1288, 1076; ^{1}H-NMR (400 MHz, CD_3OD): 5.70 (d, 2.9, H-1), 7.22 (s, H-3), 3.15 (dt, 8.5, 4.9, H-5), 2.73 (dd, 16.0, 4.5, H-6), 2.89 (dd, 16.0, 5.6, H-6), 4.70 (dq, 6.4, 6.4, H-8), 2.55 (ddd, 8.5, 6.4, 2.9, H-9), 1.46 (d, 6.7, H_3-10), 3.34 (s, OMe), 5.00 (d, 8.0, H-1′), 4.96 (dd, 8.0, 8.9, H-2′), 3.74 (t, 8.9, H-3′), 3.47 (dd, 8.7, 8.0, H-4′), 3.48 (m, H-5′), 3.99 (dd, 12.6, 1.0, H-6′), 3.75 (dd, 12.6, 5.4, H-6′), 7.42 (d, 2.0, H-2″), 7.07 (dd, 8.0, 2.0, H-4″), 7.31 (t, 8.0, H-5″), 7.49 (dd, 8.0, 2.0, H-6″); ^{13}C-NMR (100 MHz, CD_3OD): 93.8 (C-1), 153.7 (C-3), 111.6 (C-4), 26.4 (C-5), 33.7 (C-6), 175.0 (C-7), 75.6 (C-8), 39.8 (C-9), 17.2 (C-10), 167.2 (C-11), 51.7 (OMe), 97.4 (C-1′), 75.0 (C-2′), 75.2 (C-3′), 71.6 (C-4′), 78.3 (C-5′), 62.6 (C-6′), 132.2 (C-1″), 117.2 (C-2″), 158.5 (C-3″), 121.3 (C-4″), 130.5 (C-5″), 121.8 (C-6 ″), 166.8 (C-7″). *Gentiana rhodantha* (Gentianaceae).[49)]

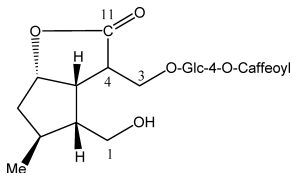
126. 6′-*O*-*p*-Coumaroyl-8-epikingiside



$C_{26}H_{30}O_{13}$: 550.1686; yellow amorphous powder; $[\alpha]_D^{26}$ −34.3° (*c*=1.8, MeOH); IR (KBr): 3421, 1707, 1604, 1514, 1441, 1279, 1167, 1077; ^{1}H-NMR (400 MHz, CD_3OD): 5.29 (d, 7.9, H-1), 7.51 (s, H-3), 2.98 (m, H-5), 2.29 (dd, 16.4, 8.5, H-6), 2.78 (dd, 16.4, 5.4, H-6), 4.34 (br q, 6.3, H-8), 2.07 (br q, 7.4, H-9), 1.41 (d, 6.3, H_3-10), 3.67 (s, OMe), 4.73 (d, 8.0, H-1′), 3.25 (dd, 8.7, 8.0, H-2′), 3.42 (dd, 8.7, 6.6, H-3′), 3.31 (m, H-4′), 3.56 (m, H-5′), 4.35 (dd, 12.0, 5.7, H-6′), 4.58 (dd, 12.0, 2.1, H-6′), 7.45 (d, 8.5, H-2″, 6″), 6.80 (d, 8.5, H-3″, 5″), 7.59 (d, 16.0, H-7″), 6.32 (d, 16.0, H-8″); ^{13}C-NMR (100 MHz, CD_3OD): 96.4 (C-1), 154.4 (C-3), 109.3 (C-4), 28.4 (C-5), 34.7 (C-6), 174.6 (C-7), 75.8 (C-8), 41.7 (C-9), 21.7 (C-10), 168.9 (C-11), 52.0 (OMe), 98.7 (C-1′), 74.6 (C-2′), 77.6 (C-3′), 71.5 (C-4′), 75.6 (C-5′), 63.6 (C-6′), 126.9 (C-1″), 131.3 (C-2″, 6″), 116.8 (C-3″, 5″), 161.3 (C-4″), 147.0 (C-7″), 114.8 (C-8″), 168.2 (C-9″). *Gentiana rhodantha* (Gentianaceae).[49)]

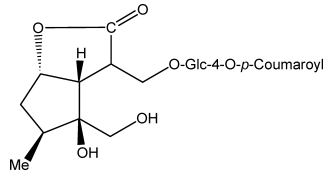
Group 4 (Secoiridoid glycosides)

127. Verbenabraside A



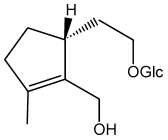
$C_{25}H_{32}O_{12}$: 524.1893; amorphous powder; $[\alpha]_D^{13}$ −86.1° (*c*=2.1, MeOH); ^{1}H-NMR (500 MHz, CD_3OD): 3.80 (dd, 11.0, 2.0, H_a-1), 3.57 (*ca.* H_b-1), 4.18 (dd, 9.5, 3.5, H_a-3), 3.91 (dd, 9.5, 4.5, H_b-3), 3.02 (m, H-4), 3.24 (m, H-5), 5.01 (br dd, 6.5, 6.5, H-6), 2.09 (br dd, 14.0, 5.5, H_a-7), 1.50 (m, H_b-7), 1.75 (*ca.* H-8), 1.77 (*ca.* H-9), 1.02 (d, H_3-10), 4.36 (d, 7.5, H-1′), 3.31 (*ca.* H-2′), 3.58 (*ca.* H-3′), 4.83 (*ca.* H-4′), 3.54 (*ca.* H-5′), 3.63 (*ca.* H_a-6′), 3.54 (*ca.* H_b-6′), 7.06 (s, H-2″), 6.79 (d, 8.0, H-5″), 6.96 (d, 8.0, H-6″), 7.60 (d, 16.0, H-7″), 6.30 (d, 16.0, H-8″), ^{13}C-NMR (125 MHz, CD_3OD): 61.5 (C-1), 70.8 (C-3), 43.7 (C-4), 46.1 (C-5), 85.4 (C-6), 42.8 (C-7), 34.1 (C-8), 52.6 (C-9), 17.7 (C-10), 180.9 (C-11), 104.6 (C-1′), 75.2 (C-2′), 75.8 (C-3′), 72.6 (C-4′), 76.3 (C-5′), 62.6 (C-6′), 127.8 (C-1″), 115.4 (C-2″), 146.9 (C-3″), 149.8 (C-4″), 116.7 (C-5″), 123.1 (C-6″), 147.7 (C-7″), 114.9 (C-8″), 168.7 (C-9″). *Verbena brasiliensis* (Verbenaceae).[57)]

128. Verbenabraside B



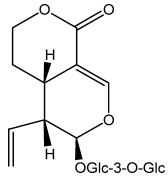
$C_{25}H_{32}O_{12}$: 524.1893; amorphous powder; $[\alpha]_D^{13}$ −39.0° (*c*=4.4, MeOH); ^{1}H-NMR (500 MHz, CD_3OD): 3.68 (d, 11.5, H_a-1), 3.61 (d, 11.5, H_b-1), 4.22 (dd, 10.0, 3.5, H_a-3), 3.97 (dd, 10.0, 5.0, H_b-3), 3.03 (ddd, 7.0, 5.0, 3.5, H-4), 3.13 (dd, 7.0, 6.5, H-5), 5.03 (br dd, 7.0, 6.5, H-6), 1.93 (*ca.* H_2-7), 2.01 (m, H-8), 0.95 (d, H_3-10), 4.38 (d, 8.0, H-1′), 3.31 (dd, 9.5, 8.0, H-2′), 3.65 (dd, 9.5, 9.5, H-3′), 4.85 (dd, 9.5, 9.5, H-4′), 3.53 (*ca.* H-5′), 3.66 (*ca.* H_a-6′), 3.56 (*ca.* H_b-6′), 7.47 (d, 8.5, H-2″, 6″), 6.82 (d, 8.5, H-3″, 5″), 7.67 (d, 16.0, H-7″), 6.36 (d, 16.0, H-8″), ^{13}C-NMR (125 MHz, CD_3OD): 65.3 (C-1), 70.3 (C-3), 44.9 (C-4), 54.2 (C-5), 84.6 (C-6), 39.8 (C-7), 37.3 (C-8), 84.3 (C-9), 11.9 (C-10), 180.5 (C-11), 104.5 (C-1′), 75.2 (C-2′), 75.8 (C-3′), 72.6 (C-4′), 76.3 (C-5′), 62.5 (C-6′), 127.2 (C-1″),131.3 (C-2″, 6″), 117.0 (C-3″, 5″), 147.3 (C-7″), 114.9 (C-8″), 168.6 (C-9″). *Verbena brasiliensis* (Verbenaceae).[57)]

129. Kankanoside D



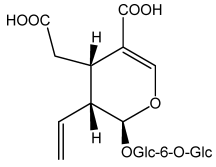
$C_{15}H_{26}O_7$: 318.1678; amorphous powder; $[\alpha]_D^{25}$ −30.6° (c=0.50, MeOH); IR (KBr): 3410, 2940, 1655, 1078; ^{1}H-NMR (500 MHz, CD_3OD): 4.04 (d, 12.2, H-1), 4.18 (d, 12.2, H-1), 3.56 (ddd, 13.2, 7.4, 2.8, H-3), 3.97 (ddd, 13.2, 8.0, 4.9, H-3), 1.41 (m, H-4), 2.06 (m, H-4), 2.90 (m, H-5), 1.51 (m, H_α-6), 2.01 (m, H_β-6), 2.23 (br dd, *ca.* 15.0, 8.0, H_α-7), 2.37 (br dd, *ca.* 15.0, 8.0, H_β-7), 1.69 (s, H_3-10), 4.25 (d, 7.7, H-1′), 3.16 (dd, 9.2, 7.7, H-2′), 3.34 (dd, 9.2, 8.9, H-3′), 3.26 (m, H-4′), 3.27 (m, H-5′), 3.66 (dd, 12.2, 5.2, H-6′), 3.86 (dd, 12.2, 1.8, H-6′). *Cistanche tubulosa* (Orobanchaceae).[25]

130. 3′-*O*-*β*-D-Glucopyranosylsweroside



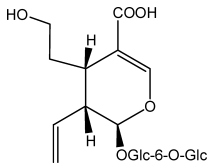
$C_{22}H_{32}O_{14}$: 520.1791; white amorphous powder; UV (MeOH): 242.6, 206.8; IR (KBr): 3404, 1697, 1616, 1072, 987; ^{1}H-NMR (500 MHz, CD_3OD) 5.49 (d, 1.5, H-1), 7.53 (s, H-3), 3.05—3.11 (m, H-5) , 1,61—1.74 (m, H_2-6), 3.83 (ddd, 10.0, 2.5, 1.5, H-7), 4.32 (ddd, 10.0, 9.0, 3.0, H-7), 5.49 (ddd, 20.5, 10.5, 5.5, H-8), 2.65 (br dd, 8.5, 5.5, H-9), 5.25 (d, 20.5, H-10), 5.22 (d, 10.5, H-10), 4.68 (d, 8.0, H-1′), 3.19—3.40 (H-2′), 4.38—4.41 (H-3′), 3.19—3.40 (H-4′, 5′), 3.51—3.65 (H_2-6′), 4.51 (d, 8.0, H-1″), 3.19—3.40 (H-2″—5″), 3.51—3.65 (H_2-6″); ^{13}C-NMR (125 MHz, CD_3OD): 98.1 (C-1), 154.0 (C-3), 105.2 (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), 168.5 (C-11), 99.5 (C-1′), 74.1 (C-2′), 87.3 (C-3′), 70.0 (C-4′), 77.8 (C-5′), 62.5 (C-6′), 106.0 (C-1″), 75.5 (C-2″), 78.1 (C-3″), 71.6 (C-4″), 78.2 (C-5″), 62.6 (C-6″). *Dipsacus asper*.[58]

131. 6′-*O*-*β*-Glucopyranosylsecologanoside



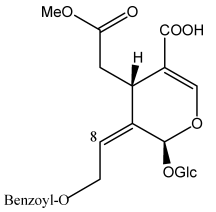
$C_{22}H_{32}O_{16}$: 552.1690; yellow amorphous powder; $[\alpha]_D^{26}$ −86.7° (c=1.8, MeOH); IR (KBr): 3425, 1639, 1074; ^{1}H-NMR (400 MHz, CD_3OD): 5.40 (d, 3.2, H-1), 7.20 (s, H-3), 3.24 (m, H-5), 2.14 (m, H-6), 2.85 (m, H-6), 5.73 (dt, 17.0, 9.6, H-8), 2.84 (m, H-9), 5.26 (dd, 15.0, 3.6, H-10), 5.31 (dd, 9.6, 3.6, H-10), 4.84 (d, 8.0, H-1′), 3.26 (m, H-2′), 3.61 (m, H-3′), 3.43—3.51 (m, H-4′, 5′), 4.41 (dd, 13.2, 4.8, H-6′), 3.84 (dd, 13.2, 2.0, H-6′), 4.48 (d, 7.2, H-1″), 3.26 (m, H-2″), 3.61 (m, H-3″), 3.43—3.51 (m, H-4″, 5″), 3.88 (dd, 12.5, 5.5, H-6″), 3.70 (dd, 12.5, 1.0, H-6″); ^{13}C-NMR (100 MHz, CD_3OD): 97.5 (C-1), 152.3 (C-3), 114.8 (C-4), 30.9 (C-5), 38.3 (C-6), 181.3 (C-7), 135.1 (C-8), 45.3 (C-9), 120.3 (C-10), 175.3 (C-11), 99.8 (C-1′), 74.8 (C-2′), 77.7 (C-3′), 71.3 (C-4′), 77.3 (C-5′), 69.8 (C-6′), 104.7 (C-1″), 74.3 (C-2″), 77.6 (C-3″), 71.4 (C-4″), 77.0 (C-5″), 62.4 (C-6″). *Gentiana rhodantha* (Gentianaceae).[49]

132. 6′-*O*-*β*-Glucopyranosylsecologanol



$C_{22}H_{34}O_{15}$: 538.1897; white amorphous powder; $[\alpha]_D^{26}$ −59.0° (c=0.5, MeOH); IR (KBr): 3425, 1639, 1074; ^{1}H-NMR (400 MHz, CD_3OD): 5.39 (d, 4.0, H-1), 7.27 (s, H-3), 3.23 (m, H-5), 1.85 (dt, 14.2, 6.5, H-6), 1.69 (ddd, 14.2, 8.7, 6.5, H-6), 4.17 (br d, 10.1, H-7), 5.67 (ddd, 17.0, 10.0, 9.5, H-8), 2.24 (ddd, 9.5, 6.8, 4.5, H-9), 5.29 (dd, 9.5, 4.0, H-10), 5.22 (dd, 14.0, 4.0, H-10), 4.79 (d, 7.6, H-1′), 3.25 (m, H-2′), 3.57 (m, H-3′), 3.32—3.48 (m, H-4′, 5′), 3.87 (dd, 12.0, 5.0, H-6′), 3.83 (dd, 12.0, 1.0, H-6′), 4.50 (d, 7.8, H-1″), 3.25 (m, H-2″), 3.57 (m, H-3″), 3.32—3.48 (m, H-4″, 5″), 3.89 (dd, 12.5, 5.5, H-6″), 3.70 (dd, 12.5, 1.0, H-6″); ^{13}C-NMR (100 MHz, CD_3OD): 97.6 (C-1), 150.3 (C-3), 111.8 (C-4), 29.7 (C-5), 33.5 (C-6), 62.2 (C-7), 134.4 (C-8), 45.0 (C-9), 120.8 (C-10), 169.5 (C-11), 99.6 (C-1′), 74.6 (C-2′), 77.7 (C-3′), 71.0 (C-4′), 77.3 (C-5′), 69.7 (C-6′), 104.4 (C-1″), 74.0 (C-2″), 77.5 (C-3″), 70.9 (C-4″), 77.1 (C-5″), 62.2 (C-6″). *Gentiana rhodantha* (Gentianaceae).[49]

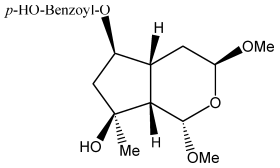
133. Alstonoside



$C_{24}H_{28}O_{13}$: 524.1529; colorless needles; mp 125—126 °C; $[\alpha]_D^{25}$ −176.0° (c=0.1, MeOH); UV (MeOH): 232 (3.88), 201 (2.45); ^{1}H-NMR (400 MHz, CD_3OD): 6.01 (s, H-1), 7.55 (s, H-3), 4.12 (dd, 10.0, 3.7, H-5), 2.56 (dd, 15.3, 10.0, H-6), 2.90 (dd, 15.3, 3.7, H-6), 6.25 (br t, 6.5, H-8), 5.11 (dd, 13.2, 6.5, H-10), 4.98 (overlapped, H-10), 4.83 (d, 7.7, H-1′), 3.32 (overlapped, H-2′, 4′), 3.38 (overlapped, H-3′), 3.40 (overlapped, H-5′), 3.68 (overlapped, H-6′), 3.88 (dd, 10.0, 1.5, H-6′), 8.02 (dd, 7.2, 1.3, H-2″, 6″), 7.46 (dd, 7.2, 1.2, H-3″, 5″), 7.60 (br t, 7.6, H-4″), 3.64 (br s, OMe); ^{13}C-NMR (100 MHz, CD_3OD): 94.2 (C-1), 154.9 (C-3), 109.4 (C-4), 32.5 (C-5), 40.7 (C-6), 173.4 (C-7), 124.1 (C-8), 131.5 (C-9), 62.6 (C-10), 169.6 (C-11), 100.9 (C-1′), 74.6 (C-2′), 78.5 (C-3′), 71.4 (C-4′), 77.9 (C-5′), 62.4 (C-6′), 134.6 (C-1″), 130.5 (C-2″, 6″), 129.6 (C-3″, 5″), 134.3 (C-4″), 167.8 (C-7″), 52.2 (OMe). *Alstonia scholaris* (Apocynaceae).[59]

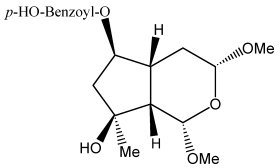
Group 5 (Iridoid aglycones and derivatives)

134. 5-Deoxy-8-deacetyl-3-*O*-methyl-6-*O*-*p*-hydroxybenzoyl-1,3-di-*epi*-clandonensine (Compound **1**)



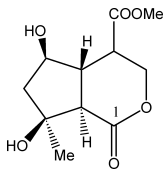
$C_{18}H_{24}O_7$: 352.1522; colorless amorphous solid; $[\alpha]_D^{25}$ −110.2° (c=0.033, MeOH); IR (KBr): 3550, 3400, 1708, 1656, 1607, 1511, 1260, 960; ^{1}H-NMR (400 MHz, CD_3OD): 4.76 (d, 3.9, H-1), 4.80 (dd, 7.1, 2.9, H-3), 1.98 (ddd, 14.1, 5.3, 2.9, H-4), 1.88 (dd, 14.1, 7.1, H-4), 2.96 (dddd, 14.1, 7.8, 7.5, 5.3, H-5),5.22 (ddd, 9.1, 7.5, 3.1, H-6), 2.45 (dd, 14.7, 9.1, H-7), 1.70 (ddd, 14.7, 3.1, 1.4, H-7), 2.27 (ddd, 7.8, 3.9, 1.4, H-9), 1.31 (s, H_3 -10), 7.79 (d, 8.8, H-2′, 6′), 6.71 (d, 8.8, H-3′, 5′); ^{13}C-NMR (100 MHz, CD_3OD): 100.1 (C-1), 96.5 (C-3), 31.1 (C-4), 40.7 (C-5), 81.7 (C-6), 48.3 (C-7), 49.0 (C-8), 53.3 (C-9), 23.8 (C-10), 55.7 (OMe-3), 56.0 (OMe-1), 122.5 (C-1′), 132.8 (C-2′, 6′), 116.1 (C-3′, 5′), 163.5 (C-4′), 168.1 (C-7′). *Tabebuia avellanedae* (Bignoniaceae).[60]

135. 5-Deoxy-8-deacetyl-3-*O*-methyl-6-*O*-*p*-hydroxybenzoyl-1-*epi*-clandonensine (Compound **2**) (C-3-epimer of **1**)



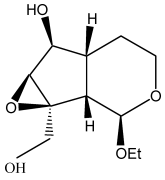
$C_{18}H_{24}O_7$: 352.1522; colorless amorphous solid; $[\alpha]_D^{25}$ −56.4° (c=0.035, MeOH), IR (KBr): 3550, 3400, 1708, 1656, 1607, 1511, 1260, 960; ^{1}H-NMR (400 MHz, CD_3OD): 4.70 (d, 5.5, H-1), 4.78 (dd, 5.6, 3.7, H-3), 1.60 (ddd, 14.7, 7.9, 5.6, H-4), 1.94 (m, H-4), 2.79 (ddd, 14.7, 7.7, 4.5, H-5), 5.22 (dd, 7.5, 4.5, H-6), 1.90 (m, H-7), 2.34 (dd, 14.9, 7.5, H-7), 2.14 (dd, 7.7, 5.5, H-9), 1.35 (s, H_3-10), 7.88 (d, 8.8, H-2′, 6′), 6.80 (d, 8.8, H-3′, 5′); ^{13}C-NMR (100 MHz, CD_3OD): 98.9 (C-1), 99.3 (C-3), 30.7 (C-4), 41.9 (C-5), 80.3 (C-6), 47.7 (C-7), 49.0 (C-8), 52.9 (C-9), 26.9 (C-10), 56.0 (OMe-1), 53.3 (MeO-3), 122.6 (C-1′), 132.6 (C-2′, 6′), 116.1 (C-3′, 5′), 163.5 (C-4′), 168.5 (C-7′). *Tabebuia avellanedae* (Bignoniaceae).[60]

136. Shanzhilactone



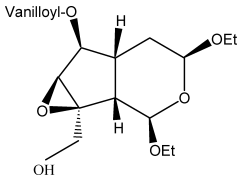
$C_{11}H_{16}O_6$: 244.0947; isolated as acetate; colorless needles; mp 182 °C; IR (KBr): 3420, 1755, 1730; ^{1}H-NMR (400 MHz, $CDCl_3$): 4.42 (dd, 12.5, 3.5, H-3), 4.37 (dd, 12.5, 9.5, H-3), 3.09 (ddd, 9.5, 6.5, 3.5, H-4), 3.16 (dd, 12.0, 6.5, H-5), 5.18 (dd, 6.5, 6.0, H-6), 2.25 (dd, 13.0, 6.5, H-7), 2.02 (dd, 13.0, 6.0, H-7), 3.34 (d, 9.5, H-9), 1.47 (s, H_3-10), 3.71 (s, OMe), 2.03 (s, OAc); ^{13}C-NMR (100 MHz, $CDCl_3$): 169.9 (C-1), 65.9 (C-3), 39.9 (C-4), 42.7 (C-5), 72.9 (C-6), 45.9 (C-7), 79.0 (C-8), 53.7 (C-9), 25.8 (C-10), 169.5 (C-11), 52.2 (OMe), 20.8, 170.0 (Ac). *Mussaenda incana* (Rubiaceae).[61]

137. Piscrocin E



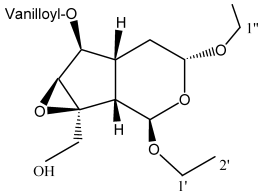
$C_{11}H_{18}O_5$: 230.1154; colorless oil; $[\alpha]_D^{20}$ −70.7° (c=0.03, MeOH); UV (MeOH): 205; IR (film): 3358, 2924, 1442, 1144, 1038; ^{1}H-NMR (300 MHz, CD_3OD): 4.24 (d, 9.0, H-1) 3.44 (dd, 12.7, 2.7, H-3), 3.84 (dd, 12.7, 7.8, H-3), 1.54 (br d, 14.1, H-4), 1.74 (m, H-4), 2.00 (m, H-5), 4.09 (br d, 9.0, H-6), 3.44 (br s, H-7), 2.14 (dd, 9.0, 7.5, H-9), 3.63 (d, 13.2, H-10), 3.92 (d, 13.2, H-10), 3.53 (dt, 7.1, 2.4, H-1′), 3.95 (m, H-1′), 1.21 (t, H_3-2′); ^{13}C-NMR (75 MHz, CD_3OD): 102.4 (C-1), 62.8 (C-3), 24.1 (C-4), 38.4 (C-5), 73.4 (C-6), 61.9 (C-7), 66.0 (C-8), 44.2 (C-9), 61.2 (C-10), 65.5 (C-1′), 15.5 (C-2″). *Neopicrorhiza scrophulariiflora* (Scrophulariaceae).[19]

138. Piscrocin F



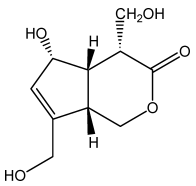
$C_{21}H_{28}O_9$: 424.1733; white amorphous powder; $[\alpha]_D^{20}$ −115.0° (c=0.02, MeOH); UV (MeOH): 205, 218, 264, 292; IR (KBr): 3357, 2974, 1710, 1597, 1515, 1285, 1030; ^{1}H-NMR (300 MHz, CD_3OD): 4.76 (d, 7.8, H-1), 4.99 (d, 3.4, H-3), 1.76 (br d, 14.7, H-4), 1.85 (m, H-4), 2.40 (m, H-5), 5.60 (dd, 9.1, 1.1, H-6), 3.75 (br s, H-7), 2.30 (t, 8.8, H-9), 3.72 (d, 13.1, H-10), 3.98 (d, 13.1, H-10), 3.59 (ddd, 14.2, 7.1, 2.2, H_a-1′), 3.79 (dd, 7.1, 2.5, H_b-1′), 1.25 (t, 7.1, H_3-2′), 3.49 (ddd, 14.1, 7.1, 2.6, H_a-1″), 3.96 (dd, 12.1, 2.2, H_b-1″), 1.22 (t, 7.1, H_3-2″), 7.55 (br s, H-2‴), 6.84 (d, 8.4, H-5‴), 7.56 (dd, 7.7, 2.2, H-6‴), 3.89 (s, OMe); ^{13}C-NMR (75 MHz, CD_3OD): 99.4 (C-1), 95.3 (C-3), 27.8 (C-4), 34.6 (C-5), 79.3 (C-6), 59.6 (C-7), 66.9 (C-8), 42.8 (C-9), 61.0 (C-10), 65.6 (C-1′), 15.6 (C-2′), 64.4 (C-1″), 15.4 (C-2″), 122.3 (C-1‴), 125.3 (C-2‴), 153.3 (C-3‴), 149.0 (C-4‴), 113.8 (C-5‴), 116.1 (C-6‴), 168.4 (C-7‴), 56.6 (OMe). *Neopicrorhiza scrophulariiflora* (Scrophulariaceae).[19]

139. Piscrocin G



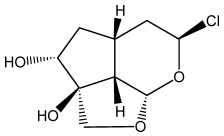
$C_{21}H_{28}O_9$: 424.1733; white amorphous powder; $[\alpha]_D$ −91.8° (c=0.03, MeOH); UV (MeOH): 205, 218, 264, 293; IR (KBr): 3358, 2975, 1711, 1604, 1524, 1240, 1042; ^{1}H-NMR (300 MHz, CD_3OD): 4.68 (d, 7.8, H-1), 4.82 (m, H-3), 1.64 (m, H-4), 1.81 (td, 16.2, 2.3, H-4), 2.42 (m, H-5), 5.36 (dd, 8.9, 1.1, H-6), 3.71 (br s, H-7), 2.34 (t, 7.8, H-9), 3.69 (d, 13.1, H-10), 3.99 (d, 13.1, H-10), 3.62 (dd, 7.1, 2.3, H-1′), 3.97 (dd, 7.1, 2.4, H-1′), 1.25 (t, 7.1, H_3-2′), 3.57 (dd, 7.1, 2.3, H-1″), 3.92 (dd, 7.1, 2.5, H-1″), 1.20 (t, 7.1, H_3-2″), 7.56 (br s, H-2‴), 6.85 (d, 8.1, H-5‴), 7.59 (dd, 8.0, 2.0, H-6‴), 3.90 (s, OMe); ^{13}C-NMR (75 MHz, CD_3OD): 100.0 (C-1), 98.7 (C-3), 29.8 (C-4), 36.4 (C-5), 77.5 (C-6), 59.9 (C-7), 66.7 (C-8), 43.9 (C-9), 60.9 (C-10), 65.5 (C-1′, 1″), 15.6 (C-2′, 2″), 122.2 (C-1‴), 125.4 (C-2‴), 153.4 (C-3‴), 149.0 (C-4‴), 113.8 (C-5‴), 116.1 (C-6‴), 168.4 (C-7‴), 56.6 (OMe). *Neopicrorhiza scrophulariiflora* (Scrophulariaceae).[19]

140. Morindacin



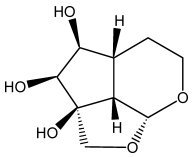
$C_{10}H_{14}O_5$: 214.0841; colorless syrup; $[\alpha]_D^{26}$ +2.0° (c=0.2, MeOH); IR (KBr): 3400, 1743, 1635, 1386, 1190, 1051; ^{1}H-NMR (400 MHz, CD_3OD): 3.79 (dd, 11.4, 4.5, H-1), 3.72 (dd, 11.4, 6.7, H-1), 2.96 (ddd, 6.0, 4.7, 3.7, H-4), 3.33 (dt, 7.7, 6.0, H-5), 5.40 (br d, 7.7, H-6), 5.84 (quin-like, H-7), 3.10 (m, H-9), 4.22 (ddd, 15.0, 2.4, 1.2, H-10), 4.16 (ddd, 15.0, 2.8, 1.7, H-10), 3.90 (dd, 10.8, 4.7, H-11), 3.84 (dd, 10.8, 3.7, H-11); ^{13}C-NMR (100 MHz, CD_3OD): 60.8 (C-1), 180.9 (C-3), 45.9 (C-4), 44.0 (C-5), 88.3 (C-6), 125.1 (C-7), 153.4 (C-8), 50.0 (C-9), 60.5 (C-10), 62.8 (C-11). *Morinda citrifolia* (Rubiaceae).[62]

141. Kankanol



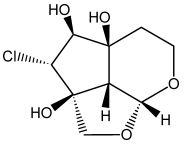
$C_9H_{13}ClO_4$: 220.0502; amorphous powder; $[\alpha]_D^{25}$ +11.1° (c=1.40, MeOH); IR (KBr): 3399, 3004, 1165, 1096, 1059, 1048, 955; ^{1}H-NMR (500 MHz, CD_3OD): 5.26 (d, 4.3, H-1), 5.17 (br d, *ca.* 3.0, H-3), 1.60 (ddd, 13.1, 5.5, 2.5, H_α-4), 1.80 (br dd, *ca.* 13.0, 3.0, H_β-4), 2.50 (m, H-5), 1.83 (br d, *ca.* 12.0, H_α-6), 2.57 (m, H_β-6), 3.80 (br s, H_β-7), 2.76 (dd, 8.0, 4.3, H-9), 3.75 (d, 9.2, H-10), 3.88 (d, 9.2, H-10), ^{13}C-NMR (125 MHz, CD_3OD): 98.1 (C-1), 95.7 (C-3), 34.3 (C-4), 26.1 (C-5), 42.3 (C-6), 79.6 (C-7), 92.7 (C-8), 54.9 (C-9), 71.5 (C-10). *Cistanche tubulosa* (Orobanchaceae).[25]

142. Piscrocin D



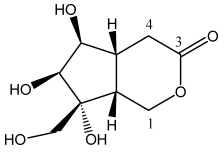
$C_9H_{14}O_5$: 202.0841; yellow amorphous powder, $[\alpha]_D^{20}$ +15.2° (c=0.1, MeOH); UV (MeOH): 205; IR (KBr): 3422, 2941, 1405, 1253, 1107, 1030; ^{1}H-NMR (300 MHz, CD_3OD): 5.29 (d, 5.9, H-1) 3.51 (ddd, 11.8, 5.1, 2.1, H_a-3), 3.92 (dd, 11.8, 2.7, H_b-3), 1.62 (br dd, 14.1, 2.0, H-4), 1.78 (m, H-4), 2.45 (m, H-5), 3.95 (dd, 8.5, 3.7, H-6) 3.70 (d, 3.7, H-7), 2.18 (dd, 10.3, 5.9, H-9), 3.62 (d, 10.1, H-10), 3.78 (d, 10.1, H-10); ^{13}C-NMR (75 MHz, CD_3OD): 101.9 (C-1), 56.4 (C-3), 22.3 (C-4), 37.1 (C-5), 74.1 (C-6), 79.4 (C-7), 85.8 (C-8), 46.8 (C-9), 75.4 (C-10). *Neopicrorhiza scrophulariiflora* (Scrophulariaceae).[19]

143. Myopochlorin



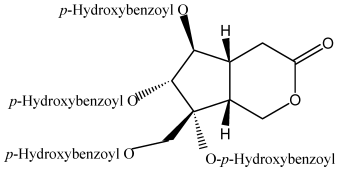
$C_9H_{12}{}^{35}ClO_5$: 235.0373; amorphous powder; $[\alpha]_D^{21}$ +71.9° (c=2.63, MeOH); IR (film): 3369, 2922, 1402, 1347, 1292, 1147, 1033; ^{1}H-NMR (400 MHz, CD_3OD): 5.41 (d, 6.0, H-1), 3.74 (ddd, 13.0, 13.0, 2.0, H-3), 3.66 (ddd, 13.0, 6.0, 2.0, H-3), 1.87 (ddd, 13.0, 2.0, 2.0, H-4), 1.62 (ddd, 13.0, 13.0, 6.0, H-4), 3.71 (d, 11.0, H-6), 4.53 (dd, 11.0, 2.0, H-7), 2.15 (d, 6.0, H-9), 4.46 (d, 10.0, H-10), 3.40 (dd, 10.0, 2.0, H-10); ^{13}C-NMR (100 MHz, CD_3OD): 102.3 (C-1), 58.5 (C-3), 32.0 (C-4), 73.1 (C-5), 76.8 (C-6), 72.4 (C-7), 84.3 (C-8), 55.7 (C-9), 72.2 (C-10). *Myoporum bontioides* (Myoporaceae).[23]

144. 6β,7β,8α,10-Tetrahydroxy-*cis*-2-oxabicyclo[4.3.0]nonan-3-one



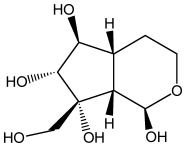
$C_9H_{14}O_6$: 218.0790; white needles; mp 164—165 °C; $[\alpha]_D^{25}$ 0.131 (c=0.45, $CHCl_3$); IR (KBr): 3381, 2927, 2855, 1713, 1466, 1380, 1095; ^{1}H-NMR (400 MHz, CD_3OD): 4.48 (dd, 12.0, 8.0, H-1), 4.33 (dd, 12.0, 6.8, H-1), 2.73 (dd, 14.4, 5.6, H-4), 2.58 (dd, 14.4, 8.0, H-4), 2.53 (dddd, 8.8, 8.0, 8.0, 5.6, H-5), 4.06 (dd, 8.0, 3.6, H-6), 3.76 (d, 3.6, H-7), 2.47 (ddd, 8.0, 8.8, 6.8, H-9), 3.73 (d, 11.2, H-10), 3.63 (d, 11.2, H-10); ^{13}C-NMR (100 MHz, CD_3OD): 68.2 (C-1), 176.3 (C-3), 33.8 (C-4), 41.0 (C-5), 79.4 (C-6), 79.9 (C-7), 82.6 (C-8), 41.2 (C-9), 66.2 (C-10). *Crescentia alata* (Bignoniaceae).[63]

145. 6β,7β,8α,10-Tetra-*p*-hydroxybenzoyl-*cis*-2-oxabicyclo[4.3.0]nonan-3-one



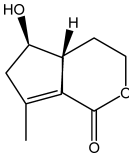
$C_{23}H_{22}O_{10}$: 458.1306; white amorphous powder; $[\alpha]_D^{25}$ +56.2° (c=0.83, $CHCl_3$); UV ($CHCl_3$): 385 (0.35), 272 (0.96), 251 (2.70); IR ($CHCl_3$): 3390, 2925, 2854, 1714, 1606, 1464, 1089; ^{1}H-NMR (400 MHz, $CDCl_3$): 4.70 (dd, 12.4, 6.4, H-1), 4.55 (dd, 12.4, 5.6, H-1), 2.91 (dd, 15.6, 6.8, H-4), 2.79 (dd, 15.6, 7.2, H-4), 3.16 (dddd, 11.6, 7.2, 6.8, 7.2, H-5), 5.50 (dd, 7.2, 4.4, H-6), 6.40 (d, 4.4, H-7), 3.33 (ddd, 11.6, 6.4, 5.6, H-9), 5.36 (d, 12.4, H-10), 5.10 (d, 12.4, H-10), 7.61 (d, 8.4, H-2′, 6′), 7.46 (d, 8.4, H-3′, 5′), 7.77 (d, 8.8, H-2″, 6″), 7.53 (d, 8.8, H-3″, 5″), 7.95 (d, 8.4, H-2‴, 6‴), 7.66 (d, 8.4, H-3‴, 5‴), 7.73 (d, 8.4, H-2⁗, 6⁗), 7.54 (d, 8.4, H-3⁗, 5⁗); ^{13}C-NMR (100 MHz, $CDCl_3$): 65.7 (C-1), 170.6 (C-3), 32.2 (C-4), 38.2 (C-5), 77.0 (C-6), 75.9 (C-7), 88.1 (C-8), 42.0 (C-9), 63.5 (C-10), 128.0 (C-1′), 131.0 (C-2′, 6′), 132.1 (C-3′, 5′), 129.1 (C-4′), 164.9 (C-7′), 127.7 (C-1″), 131.2 (C-2″, 6″), 132.1 (C-3″, 5″), 129.4 (C-4″), 164.4 (C-7″), 127.8 (C-1‴), 131.3 (C-2‴, 6‴), 132.4 (C-3‴, 5‴), 129.6 (C-4‴), 164.4 (C-7‴), 127.6 (C-1⁗), 131.5 (C-2⁗, 6⁗), 132.2 (C-3⁗, 5⁗), 129.0 (C-4⁗), 165.0 (C-7⁗). *Crescentia alata* (Bignoniaceae).[63]

146. 1β,6β,7α,8α,10-Pentahydroxy-*cis*-2-oxabicyclo[4.3.0]nonane



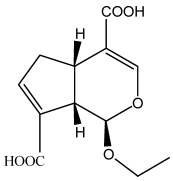
$C_9H_{16}O_6$: 220.0947; white amorphous powder; $[\alpha]_D^{25}$ +78.2° (c=0.11, $CHCl_3$); IR ($CHCl_3$): 3382, 2918, 2851, 1043; ^{1}H-NMR (400 MHz, $CDCl_3$): 5.40 (d, 5.2, H-1), 3.90 (ddd, 12.0, 12.0, 2.8, H-3), 3.63 (ddd, 12.0, 5.2, 2.0, H-3), 1.84 (dddd, 14.8, 12.0, 6.0, 1.2, H-4), 1.71 (dd, 14.8, 2.8, H-4), 2.28 (dddd, 10.0, 10.0, 6.0, 2.0, H-5), 3.99 (dd, 10.0, 10.0, H-6), 4.14 (dd, 10.0, 2.0, H-7), 2.42 (dd,10.0, 5.2, H-9), 4.49 (d, 10.4, H-10), 3.51 (dd, 10.4, 2.0, H-10); ^{13}C-NMR (100 MHz, $CDCl_3$): 100.1 (C-1), 55.8 (C-3), 21.1 (C-4), 35.2 (C-5), 75.6 (C-6), 73.6 (C-7), 85.0 (C-8), 44.3 (C-9), 72.4 (C-10). *Crescentia alata* (Bignoniaceae).[63]

147. 6β-Hydroxy-2-oxabicyclo[4.3.0]non-8-en-1-one



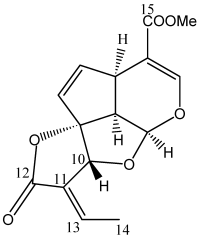
$C_9H_{12}O_3$: 168.0786; yellow oil; $[\alpha]_D^{25}$ +0.68° (c=0.06, $CHCl_3$); UV ($CHCl_3$): 246 (1.84); IR ($CHCl_3$): 3365, 1727, 1652, 1603, 1043; ^{1}H-NMR (400 MHz, $CDCl_3$): 4.43 (ddd, 11.2, 4.8, 2.8, H-3), 4.27 (ddd, 11.2, 12.0, 2.8, H-3), 1.67 (dddd, 13.6, 12.0, 12.0, 4.8, H-4), 2.20 (m, H-4), 2.87 (m, H-5), 4.20 (dt, 7.6, 8.8, H-6), 2.65 (ddd, 16.8, 8.0, 1.2, H-7), 2.54 (ddd, 16.8, 8.8, 1.6, H-7), 2.20 (s, H_3-10); ^{13}C-NMR (100 MHz, $CDCl_3$): 164.1 (C-1), 69.4 (C-3), 28.3 (C-4), 50.1 (C-5), 78.6 (C-6), 46.9 (C-7), 157.0 (C-8), 122.6 (C-9), 17.0 (C-10). *Crescentia alata* (Bignoniaceae).[63]

148. Tarennin (artifact)



$C_{12}H_{14}O_6$: 254.0790; amorphous powder; $[\alpha]_D^{23}$ +87.2° (c=0.45, MeOH); UV (MeOH): 342 (2.38), 325 (2.45); IR (KBr): 3431,1690, 1637, 1624, 1558, 1408, 1271, 1163, 1038, 743; ^{1}H-NMR (400 MHz, CD_3OD): 5.28 (d, 3.6, H-1), 7.40 (s, H-3), 3.21 (m, H-5), 2.83 (dd, 18.0, 7.8, H-6), 2.35 (d, 18.0, H-6), 6.57 (br s, H-7), 3.15 (br s, H-9), 3.82 (dq, 9.7, 7.1, H-1′), 3.59 (dq, 9.7, 7.1, H-1′), 1.18 (t, 7.1, H_3-2′); ^{13}C-NMR (100 MHz, CD_3OD): 100.3 (C-1), 152.9 (C-3), 113.6 (C-4), 34.8 (C-5), 40.1 (C-6), 142.0 (C-7), 140.4 (C-8), 48.4 (C-9), 171.4 (C-10), 172.0 (C-11), 65.8 (C-1′), 15.4 (C-2′). *Tarenna attenuata* (Rubiaceae).[36]

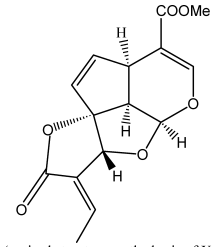
149. Plumericin



(revised structure on the basis of X-ray crystal study)

$C_{15}H_{14}O_6$: 290.0790; colorless crystals; mp 205—208 °C (dec); $[\alpha]_D^{20}$ +179.0° (c=14.6, $CHCl_3$); UV (MeCN): 237 sh (4.05), 213 sh (4.27), 200 (4.32); IR ($CHCl_3$): 1755, 1796, 1635, 1524; ^{1}H-NMR (500 MHz, $CDCl_3$): 5.55 (d, 6.0, H-1), 7.44 (s, H-3), 4.01 (td, 9.5, 6.0, H-5), 5.65 (dd, 5.5, 2.2, H-6), 6.05 (dd, 5.5, 2.2, H-7), 3.45 (dd, 9.5, 6.0, H-9), 5.11 (s, H-10), 7.15 (dq, 7.5, 1.5, H-13), 2.10 (d, 7.5, H_3-14), 3.75 (s, OMe); ^{13}C-NMR (125 MHz, $CDCl_3$): 102.3 (C-1), 152.3 (C-3), 104.6 (C-4), 38.4 (C-5), 126.3 (C-6), 141.1 (C-7), 109 (C-8), 53.7 (C-9), 80.3 (C-10), 127.4 (C-11), 168.2 (C-12), 145.6 (C-13), 16.2 (C-14), 166.6 (C-15), 51.7 (OMe). *Plumeria rubra*.[64] This revised structure was not in agreement with vibrational CD spectra.[65]

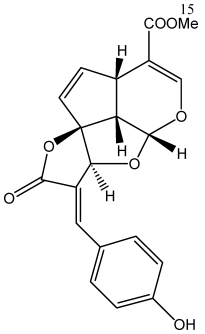
150. Isoplumericin



(revised structure on the basis of X-ray crystal study)

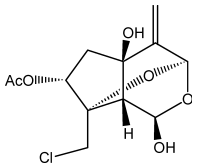
$C_{15}H_{14}O_6$: 290.0790; colorless crystals; mp 207—211 °C; $[\alpha]_D^{20}$ +179.0° (c=14.6, $CHCl_3$); UV (MeCN): 238 sh (4.07), 210 (4.30); ^{1}H-NMR (500 MHz, $CDCl_3$): 5.55 (d, 6.0, H-1), 7.44 (s, H-3), 4.01 (td, 9.5, 6.0, H-5), 5.65 (dd, 5.5, 2.2, H-6), 6.05 (dd, 5.5, 2.2, H-7), 3.45 (dd, 9.5, 6.0, H-9), 5.11 (s, H-10), 6.84 (dq, 7.5, 1.5, H-13), 2.35 (d, 6.5, H_3-14), 3.75 (s, OMe); ^{13}C-NMR (125 MHz, $CDCl_3$): 101.3 (C-1), 152.3 (C-3), 104.1 (C-4), 38.4 (C-5), 126.1 (C-6), 141.1 (C-7), 109.2 (C-8), 51.7 (C-9), 83.7 (C-10), 125.4 (C-11), 168.2 (C-12), 145.6 (C-13), 14.8 (C-14), 166.6 (C-15), 51.6 (OMe). *Plumeria rubra*.[64]

151. Prismatomerin



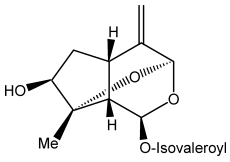
$C_{20}H_{16}O_7$: 368.0896; white needles; mp 134—135 °C, $[\alpha]_D^{25}$ −136.0° (c=0.01, EtOH); UV ($CDCl_3$): 317 (4.07); IR (KBr); 3512, 3123, 2962, 1732, 1696, 1644; ^{1}H-NMR (500 MHz, $CDCl_3$): 5.67 (d, 5.8, H-1), 7.50 (s, H-3), 4.08 (tt, 9.5, 2.0, H-5), 6.07 (dd, 5.4, 2.1, H-6), 5.67 (overlapped, H-7), 3.56 (dd, 9.5, 5.8, H-9), 5.25 (br s, H-10), 7.81 (br s, H-13), 3.81 (s, H-15), 7.71 (d, 8.6, H-2′, 6′), 6.97 (d, 8.6, H-3′, 5′), 5.73 (br s, HO-4′); ^{13}C-NMR (125 MHz,$CDCl_3$): 102.4 (C-1), 152.9 (C-3), 109.6 (C-4), 38.5 (C-5), 141.1 (C-6), 126.5 (C-7), 104.5 (C-8), 54.2 (C-9), 82.0 (C-10), 120.2 (C-11), 170.2 (C-12), 144.4 (C-13), 166.8 (C-14), 51.7 (OMe), 126.2 (C-1′), 133.3 (C-2′, 6′), 116.3 (C-3′, 5′), 158.9 (C-4′). *Prismatomeris tetrandra* (Rubiaceae).[65,66]

152. 1,5-Dihydroxy-3,8-epoxyvalechlorine A



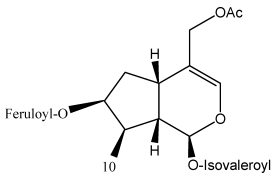
$C_{12}H_{15}ClO_6$: 290.0557; colorless oil; $[\alpha]_D^{20}$ +86.2° (c=0.1, MeOH); IR (KBr): 3436, 2920, 1736, 1628, 1247, 1108, 963; ^{1}H-NMR (600 MHz, $CDCl_3$): 5.60 (d, 3.2, H-1), 5.30 (s, H-3), 2.59 (dd, 14.3, 7.3, H-6), 2.03 (dd, 14.3, 2.6, H-6), 4.95 (dd, 7.3, 2.6, H-7), 2.64 (d, 3.2, H-9), 3.78 (d, 11.5, H-10), 3.73 (d, 11.5, H-10), 5.38 (s, H-11), 5.12 (s, H-11), 2.08 (s, OAc); ^{13}C-NMR (150 MHz, $CDCl_3$): 90.5 (C-1), 94.1 (C-3), 151.6 (C-4), 77.4 (C-5), 46.5 (C-6), 74.6 (C-7), 82.5 (C-8), 46.6 (C-9), 45.5 (C-10), 108.3 (C-11), 21.0, 169.6 (OAc). *Valeriana wallichii* (Valerianaceae).[67)]

153. Rupesin E



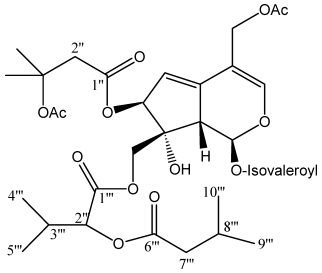
$C_{15}H_{22}O_5$: 282.1467; colorless oil; $[\alpha]_D^{20}$ +22.0° (c=0.89, MeCOMe); IR (KBr): 3477, 1742, 1670; ^{1}H-NMR (400 MHz, $CDCl_3$): 6.18 (d, 3.3, H-1), 5.08 (s, H-3), 3.00 (dd, 8.0, 4.2, H-5), 1.92 (m, H-6), 1.77 (m, H-6), 3.63 (m, H-7), 2.33 (dd, 4.2, 3.3, H-9), 1.26 (s, H_3-10), 4.87 (br s, H-11), 4.77 (br s, H-11), 2.13 (m, H_2-2′), 1.92 (m, H-3′), 0.88 (d, 1.8, H_3-4′, 5′); ^{13}C-NMR (100 MHz, $CDCl_3$): 90.5 (C-1), 93.3 (C-3), 149.4 (C-4), 36.8 (C-5), 43.0 (C-6), 78.1 (C-7), 82.8 (C-8), 41.8 (C-9), 19.5 (C-10), 107.9 (C-11), 171.8 (C-1′), 43.4 (C-2′), 25.8 (C-3′), 22.7 (C-4′, 5′). *Patrinia rupestris*.[68)]

154. 8-Methylvalepotriate



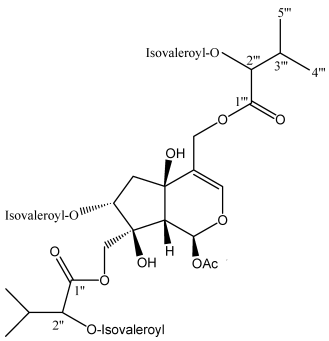
$C_{27}H_{34}O_9$; 502.2202; yellow oil; $[\alpha]_D^{20}$ −50.0° (c=0.1, MeOH); IR (KBr): 3436, 1740, 1627, 1599, 1516, 1458, 1270, 1157; ^{1}H-NMR (600 MHz, $CDCl_3$): 6.02 (d, 3.7, H-1), 6.34 (s, H-3), 2.93 (m, H-5), 1.98 (m, H-6), 2.10 (m, H-6), 5.33 (td, 5.2, 2.2, H-7), 2.10 (m, H-8), 2.19 (m, H-9), 1.11 (d, 6.7, H_3-10), 4.57 (d, 12.1, H-11), 4.42 (d, 12.1, H-10), 2.07 (s, Ac), 2.14 (m, H-2′), 2.11 (m, H-3′), 0.99 (d, 6.7, H_3-4′), 0.98 (d, 6.7, H_3-5′), 7.03 (d, H-2″), 6.92 (d, 8.3, H-5″), 7.08 (dd, 8.3, 1.7, H-6″), 3.93 (s, MeO-3″), 7.61 (d, 15.8, H-7″), 6.28 (d, 15.8, H-8″); ^{13}C-NMR (150 MHz, $CDCl_3$): 91.0 (C-1), 139.9 (C-3), 113.4 (C-4), 32.2 (C-5), 37.3 (C-6), 76.7 (C-7), 39.2 (C-8), 45.8 (C-9), 12.9 (C-10), 64.0 (C-11), 20.9, 170.9 (Ac), 171.8 (C-1′), 43.4 (C-2′), 25.6 (C-3′), 22.3 (C-4′, 5′), 126.9 (C-1″), 109.4 (C-2″), 146.8 (C-3″), 148.0 (C-4″), 114.7 (C-5″), 123.0 (C-6″), 55.9 (MeO-3″), 145.0 (C-7″), 115.4 (C-8″), 166.7 (C-9″). *Valeriana wallichii* (Valerianaceae).[67)]

155. Valeriotetrate B



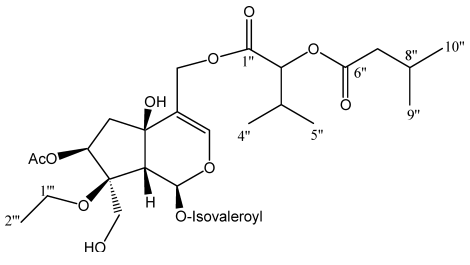
$C_{34}H_{50}O_{14}$; 682.3200; colorless oil; $[\alpha]_D^{20}$ +190.2° (c=0.1, MeOH); ^{1}H-NMR (600 MHz, $CDCl_3$): 6.22 (d, 10.0, H-1), 6.68 (s, H-3), 5.75 (dd, 2.6, 2.4, H-6), 5.38 (d, 2.6, H-7), 2.89 (dd, 10.0, 2.4, H-9), 4.70 (d, 11.4, H-10), 4.28 (d, 11.4, H-10), 4.71 (d, 12.4, H-11), 4.62 (d, 12.4, H-11), 2.03 (s, OAc), 1.95 (s, OAc), 2.31 (m, H-2′), 2.15 (m, H-3′), 0.97 (d, 6.4, H-4′), 0.96 (d, 6.4, H-5′), 2.98 (d, 14.2, H-2″), 2.80 (d, 14.2, H-2″), 1.51 (s, H_3-4″), 1.50 (s, H_3-5″), 4.72 (d, 4.2, H-2‴), 2.24 (m, H-3‴), 1.00 (d, 6.4, H_3-4‴), 0.99 (d, 6.4, H_3-5‴), 2.34 (m, H_2-7‴), 2.09 (m, H-8‴), 1.02 (d, 6.4, H_3-9‴), 0.98 (d, 6.4, H_3-10‴); ^{13}C-NMR (125 MHz, $CDCl_3$): 92.5 (C-1), 148.2 (C-3), 108.6 (C-4), 139.1 (C-5), 117.3 (C-6), 83.2 (C-7), 80.0 (C-8), 48.3 (C-9), 65.5 (C-10), 60.8 (C-11), 20.9, 170.8 (OAc-11), 22.2, 170.3 (OAc-3″) 170.7 (C-1′), 42.9 (C-2′), 25.5 (C-3′), 22.3 (C-4′, 5′), 168.9 (C-1″), 44.1 (C-2″), 79.3 (C-3″), 26.4 (C-4″), 26.5 (C-5″), 169.6 (C-1‴), 76.8 (C-2‴), 30.0 (C-3‴), 18.6 (C-4‴), 17.1 (C-5‴), 173.7 (C-6‴), 43.0 (C-7‴), 25.6 (C-8‴), 22.3 (C-9‴, 10‴). *Valeriana wallichii* (Valerianaceae).[67)]

156. Valeriotetrate C



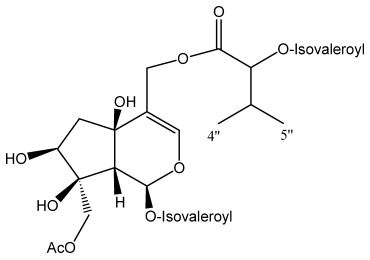
$C_{37}H_{58}O_{15}$; 742.3775; colorless needles; mp 54—55 °C; $[\alpha]_D^{20}$ −63.8° (c=0.1, MeOH); IR (KBr): 3460, 1742, 1659, 1247, 1186; ^{1}H-NMR (600 MHz, $CDCl_3$): 6.57 (d, 1.4, H-1), 6.61 (s, H-3), 2.60 (dd, 13.2, 6.2, H-6), 2.11 (m, H-6), 4.93 (dd, 6.2, 2.4, H-7), 2.58 (d, 1.4, H-9), 4.27 (d, 11.4, H-10), 4.23 (d, 11.4, H-10), 4.91 (d, 12.7, H-11), 4.69 (d, 12.7, H-11), 2.29 (m, H-2′), 2.08 (m, H-3′), 0.98 (overlapped, H_3-4′), 0.99 (overlapped, H_3-5′), 4.79 (d, 4.8, H-2″), 2.21 (m, H-3″), 1.00 (overlapped, H_3-4″), 0.99 (overlapped, H_3-5″), 2.28 (m, H_2-7″), 2.09 (m, H-8″), 0.96 (overlapped, H_3-9″), 0.97 (overlapped, H_3-10″), 4.80 (d, 4.8, H-2‴), 2.21 (m, H-3‴), 1.01 (d, 6.4, H_3-4‴), 0.99 (d, 6.4, H_3-5‴), 2.26 (m, H_2-7‴), 2.09 (m, H-8‴), 0.96 (overlapped, H_3-9‴), 0.97 (overlapped, H_3-10‴), 2.09 (s, OAc); ^{13}C-NMR (150 MHz, $CDCl_3$): 89.0 (C-1), 145.0 (C-3), 112.5 (C-4), 69.6 (C-5), 40.5 (C-6), 79.8 (C-7), 79.1 (C-8), 53.3 (C-9), 67.3 (C-10), 61.9 (C-11), 20.7, 170.7 (OAc),171.2 (C-1′), 43.1 (C-2′), 25.7 (C-3′), 22.3 (C-4′, 5′), 169.6 (C-1″), 76.6 (C-2″), 29.9 (C-3″), 17.3 (C-4″), 18.6 (C-5″), 173.0 (C-6″), 43.0 (C-7″), 25.6 (C-8″), 22.3 (C-9″, 10″) 169.9 (C-1‴), 76.7 (C-2‴), 30.0 (C-3‴), 17.2 (C-4‴), 18.9 (C-5‴), 173.2 (C-6‴), 42.9 (C-7‴), 25.7 (C-8‴), 22.4 (C-9‴,10‴). *Valeriana wallichii* (Valerianaceae).[67)]

157. Valeriotriate A



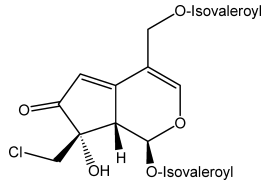
$C_{29}H_{46}O_{12}$: 586.2989; colorless oil; ^{1}H-NMR (500 MHz, CD_3COCD_3): 6.55 (d, 1.8, H-1), 6.59 (s, H-3), 2.53 (dd, 13.5, 7.4, H-6), 2.06 (m, H-6), 4.95 (dd, 7.4, 7.0, H-7), 2.68 (s, H-9), 3.60 (m, H_2-10), 4.74 (d, 12.9, H-11), 4.80 (d, 12.9, H-11), 2.24 (m, H_2-2′), 2.23 (m, H-3′), 0.96 (d, 6.7, H_3-4′)[a], 0.97 (d, 6.7, H_3-5′)[a], 4.86 (d, 4.3, H-2″), 2.10 (m, H-3″), 0.95 (d, 6.7, H_3-4″)[a], 0.97 (d, 6.7, H_3-5″)[a], 2.28 (m, H_2-7″), 2.02 (m, H-8″), 0.96 (d, 6.7, H_3-9″)[a], 0.99 (d, 6.7, H_3-10″)[a], 3.55 (q, 7.0, H_2-1‴), 1.17 (t, 7.0, H_3-2‴), 2.05 (s, Ac); ^{13}C-NMR (125 MHz, CD_3COCD_3): 91.3 (C-1), 144.8 (C-3), 115.3 (C-4), 71.5 (C-5), 43.4 (C-6), 81.1 (C-7), 82.0 (C-8), 55.7 (C-9), 75.2 (C-10), 63.8 (C-11), 172.2 (C-1′), 44.3 (C-2′), 27.1 (C-3′), 23.2 (C-4′, 5′), 170.8 (C-1″), 77.9 (C-2″), 31.4 (C-3″), 19.8 (C-4″), 17.5 (C-5″), 173.6 (C-6″), 44.2 (C-7″), 26.9 (C-8″), 23.3 (C-9″, 10″), 68.2 (C-1‴), 16.0 (C-2‴), 21.6, 171.6 (Ac). *Valeriana jatamansi* (Valerianaceae).[69)]

158. Valeriotriate B



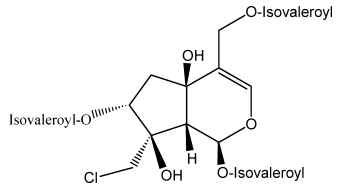
$C_{27}H_{42}O_{12}$: 558.2676; colorless oil; ^{1}H-NMR (500 MHz, CD_3COCD_3): 6.65 (d, 1.8, H-1), 6.57 (s, H-3), 2.37 (dd, 13.2, 5.0, H-6), 2.11 (m, H-6), 3.82 (dd, 7.5, 5.1, H-7), 2.72 (d, 1.8, H-9), 4.14 (d, 11.9, H-10), 4.04 (d, 11.9, H-10), 4.74 (d, 12.5, H-11), 4.78 (d, 12.5, H-11), 2.28 (m, H_2-2′), 2.08 (m, H-3′), 0.97 (d, 6.5, H_3-4′)[a], 0.99 (d, 6.5, H_3-5′)[a], 4.80 (d, 4.3, H-2″), 2.09 (m, H-3″), 0.94 (d, 6.5, H_3-4″)[a], 0.96 (d, 6.5, H_3-5″)[a], 2.29 (m, H_2-7″), 2.24 (m, H-8″), 0.97 (d, 6.5, H_3-9″)[a], 0.98 (d, 6.5, H_3-10″)[a], 2.05 (s, Ac) a: may be exchangeable. ^{13}C-NMR (125 MHz, CD_3COCD_3): 89.6 (C-1), 143.4 (C-3), 115.9 (C-4), 69.3 (C-5), 43.4 (C-6), 72.0 (C-7), 79.2 (C-8), 55.6 (C-9), 66.7 (C-10), 62.7 (C-11), 171.6 (C-1′), 43.4 (C-2′), 26.4 (C-3′), 22.6 (C-4′, 5′), 170.2 (C-1″), 77.3 (C-2″), 30.7 (C-3″), 19.1 (C-4″), 18.2 (C-5″), 173.1 (C-6″), 43.4 (C-7″), 26.2 (C-8″), 22.5 (C-9″, 10″), 20.8, 171.1 (Ac). *Valeriana jatamansi* (Valerianaceae).[69]

159. Rupesin A



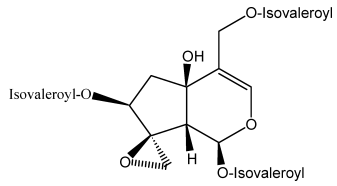
$C_{20}H_{27}ClO_7$: 414.1445; yellow oil; $[\alpha]_D^{20}$ −155.0° (c=0.40, MeOH); UV (MeOH): 303 (4.30); IR (KBr): 1766, 1735, 1708, 1602, 753; ^{1}H-NMR (400 MHz, $CDCl_3$): 6.37 (d, 8.1, H-1), 7.05 (s, H-3), 6.01 (s, H-6), 3.49 (dd, 8.1, 1.8, H-9), 3.83 (d, 7.8, H-10), 3.60 (d, 7.8, H-10), 4.82 (d, 9.3, H-11), 4.76 (d, 9.3, H-11), 2.33 (m, H-2′, 2″), 2.06 (m, H-2′, 2″), 2.18 (m, H-3′, 3″), 1.01 (d, 5.1, H-4′, 4″), 0.93 (d, 4.8, H-5′, 5″); ^{13}C-NMR (100 MHz, $CDCl_3$): 92.9 (C-1), 154.4 (C-3), 109.7 (C-4), 165.3 (C-5), 119.1 (C-6), 204.1 (C-7), 76.1 (C-8), 44.1 (C-9), 44.2 (C-10), 60.0 (C-11), 170.7 (C-1′), 43.4 (C-2′), 25.9 (C-3′), 22.6 (C-4′), 22.5 (C-5′), 173.1 (C-1″), 43.2 (C-2″), 25.9 (C-3″), 22.5 (C-4″), 22.4 (C-5″). *Patrinia rupestris* (Valerianaceae).[68]

160. Rupesin C



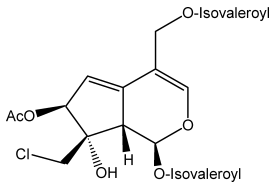
$C_{25}H_{39}{}^{35}ClO_9$: 518.2448; colorless prisms; mp 120—121 °C; $[\alpha]_D^{20}$ −61.8° (c=1.6, MeOH); IR (KBr): 3470, 1759, 1722, 1664; ^{1}H-NMR (400 MHz, $CDCl_3$): 6.50 (d, 5.4, H-1), 6.52 (s, H-3), 2.55 (dd, 15.0, 9.9, H-6), 4.89 (dd, 12.9, 6.6, H-7), 3.03 (d, 2.0, H-9), 3.60 (d, 11.7, H-10), 3.70 (d, 11.7, H-10), 4.67 (d, 12.3, H-11), 4.74 (d, 12.3, H-11), 2.19 (m, H_2-2′, 2″, 2‴), 2.11 (m, H-3′, 3″, 3‴), 0.96 (d, 6.6, H_3-4′, 5′, 4″, 5″, 4‴, 5‴); ^{13}C-NMR (100 MHz, $CDCl_3$): 89.5 (C-1), 143.2 (C-3), 113.8 (C-4), 70.9 (C-5), 41.3 (C-6), 79.7 (C-7), 80.6 (C-8), 54.4 (C-9), 49.7 (C-10), 61.5 (C-11), 171.0 (C-1′), 43.6 (C-2′), 25.9 (C-3′, 3″, 3‴), 22.5 (C-4′, 5′, 4″, 5″, 4‴, 5‴), 173.1 (C-1″), 43.4 (C-2″), 173.3 (C-1‴), 43.3 (C-2‴). *Patrinia rupestris* (Valerianaceae).[68]

161. Rupesin D



$C_{25}H_{38}O_9$: 482.2515; colorless prisms; mp 84—85 °C; $[\alpha]_D^{20}$ −117.8° (c=1.40, MeOH); IR (KBr): 3481, 1760, 1720, 1663, 1080; ^{1}H-NMR (400 MHz, $CDCl_3$): 6.08 (d, 2.4, H-1), 6.62 (s, H-3), 1.99 (dd, 13.2, 10.2, H-6), 2.79 (dd, 13.2, 7.0, H-6), 4.87 (dd, 10.2, 7.0, H-7), 2.91 (d, 2.4, H-9), 2.82 (d, 5.0, H-10), 3.12 (d, 5.0, H-10), 4.75 (d, 12.3, H-11), 4.90 (d, 12.3, H-11), 2.19 (m, H-2′, 2″, 2‴), 2.12 (m, H-3′), 0.96 (d, 6.6, H-4′, 5′, 4″, 5″, 4‴, 5‴), 2.11 (m, H-3″, 3‴); ^{13}C-NMR (100 MHz, $CDCl_3$): 88.1 (C-1), 144.4 (C-3), 111.6 (C-4), 69.3 (C-5), 40.2 (C-6), 72.6 (C-7), 62.0 (C-8), 47.8 (C-9), 48.7 (C-10), 60.7 (C-11), 170.7 (C-1′), 42.9 (C-2′, 2″), 25.4 (C-3′, 3″), 22.1 (C-4′, 5′, 4″, 5″, 4‴, 5‴), 173.1 (C-1″), 171.5 (C-1‴), 43.7 (C-2‴). *Patrinia rupestris* (Valerianaceae).[68]

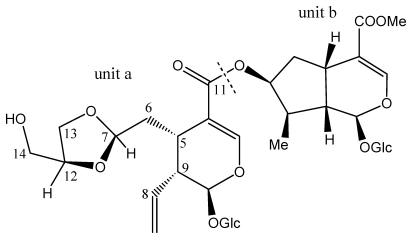
162. Rupesin B



$C_{22}H_{31}ClO_8$: 458.1707; colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$): 6.20 (d, 9.9, H-1), 6.63 (s, H-3), 5.69 (t, 2.8, H-6), 5.42 (d, 2.8, H-7), 2.89 (dd, 9.9, 2.4, H-9), 3.93 (d, 11.2, H-10), 3.73 (d, 11.2, H-10), 4.65 (d, 12.4, H-11), 4.58 (d, 12.4, H-11), 2.25 (m, H_2-2′), 2.11 (m, H-3′), 0.96 (d, 6.6, H-4′, 5′), 2.12 (m, H_2-2″), 2.11 (m, H-3″), 0.96 (d, 6.6, H_3-4″,5″), 2.13 (s, Ac); ^{13}C-NMR (100 MHz, $CDCl_3$): 92.4 (C-1), 148.1 (C-3), 108.9 (C-4), 139.6 (C-5), 117.3 (C-6), 83.5 (C-7), 80.4 (C-8), 49.5 (C-9), 48.6 (C-10), 60.4 (C-11), 170.6 (C-1′), 43.2 (C-2′), 25.6 (C-3′), 22.1 (C-4′, 5′), 170.0 (C-1″), 43.1 (C-2″), 25.6 (C-3″), 22.1 (C-4″, 5″), 173.1, 20.9 (Ac). *Patrinia rupestris* (Valerianaceae).[68]

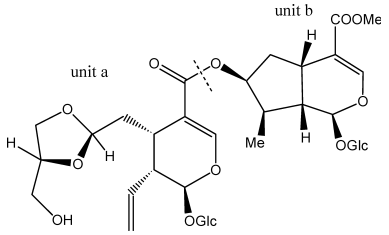
Group 6 (Bis- and tetrakis-iridoid glycosides)

163. Dipsanoside C



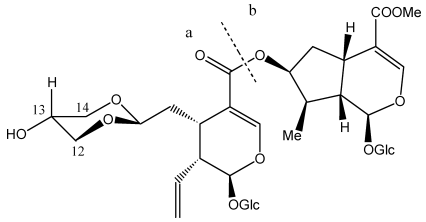
$C_{36}H_{52}O_{21}$: 820.3000; white amorphous powder; $[\alpha]_D^{20}$ −34.8° (c=0.209, MeOH); UV (MeOH): 234.4; IR (KBr): 3431 , 1701, 1637, 1292, 1074; ^{1}H- NMR (500 MHz, CD_3OD): (unit a) 5.50 (d, 6.0, H-1), 7.38 (s , H-3), 2.97 (br q, 5.5, H-5), 1.7 (dddd, 14.0 , 6.0, 4.0, 2.0, H-6), 1.95 (ddd, 14.0, 6.0, 6.0, H-6), 4.93 (dd, 6.0, 4.0, H-7), 5.70 (ddd, 17.5, 10.5, 9.0, H-8), 2.67 (ddd, 9.0, 6.0, 5.5, H-9), 5.24 (d, 17.5, H-10), 5.20 (d, 10.5, H-10), 4.02 (ddd, 7.0, 5.5, 5.0, H-12), 3.72 (dd, 8.0, 5.0, H-13), 3.80 (dd, 8.0, 7.0, H-13), 3.50 (dd, 11.0, 5.0, H-14), 3.45 (dd, 11.0, 5.5, H-14), 4.63 (d, 8.0, H-1′), 3.14 (dd, 9.0, 8.0, H-2′), 3.31 (t, 8.5, H-3 ′), 3.20—3.28 (H-4′, 5′), 3.61 (dd, 12.0, 5.5, H-6′), 3.80 (br d, 11.5, H-6′); (unit b) 5.27 (d, 4.0, H-1), 7.36 (s, H-3), 3.06 (br q, 8.0, H-5), 1.82 (ddd, 14.0, 8.0, 4.0, H-6), 2.25 (dd, 14.0, 8.0, H-6), 5.13 (dd, 8.0, 4.0, H-7), 2.03—2.09 (m, H-8), 2.12 (ddd, 9.0, 8.0, 4.0, H-9), 1.01 (d, 7.0, H_3-10), 3.64 (s, OMe), 4.60 (d, 8.0, H-1′), 3.14 (dd, 8.5, 8.0, H-2′), 3.31 (t, 8.5, H-3′), 3.28—3.20 (H-4′, 5′),, 3.61 (dd, 12.0, 5.5, H-6′), 3.80 (br d, 11.5, H-6′); ^{13}C-NMR (125 MHz, CD_3OD): (unit a) 97.7 (C-1), 153.5 (C-3), 113.5 (C-4), 30.0 (C-5), 35.2 (C-6), 104.8 (C-7), 135.8 (C-8), 45.4 (C-9), 119.8 (C-10), 168.4 (C-11), 77.7 (C-12), 68.1 (C-13), 64.1 (C-14), 100.2 (C-1′), 74.7 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.8 (C-6′); (unit b) 97.2 (C-1), 152.3 (C-3), 111.8 (C-4), 32.3 (C-5), 40.4 (C-6), 78.6 (C-7), 40.9 (C-8), 47.0 (C-9), 13.5 (C-10), 169.3 (C-11), 51.7 (OMe), 100.1 (C-1′), 74.7 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.7 (C-6′). *Dipsacus asper*.[58]

164. Dipsanoside D



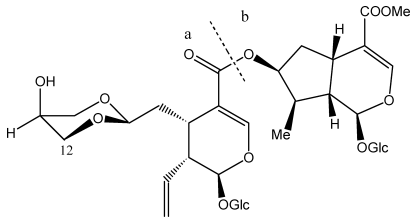
$C_{36}H_{52}O_{21}$: 820.3000; white amorphous powder; $[\alpha]_D^{20}$ −36.6° (c=0.260, MeOH); UV (MeOH): 236.4; IR (KBr): 3408, 1697, 1570, 1290, 1074, 1018; ^{1}H-NMR (500 MHz, CD_3OD): (unit a) 5.49 (d, 5.5, H-1), 7.38 (s , H-3), 2.96 (br q, 6.0, H-5), 1.77 (ddd, 14.0, 6.0, 4.0, H-6), 1.90 (ddd, 14.0, 6.0, 6.0, H-6), 5.06 (dd, 6.0, 4.0, H-7), 5.70 (ddd, 17.5, 10.5, 9.0, H-8), 2.67 (ddd, 9.0, 6.0, 5.5, H-9), 5.24 (d, 17.5, H-10), 5.20 (d, 10.5, H-10), 4.06 (ddd, 11.5, 4.5, 3.0, H-12), 3.59—3.85 (overlapped, H-13), 4.04 (dd, 7.5, 4.5, H-13), 3.51—3.56 (overlapped, H-14), 4.63 (d, 8.0, H-1′), 3.11—3.33 (H-2′—5′), 3.59—3.85 (H_a-6′), 3.84 (d, 11.5, H_b-6′); (unit b) 5.27 (d, 4.0, H-1), 7.36 (s, H-3), 3.06 (br q, 8.0, H-5), 1.70 (ddd, 14.0, 9.0, 5.0, H-6), 2.25 (br dd, 14.0, 8.0, H-6), 5.12 (dd, 5.0, 3.5, H-7), 2.03—2.13 (m, H-8), 2.11 (ddd, 9.5, 8.0, 4.0, H-9), 1.02 (d, 6.5, H_3-10), 3.85 (s, OMe), 4.60 (d, 8.0, H-1′), 3.11—3.33 (H-2′, 5′), 3.51—3.56 (H-6′); ^{13}C-NMR (125 MHz, CD_3OD): (unit a) 97.7 (C-1),153.4 (C-3), 113.5 (C-4), 30.0 (C-5), 32.3 (C-6), 104.5 (C-7), 135.8 (C-8), 45.4 (C-9), 119.8 (C-10), 168.4 (C-11), 77.4 (C-12), 68.0 (C-13), 63.4 (C-14), 100.2 (C-1′), 74.7 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.8 (C-6′); (unit b) 97.3 (C-1), 152.3 (C-3), 111.9 (C-4), 35.2 (C-5), 40.4 (C-6), 78.6 (C-7), 40.9 (C-8), 47.1 (C-9), 13.5 (C-10), 169.3 (C-11), 51.7 (OMe), 100.1 (C-1′), 74.7 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.8 (C-6′). *Dipsacus asper*.[58)]

165. Dipsanoside E



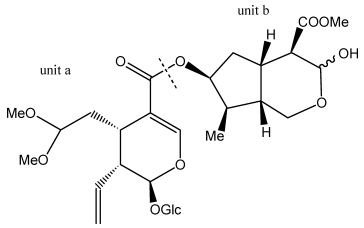
$C_{36}H_{52}O_{21}$: 820.3000; white amorphous powder; $[\alpha]_D^{20}$ −28.3° (c=0.198, MeOH); UV (MeOH): 234.0; IR (KBr): 3446, 695, 1635, 1624, 1074; ^{1}H-NMR (500 MHz, CD_3OD): (unit a) 5.46 (d, 6.0, H-1), 7.38 (s, H-3), 2.94 (ddd, 9.0, 6.0, 4.0, H-5), 1.68 (ddd, 14.0, 7.0, 6.0, H-6), 1.87 (ddd, 14.0, 6.5, 4.0, H-6), 4.50 (dd, 7.0, 6.5, H-7), 5.70 (ddd, 17.0, 10.5, 8.0, H-8), 2.62 (ddd, 9.0, 8.0, 6.0, H-9) 5.24 (d, 17.0, H-10), 5.19 (d, 10.5, H-10), 3.98 (ddd, 10.5, 5.0, 1.5, H-12), 3.19—3.32 (overlapped, H-12), 3.66 (dd, 10.0, 5.0, H-13), 4.02 (ddd, 10.5, 5.0, 1.5, H-14), 3.19—3.32 (overlapped, H-14), 4.63 (d, 8.0, H-1′), 3.13—3.17 (dd , 8.0, 6.5, H-2′), 3.19—3.32 (H-3′—5′), 3.59—3.68 (H_a-6′), 3.83—3.86 (H_b-6′); (unit b) 5.28 (d, 4.5, H-1), 7.35 (s, H-3), 3.07 (q, 7.5, H-5), 1.69 (ddd, 14.5, 7.5, 5.0, H-6), 2.24 (br dd, 14.5, 7.5, H-6), 5.11 (dd, 7.5, 5.0, H-7), 2.03—2.06 (m, H-8), 2.18 (ddd, 9.0, 7.5, 4.5, H-9), 1.02 (d, 6.5, H_3-10), 3.63 (s, OMe), 4.60 (d, 8.0, H-1′), 3.13—3.17 (dd, 8.5, 6.5, H-2′), 3.19—3.32 (H-3′—5′), 3.59—3.68 (H_a-6′), 3.83—3.86 (H_b-6′); ^{13}C-NMR (125 MHz, CD_3OD): (unit a) 97.7 (C-1), 153.3 (C-3), 113.6 (C-4), 30.0 (C-5), 35.7 (C-6), 101.7 (C-7), 135.9 (C-8), 45.5 (C-9), 119.7 (C-10), 168.4 (C-11), 72.6 (C-12), 61.9 (C-13), 71.4 (C-14), 100.2 (C-1′), 74.7 (C-2′), 78.0 (C-3′), 71.5 (C-4′), 78.4 (C-5′), 62.7 (C-6′); (unit b) 97.2 (C-1), 152.2 (C-3), 112.0 (C-4), 32.1 (C-5), 40.5 (C-6), 78.6 (C-7), 40.9 (C-8), 46.9 (C-9), 13.4 (C-10), 169.4 (C-11), 51.7 (OMe), 100.1 (C-1′), 74.6 (C-2′), 78.0 (C-3′), 71.4 (C-4′), 78.3 (C-5′), 62.6 (C-6′). *Dipsacus asper*.[58)]

166. Dipsanoside F



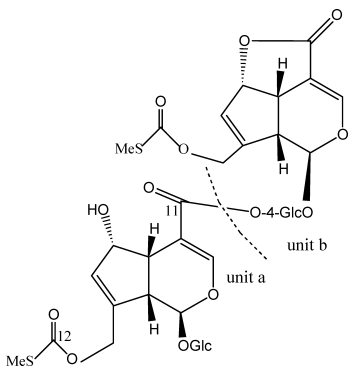
$C_{36}H_{52}O_{21}$: 820.3000; white amorphous powder; $[\alpha]_D^{20}$ −10.2° (c=0.885, MeOH); UV (MeOH): 235.2; IR (KBr): 3388, 1693, 1631, 1074; ^{1}H-NMR (500 MHz, CD_3OD): (unit a) 5.49 (d, 6.0, H-1), 7.39 (s, H-3), 2.94 (br q, 6.0, H-5), 1.68 (ddd, 14.0, 6.0, 6.0, H-6), 1.93 (ddd, 14.0, 6.0, 6.0, H-6), 4.66 (q, 6.0, H-7), 5.71 (ddd, 17.0, 11.0, 8.0, H-8), 2.62 (br dd, 8.0, 6.0, H-9), 5.25 (d, 17.0, H-10), 5.19 (d, 11.0, H-10), 3.79—3.88 (overlapped, H-12), 3.20—3.33 (overlapped, H-12), 3.60 (dd, 5.5, 3.0, H-13), 3.79—3.88 (overlapped, H-14), 3.20—3.33 (overlapped, H-14), 4.65 (d, 8.0, H-1′), 3.12—3.16 (H-2′), 3.20—3.33 (H-3′—5′), 3.59—3.64 (H_a-6′), 3.81—3.88 (H_b-6′); (unit b) 5.25 (d, 4.0, H-1), 7.36 (s, H-3), 3.08 (br ddd, 9.0, 7.5, 7.0, H-5), 1.69 (ddd, 14.0, 7.0, 5.0, H-6), 2.25 (dd, 14.0, 7.5, H-6), 5.14 (br s, H-7), 2.08 (overlapped, H-8, 9), 1.01 (d, 6.0, H_3-10), 3.64 (s, OMe), 4.59 (d, 8.0, H-1′), 3.12—3.16 (H-2′), 3.19—3.33 (H-3′—5′), 3.59—3.64 (H_a-6′), 3.81—3.88 (H_b-6′); ^{13}C-NMR (125 MHz, CD_3OD): (unit a) 97.7 (C-1),153.3 (C-3), 113.4 (C-4), 32.0 (C-5), 36.0 (C-6), 102.3 (C-7), 135.9 (C-8), 45.5 (C-9), 119.6 (C-10), 168.4 (C-11), 72.5 (C-12), 65.0 (C-13), 72.3 (C-14), 100.3 (C-1′), 74.7 (C-2′), 78.4 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.8 (C-6′); (unit b) 97.4 (C-1), 152.4 (C-3), 112.2 (C-4), 29.7 (C-5), 40.4 (C-6), 78.0 (C-7), 41.0 (C-8), 47.1 (C-9), 13.7 (C-10), 169.4 (C-11), 51.7 (OMe), 100.2 (C-1′), 74.7 (C-2′), 78.4 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.8 (C-6′). *Dipsacus asper*.[58)]

167. Dipsanoside G



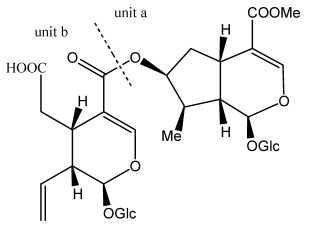
$C_{29}H_{44}O_{15}$: 632.2680; white amorphous powder, $[\alpha]_D^{20}$ −3.4° (c=1.277, MeOH); UV (MeOH): 235.0; IR (KBr): 3417, 1732, 1699, 1633, 1385, 1074; ^{1}H-NMR (500 MHz, CD_3OD): (unit a) 5.45 (d, 5.5, H-1), 7.35 (s, H-3), 3.13 (ddd, 8.0, 7.5, 2.0, H-5) , 1.56—1.58 (m, H-6), 1.92—1.96 (m, H-6), 5.22 (dd, 6.0, 4.0, H-7), 5.67 (ddd, 18.0, 10.0, 8.5, H-8), 2.84 (br dd, 8.5, 5.5, H-9), 5.24 (d, 18.0, H-10), 2.10 (d, 10.0, H-10), 3.25 (s, OMe), 4.60 (d, 7.5, H-1′), 3.08—3.31 (H-2′—5′), 3.58—3.64 (H-6′); (unit b) 3.80—3.88 (br q, 11.0, H-1), 4.66 (dd, 6.5, 2.0, H-3), 2.17 (dd, 9.0, 6.5, H-4), 2.43—2.48 (m, H-5), 1.75—1.82 (m, H-6), 2.10 (ddd, 7.0, 6.0, 4.5, H-6), 4.45 (br d, 4.5, H-7), 2.00 (m, H-8), 2.61 (br d, 4.0, H-9), 0.93 (d, 7.0, H_3-10), 3.64 (s, OMe); ^{13}C-NMR (125 MHz, CD_3OD): (unit a) 97.8 (C-1), 153.2 (C-3), 112.1 (C-4), 29.3 (C-5), 44.3 (C-6), 104.3 (C-7), 135.8 (C-8), 44.3 (C-9), 119.8 (C-10), 168.3 (C-11), 52.8 (OMe), 52.3 (OMe), 100.1 (C-1′), 74.6 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.8 (C-6′); (unit b) 64.8 (C-1), 97.1 (C-3), 54.0 (C-4), 39.9 (C-5), 38.2 (C-6), 78.1 (C-7), 38.7 (C-8), 43.8 (C-9), 12.4 (C-10), 175.1 (C-11), 53.7 (OMe). *Dipsacus asper*.[58)]

168. Paederoside B



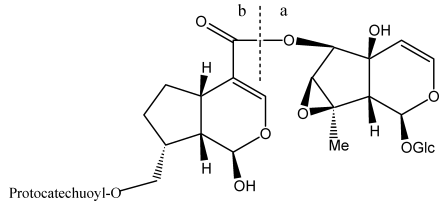
$C_{36}H_{44}O_{22}S_2$: 892.1765: yellow powder; $[\alpha]_D^{25}$ −42.0° (c=0.12, MeOH); UV (MeOH): 234.0 (4.13); IR (KBr): 3427, 1709, 1657, 1628, 1159; ^{1}H-NMR (600 MHz, CD_3OD): (unit a) 5.07 (d, 8.3, H-1), 7.71 (d, 1.2, H-3), 3.05 (ddd, 8.3, 6.7, 1.2, H-5), 4.85 (d, 6.7, H-6), 6.02 (br s, H-7), 2.65 (t, 8.3, H-9), 4.96 (d, 14.9, H-10), 5.05 (d, 14.9, H-10), 2.32 (s, SMe), 4.73 (d, 7.9, H-1′), 3.35 (m, H-2′), 3.41 (m, H-3′), 3.24 (m, H-4′), 3.30 (m, H-5′), 3.80 (dd, 12.1, 2.0, H-6′), 3.64 (dd, 12.1, 6.4, H-6′); (unit b) 5.82 (d, 1.1, H-1), 7.30 (d, 1.9, H-3), 3.68 (ddd, 7.3, 6.5, 1.9, H-5), 5.58 (d, 6.5, H-6), 5.76 (s, H-7), 3.27 (dd, 7.3, 1.1, H-9), 4.64 (d, 15.3, H-10), 4.82 (d, 15.3, H-10), 2.31 (s, SMe), 4.71 (d, 8.1, H-1′), 3.22 (m, H-2′), 3.60 (dd, 9.5, 8.6, H-3′), 4.16 (dd, 8.6, 8.0, H-4′), 3.38 (m, H-5′), 3.59 (dd, 12.0, 1.7, H-6′), 3.74 (dd, 12.0, 6.0, H-6′); ^{13}C-NMR (150 MHz, CD_3OD): (unit a) 101.4 (C-1), 155.8 (C-3), 108.1 (C-4), 42.6 (C-5), 75.8 (C-6), 132.4 (C-7), 145.6 (C-8), 46.3 (C-9), 66.2 (C-10), 168.6 (C-11), 172.8 (C-12), 13.6 (SMe), 100.7 (C-1′), 74.9 (C-2′), 77.9 (C-3′), 71.6 (C-4′), 78.6 (C-5′), 63.0 (C-6′); (unit b) 93.0 (C-1), 150.1 (C-3), 106.2 (C- 4), 37.4 (C-5), 86.2 (C-6), 130.0 (C-7), 143.5 (C-8), 45.2 (C-9), 64.4 (C-10), 172.4 (C-11), 172.6 (C-12), 13.7 (SMe), 99.9 (C-1′), 74.6 (C-2′), 75.6 (C-3′), 72.4 (C-4′), 77.7 (C-5′), 62.6 (C-6′). *Paederia scandens* (Rubiaceae).[70]

169. Axillaroside



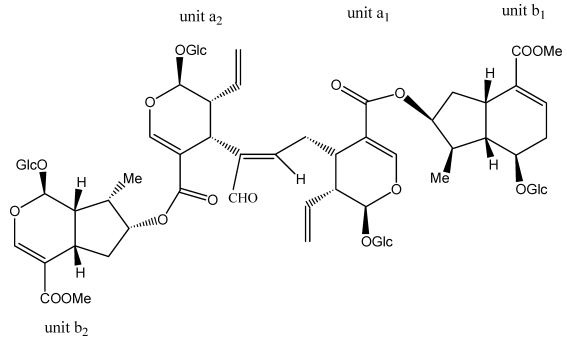
$C_{33}H_{46}O_{20}$: 762.2582; white powder, $[\alpha]_D^{25}$ −60.0° (c=0.6, MeOH); UV (MeOH): 234 (4.24); IR (KBr): 3421, 1697, 1636; ^{1}H-NMR (500 MHz, CD_3OD): (unit a) 5.28 (d, 5.0, H-1), 7.24 (d, 1.5, H-3), 3.11 (br q, 8.0, H-5), 1.74 (ddd, 14.5, 8.0, 5.0, H-6), 2.29 (ddd, 14.5, 7.5, 1.5, H-6), 5.20 (br t, 5.5, H-7), 2.10—2.18 (m, H-8), 2.07 (td, 9.0, 5.0, H-9), 1.07 (d, 6.5, H_3-10), 3.69 (s, OMe), 4.66 (d, 8.0, H-1′), 3.22 (dd, 9.0, 8.0, H-2′), 3.36 (t, 9.0, H-3′), 3.28 (br t, 9.0, H-4′), 3.26—3.38 (m, H-5′), 3.66 (dd, 12.0, 6.0, H-6′), 3.90 (dd, 12.0, 2.0, H-6′); (unit b) 5.50 (d, 4.5, H-1), 7.49 (d, 2.0, H-3), 3.28—3.38 (m, H-5), 2.30 (dd, 16.5, 9.0, H-6), 2.91 (dd, 16.5, 4.0, H-6), 5.66 (br dt, 17.0, 10.0, H-8), 2.81 (br dt, 9.0, 5.0, H-9), 5.23 (dd, 10.0, 1.5, H-10), 5.27 (dd, 17.0, 1.0, H-10), 4.68 (d, 8.0, H-1′), other sugar protons appeared in the same region as that of sugar protons of unit a; ^{13}C-NMR (125 MHz, CD_3OD): (unit a) 97.6 (C-1), 152.7 (C-3), 113.3 (C-4), 32.7 (C-5), 40.4 (C-6), 78.3 (C-7), 41.4 (C-8), 47.2 (C-9), 13.9 (C-10), 169.5 (C-11), 51.8 (OMe), 100.3 (C-1′), 74.7 (C-2′), 78.1 (C-3′), 71.6 (C-4′), 78.5 (C-5′), 62.8 (C-6′); (unit b) 97.7 (C-1), 153.7 (C-3), 110.5 (C-4), 29.1 (C-5), 35.3 (C-6), 176.1 (C-7), 134.5 (C-8), 45.4 (C-9), 120.6 (C-10), 168.0 (C-11), 100.1 (C-1′), 74.8 (C-2′), 78.1 (C-3′), 71.7 (C-4′), 78.5 (C-5′), 62.8 (C-6′). *Strychnos axillaris* (Loganiaceae).[71]

170. Incaside



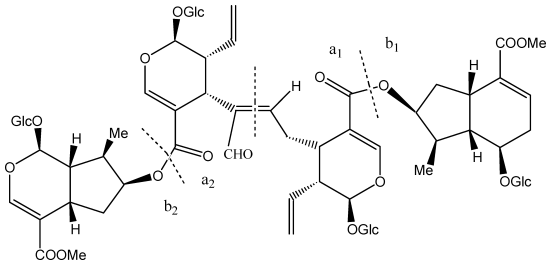
$C_{32}H_{38}O_{17}$: 694.2108; viscous oil; ^{1}H-NMR (400 MHz, CD_3OD): (unit a) 5.39 (d, 6.0, H-1), 6.31 (d, 6.3, H-3), 4.92 (d, 6.3, H-4), 4.98 (d, 3.0, H-6), 3.49 (s, H-7), 2.46 (d, 6.0, H-9), 1.50 (s, H_3-10), 4.47 (d, 8.0, H-1′), 3.28 (dd, 9.0, 8.0, H-2′), 3.38 (dd, 9.2, 9.0, H-3′), 3.47 (dd, 9.5, 9.2, H-4′), 3.31 (m, H-5′), 3.86 (dd, 12.5, 2.0, H-6′), 3.67 (dd, 12.5, 5.0, H-6′); (unit b) 5.19 (d, 5.0, H-1), 7.48 (d, 1.0, H-3), 2.86 (m, H-5), 2.16 (m, H-6), 1.34 (m, H-6), 1.18 (m, H-7), 1.88 (m, H-7), 2.23 (m, H-8), 1.99 (m, H-9), 4.14 (dd, 11.0, 6.5, H-10), 4.10 (dd, 11.0, 6.1, H-10), 7.60 (d, 2.0, H-2′), 6.92 (d, 8.5, H-5′), 7.38 (dd, 8.5, 2.0, H-6′); ^{13}C-NMR of its octaacetate (100 MHz, $CDCl_3$): (unit a) 95.8 (C-1), 141.6 (C-3), 106.8 (C- 4), 73.3 (C-5), 77.8 (C-6), 63.1 (C-7), 66.8 (C-8), 55.8 (C-9), 17.4 (C-10), 101.4 (C-1′), 71.4 (C-2′), 72.8 (C-3′), 68.3 (C-4′), 71.9 (C-5′), 61.8 (C-6′); (unit b) 87.8 (C-1), 152.0 (C-3), 112.8 (C-4), 35.0 (C-5), 29.7 (C-6), 33.5 (C-7), 42.5 (C-8), 45.0 (C-9), 66.2 (C-10), 170.7 (C-11), 122.8 (C-1′), 120.5 (C-2′), 145.1 (C-3′), 151.4 (C-4′), 114.3 (C-5′), 124.2 (C-6′), 166.7 (C-7′), 20.4, 20.5×2, 20.6×3, 20.9×2, 168.4, 168.8, 169.3, 169.4, 169.7, 170.3, 171.1×2 (8×Ac). *Mussaenda incana* (Rubiaceae).[72]

171. Dipsanoside A



$C_{66}H_{90}O_{37}$: 1474.5159; white amorphous powder; UV (MeOH): 235.8 (3.2); IR (KBr): 3399, 1693, 1637; ^{1}H-NMR (500 MHz, CD_3OD): (unit a_1) 5.52 (d, 4.0, H-1), 7.42 (s, H-3), 2.95 (br m, H-5), 3.16 (dd, 9.0, 8.0, H-6), 2.33 (dd, 8.5, 6.0, H-6), 6.71 (dd, 7.0, 6.5, H-7), 5.72 (ddd, 18.0, 10.0, 8.0, H-8), 2.51 (ddd, 7.3, 6.4, 6.0, H-9), 5.32 (d, 17.0, H-10), 5.25 (d, 10.5, H-10), 4.61 (d, 8.0, H-1′), 3.14—3.35 (H-2′, 3′, 4′, 5′), 3.58—3.66 (H-6′), 3.82—3.86 (H-6′); (unit b_1) 5.12 (d, 4.0, H-1), 7.38 (s, H-3), 3.06 (br q, 8.0, H-5), 1.71 (ddd, 13.5, 8.0, 5.0, H-6), 2.26 (br dd, 14.5, 7.0, H-6), 5.21 (d, 5.5, H-7), 2.14 (m, H-8), 2.01 (ddd, 7.0, 5.0, 4.0, H-9), 1.03 (d, 6.5, H_3-10), 3.64 (s, OMe), sugar protons appeared at the same values at that of unit a_1; (unit a_2) 5.43 (d, 5.5, H-1), 7.49 (s, H-3), 4.05 (d, 5.5, H-5), 9.26 (s, H-7), 5.57 (ddd, 17.5, 10.0, 7.5, H-8), 2.75 (ddd, 8.5, 5.7, 5.5, H-9), 4.99 (d, 19.5, H-10), 4.96 (d, 11.5, H-10), sugar protons appeared at the same values as that of unit a_1; (unit b_2) 5.20 (d, 5.5, H-1), 7.39 (s, H-3), 2.96 (ddd, 10.0, 9.5, 7.5, H-5), 1.55 (ddd, 9.0, 8.5, 4.5, H-6), 2.08 (dd, 14.0, 8.5, H-6), 5.13 (d, 6.0, H-7), 2.14 (m, H-8), 1.90 (ddd, 7.5, 7.0, 5.0, H-9), 0.95 (d, 6.5, H_3-10), 3.64 (s, OMe), sugar protons appeared at the same values at that of unit a_1; ^{13}C-NMR (125 MHz, CD_3OD): (unit a_1) 98.3 (C-1), 154.1 (C-3), 113.1 (C-4), 32.9 (C-5), 29.6 (C-6), 156.1 (C-7), 135.5 (C-8), 46.6 (C-9), 120.6 (C-10), 168.2 (C-11), 101.2 (C-1′), 74.7 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 78.3 (C-5′), 62.8 (C-6′); (unit b_1) 97.9 (C-1), 153.2 (C-3), 112.6 (C-4), 33.6 (C-5), 40.4 (C-6), 78.6 (C-7), 41.4 (C-8), 47.1 (C-9), 14.3 (C-10), 169.4 (C-11), 51.9 (OMe), 99.6 (C-1′), 74.7 (C-2′), 78.2 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.8 (C-6′); (unit b_1) 97.2 (C-1), 151.9 (C-3), 109.8 (C- 4), 30.7 (C-5), 143.7 (C-6), 197.2 (C-7), 135.4 (C-8), 45.3 (C-9), 119.6 (C-10), 168.2 (C-11), 101.2 (C-1′), 74.6 (C-2′), 78.0 (C-3′), 71.5 (C-4′), 78.3 (C-5′), 62.8 (C-6′); (unit b_2) 97.7 (C-1), 152.7 (C-3), 111.1 (C-4), 33.0 (C-5), 40.3 (C-6), 77.8 (C-7), 41.1 (C-8), 46.9 (C-9), 14.2 (C-10), 169.4 (C-11), 51.8 (OMe), 100.4 (C-1′), 74.7 (C-2′), 78.2 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.8 (C-6′). *Dipsacus asper*.[73]

172. Dipsanoside B



$C_{66}H_{90}O_{37}$: 1474.5159; white amorphous powder; ^{1}H-NMR (500 MHz, CD_3OD): (unit a_1) 5.34 (d, 6.5, H-1), 7.60 (s, H-3), 2.93 (d, 4.0, H-5), 1.31 (d, 6.5, H_2-6), 6.30 (t, 8.0, H-7), 5.37 (ddd, 17.5, 11.0, 6.5, H-8), 2.67 (ddd, 6.1, 5.8, 4.6, H-9), 5.02 (d, 11.0, H-10), 5.08 (d, 17.5, H-10), 4.66 (d, 8.0, H-1′), 3.11—3.33 (H-2′, 3′, 4′, 5′), 3.60—3.64 (H-6′), 3.80—3.86 (H-6′); (unit b_1) 5.15 (d, 5.5, H-1), 7.37 (s, H-3), 3.04 (dd, 8.0, 8.0, H-5), 1.59 (ddd, 14.0, 8.5, 5.0, H-6), 2.16 (dd, 14.0, 8.0, H-6), 5.16—5.18 (d, 6.0, H-7), 2.02 (m, H-8), 2.09 (ddd, 8.0, 7.0, 6.5, H-9), 1.03 (d, 6.5, H_3-10), 3.25 (s, OMe), 4.60 (d, 8.0, H-1′), other sugar protons appeared at the same values at that of sugar protons of unit a_1; (unit a_2) 5.46 (d, 5.5, H-1), 7.47 (s, H-3), 4.06 (d, 6.0, H-5), 10.00 (s, H-7), 5.71 (ddd, 17.5, 10.5, 8.0, H-8), 2.67 (ddd, 7.5, 6.0, 5.5, H-9), 5.22 (d, 11.0, H-10), 5.27 (d, 17.5, H-10), 4.63 (d, 8.0, H-1′), other sugar protons appeared at the same values at that of unit a_1; (unit b_2) 5.24 (d, 5.0, H-1), 7.37 (s, H-3), 2.90 (ddd, 8.5, 8.0, 7.0, H-5), 1.69—1.74 (m, H-6), 2.24 (dd, 14.0, 8.5, H-6), 5.02—5.10 (d, 6.0, H-7), 2.02 (m, H-8), 1.91 (ddd, 8.5, 6.5, 5.5, H-9), 1.01 (d, 6.5, H_3-10), 3.25 (s, OMe), 4.60 (d, 8.0, H-1′), other sugar protons appeared at the same values at that of sugar protons of unit a_1; ^{13}C-NMR (125 MHz, CD_3OD): (unit a_1) 97.5 (C-1), 154.9 (C-3), 110.4 (C-4), 33.0 (C-5), 21.4 (C-6), 150.8 (C-7), 135.4 (C-8), 45.8 (C-9), 120.5 (C-10), 168.0 (C-11), 100.3 (C-1′), 74.6 (C-2′), 78.0 (C-3′), 71.5 (C-4′), 78.4 (C-5′), 62.8 (C-6′); (unit b_1) 97.8 (C-1), 152.8 (C-3), 113.1 (C-4), 33.0 (C-5), 40.6 (C-6), 78.7 (C-7), 41.2 (C-8), 47.1 (C-9), 14.2 (C-10), 169.4 (C-11), 51.9 (OMe), 100.2 (C-1′), 74.7 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.8 (C-6′); (unit a_2) 98.0 (C-1), 154.0 (C-3), 110.0 (C-4), 34.2 (C-5), 141.1 (C-6), 192.1 (C-7), 135.2 (C-8), 45.2 (C-9), 120.1 (C-10), 167.7 (C-11), 100.1 (C-1′), 74.6 (C-2′), 78.0 (C-3′), 71.4 (C-4′), 78.4 (C-5′), 62.6 (C-6′); (unit b_2) 97.5 (C-1), 152.6 (C-3), 113.1 (C-4), 32.6 (C-5), 40.2 (C-6), 77.3 (C-7), 41.0 (C-8), 46.8 (C-9), 14.1 (C-10), 169.4 (C-11), 51.9 (OMe), 100.2 (C-1′), 74.7 (C-2′), 78.2 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.8 (C-6′). *Dipsacus asper*.[73]

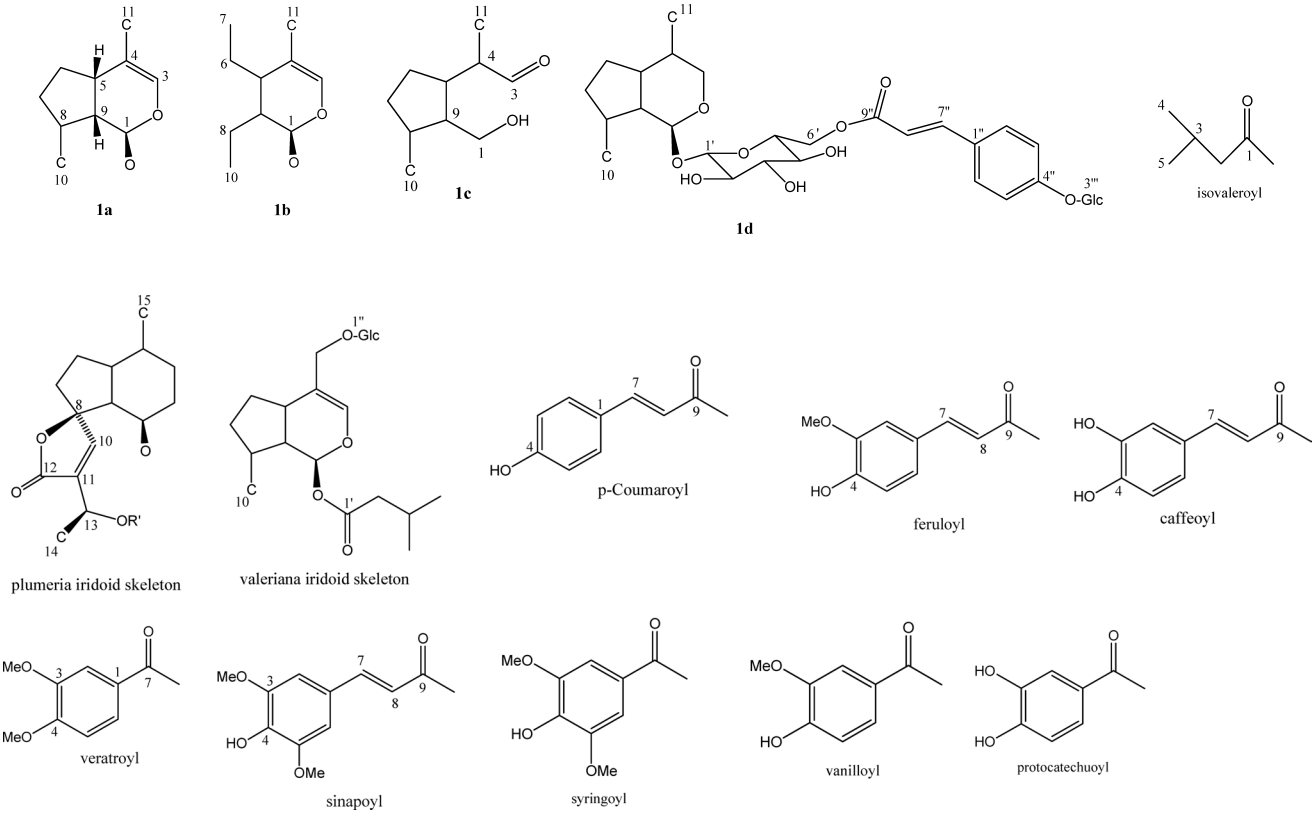


Fig. 1

cally listed in Table 2.

In spite of exhaustive efforts, some new iridoids and secoiridoids may be omitted in the list because of non-availability of the published papers and hence this review should not be used as the only source of new iridoids and secoiridoids reported during the period (2005—2008) of the review.

Biological and Pharmacological Activity of Naturally Occurring Iridoids and Secoiridoids

At present a good number of plant extracts containing iridoids/secoiridoids as chemical constituents are used in preparation of bitter tonics, sedatives, febrifuges, cough medicines, anti-inflammatory, antirheumatic, antiulcer, hypo and

Table 2. Alphabetical Index of Iridoids Cited in Table 1

6-*O*-Acetylantirrinoside **4**
8-*O*-Acetylharpagide-6-*O*-β-glucoside **8**
Alstonoside **133**
Axillaroside **169**
10-*O*-Benzoyl-10-*O*-deacetylasperuloside **100**
10-*O*-Benzoyl-10-*O*-deacetyldaphylloside **91**
10-*O*-Benzoyl-10-*O*-deacetyl-11-demethoxy-11-ethoxydaphylloside **92**
6-*O*-(3″-*O*-Benzoyl) α-L-rhamnopyranosylcatalpol **28**
6-*O*-Caffeoylharpagide **11**
6′-*O*-[(*E*)-Caffeoyl]-deacetylasperulosidic acid methyl ester **88**
6-*O*-*E*-Cinnamoyl-*E*-harpagoside **19**
6-*O*-(3″-*O*-*E*-Cinnamoyl)-α-L-rhamnopyranosylcatalpol **29**
6-*O*-(3″-*O*-*Z*-Cinnamoyl)-α-L-rhamnopyranosylcatalpol **30**
Citrifoside **2**
(Compound **1**) 5-Deoxy-8-deacetyl-3-*O*-methyl-6-*O*-*p*-hydroxybenzoyl-1, 3-di-*epi*-clandonensine **134**

(Compound **2**) 5-Deoxy-8-deacetyl-3-*O*-methyl-6-*O*-*p*-hydroxybenzoyl-1-*epi*-clandonensine **135**
10-*O*-(*E*)-*p*-Coumaroyl deacetylasperulosidic acid **49**
10-*O*-(*Z*)-*p*-Coumaroyl desacetylasperulosidic acid **50**
10-*O*-Coumaroyl-10-*O*-deacetylasperuloside **99**
10-*O*-*p*-Coumaroyl-10-*O*-deacetyldaphylloside **89**
10-*O*-*p*-Coumaroyl-10-*O*-deacetyl-11-demethoxy-11-ethoxydaphylloside **90**
10-(*E*)-*p*-Coumaroyl-6,7-dihydromonotropein **45**
10-(*Z*)-*p*-Coumaroyl-6,7-dihydromonotropein **46**
6′-*O*-*E*-*p*-Coumaroyl-3,4-dihydrocatalpol (Piscroside B) **25**
6′-*O*-(*E*)-*p*-Coumaroyl-8-*epi*-loganic acid **44**
10-*O*-(*E*)-*p*-Coumaroylscandoside **47**
10-*O*-(*Z*)-*p*-Coumaroylscandoside **48**
6′-*O*-*p*-Coumaroyl-8-epikingiside **126**
6′-*O*-*E*-*p*-Coumaroylgardoside **72**
4″-*O*-[(*E*)-*p*-Coumaroyl]-gentiobiosylgenipin **82**
6′-*O*-Cyclopropanoyltheviridoside **79**
Daphmacropodosidine A **122**
Daphmacropodosidine B **123**
6,7-Dehydro-8-acetylharpagide **9**
5-Dehydro-8-*epi*-adoxosidic acid **56**
7,8-Dehydroharpagide **3**
5-Dehydro-8-*epi*-mussaenoside **110**
11-Demethoxy-11-ethoxydaphylloside **93**
7-Deoxyloganic acid-β-D-glucopyranosyl ester **96**
8-Deoxyshanzhiside **69**
6,8-Diacetylharpagide **16**
6,8-Diacetylharpagide-1-*O*-β-(2′,3′-di-*O*-acetylglucoside) **17**
1,5-Dihydroxy-3,8-epoxyvalechlorine A **152**
10-*O*-Dihydroferuloyl-10-*O*-deacetyldaphylloside **94**
Dipsanoside A **171**
Dipsanoside B **172**
Dipsanoside C **163**
Dipsanoside D **164**
Dipsanoside E **165**
Dipsanoside F **166**
Dipsanoside G **167**
Eucomoside A **95**
Eucomoside B **84**
Eucomoside C **85**
6-*epi*-Barlerin **108**
13(*R*)-*epi*-Epoxygaertneroside **119**
13(*R*)-*epi*-Gaertneroside **118**
Eriobioside (Ipolamiide 6′-*O*-β-glucopyranoside) **111**
6′-*O*-Feruloylharpagide **12**
6′-*O*-α-D-Galactopyranosylbarlerin **107**
6′-*O*-α-D-Galactopyranosylphlorigidoside C **103**
6′-*O*-α-D-Galactopyranosylshanzhiside methyl ester **109**
6′-*O*-α-D-Galactopyranosylsesamoside **105**
Gardaloside **43**
Genameside A **73**
Genameside B **74**
Genameside C **75**
Genameside D **76**
Genestifolioside **15**
Genipin-1-*O*-α-L-rhamnopyranosyl(1→6)-β-D-glucopyranoside **78**
Globularioside **1**
6′-*O*-β-D-Glucopyranosylbarlerin **106**
6′-*O*-Glucopyranosylharpagoside **13**
5-*O*-β-Glucopyranosylharpagide **14**
6′-*O*-β-D-Glucopyranosylphlorigidoside C **102**
6′-*O*-β-Glucopyranosylsecologanoside **131**
6′-*O*-β-D-Glucopyranosylsecologanol **132**
6′-*O*-β-D-Glucopyranosylsesamoside **104**
3′-*O*-β-D-Glucopyranosylsweroside **130**
Harpagide 6-*O*-β-glucoside **7**
Harprocumbide A (6′-*O*-α-D-Galactopyranosyl-harpagoside) **18**
Harprocumbide B (6′-*O*-(*cis*-*p*-Coumaroylprocumbide)) **6**
Hedycoryside A **83**
Hedycoryside B **86**
Hedycoryside C **51**
6′-*O*-*p*-Hydroxybenzoylantirrinoside **5**
2′-*O*-(3″-Hydroxybenzoyl)-8-epikingiside **124**
2′-*O*-(3″-Hydroxybenzoyl)-kingiside **125**
10-*O*-*p*-Hydroxybenzoyltheveridoside **80**
6β-Hydroxy-7-epigardoside methyl ester **114**
6β-Hydroxy-2-oxabicyclo[4.3.0]non-8-en-1-one **147**
Incaside **170**
Isoplumericin **150**
10-Isovalerylkanokoside C **117**
Kankanol **141**
Kankanoside A **42**
Kankanoside B **33**
Kankanoside C **34**
Kankanoside D **129**
6-Keto-8-acetylharpagide **10**
Lamalbidic acid **70**
Lamerioside **112**
Loganic acid 11-*O*-β-glucopyranosyl ester **97**
Marinoid A **64**
Marinoid B **65**
Marinoid C **66**
Marinoid D **54**
Marinoid E **55**
2′-*O*-(4-Methoxycinnamoyl)mussaenosidic acid **68**
8-Methylvalepotriate **154**
Morindacin **140**
Myobontioside A **36**
Myobontioside B **31**
Myopochlorin **143**
Paederoside B **168**
Pensteminoside **27**
1β,6β,7α,8α,10-Pentahydroxy-*cis*-2-oxabicyclo[4.3.0]nonane **146**
2′-*O*-[(2*E*,4*E*)-5-Phenylpenta-2,4-dienoyl]mussaenosidic acid **67**
Picroroside A **38**
Picroroside B **39**
Picroroside C **40**
Piscrocin D **142**
Piscrocin E **137**
Piscrocin F **138**
Piscrocin G **139**
Piscroside A (7-Deoxy-7-α-Cl-pikuroside) **37**
Piscroside B (6′-*O*-*E*-Cinnamoyl-3β-methoxy-3,4-dihydro-catalpol) **26**
Plumericin **149**
Prismatomerin **151**
Rupesin A **159**
Rupesin B **162**
Rupesin C **160**
Rupesin D **161**
Rupesin E **153**
Scutelloside **41**
Scyphiphorin A (10-*O*-Benzoylgeniposidic acid) **52**
Scyphiphorin B **53**
Shanzhilactone **136**
6′-*O*-[(*E*)-Sinapoyl]gardoside **71**

6′-*O*-Sinapoylgeniposide **77**
Stachysoside E (3″-*O*-*p*-Coumaroyl ester of melittoside) **20**
Stachysoside F **21**
Stachysoside G **22**
Stachysoside H **23**
Stereospermoside (6-*O*-*trans*-*p*-Coumaroyl-decinnamoyl globularimin) **35**
Tarennin (artifact) **148**
Tarenninoside A **57**
Tarenninoside B **58**
Tarenninoside C **59**
Tarenninoside D **60**
Tarenninoside E **61**
Tarenninoside F **62**
Tarenninoside G **63**
Teneoside A (10-*O*-(α-L-Rhamno) deacetylasperuloside) **98**
Teneoside B **87**
6β,7β,8α,10-Tetrahydroxy-*cis*-2-oxabicyclo[4.3.0]nonan-3-one **144**
6β,7β,8α,10-Tetra-*p*-hydroxybenzoyl-*cis*-2-oxabicyclo[4.3.0]nonan-3-one **145**
Tudoside **113**
(*E*)-Uenfoside **120**
(*Z*)-Uenfoside **121**
Valeriotetrate C **156**
Valeriotriate A **157**
Valeriotriate B **158**
10-*O*-Vanilloyltheviridoside **81**
6′-*O*-Vanilloyl-3,4-dihydrocatalpol (Piscroside A) **24**
Verbenabraside A **127**
Verbenabraside B **128**
Versibirioside **32**
Viburtinoside A **115**
Viburtinoside B **116**
Wendoside **101**

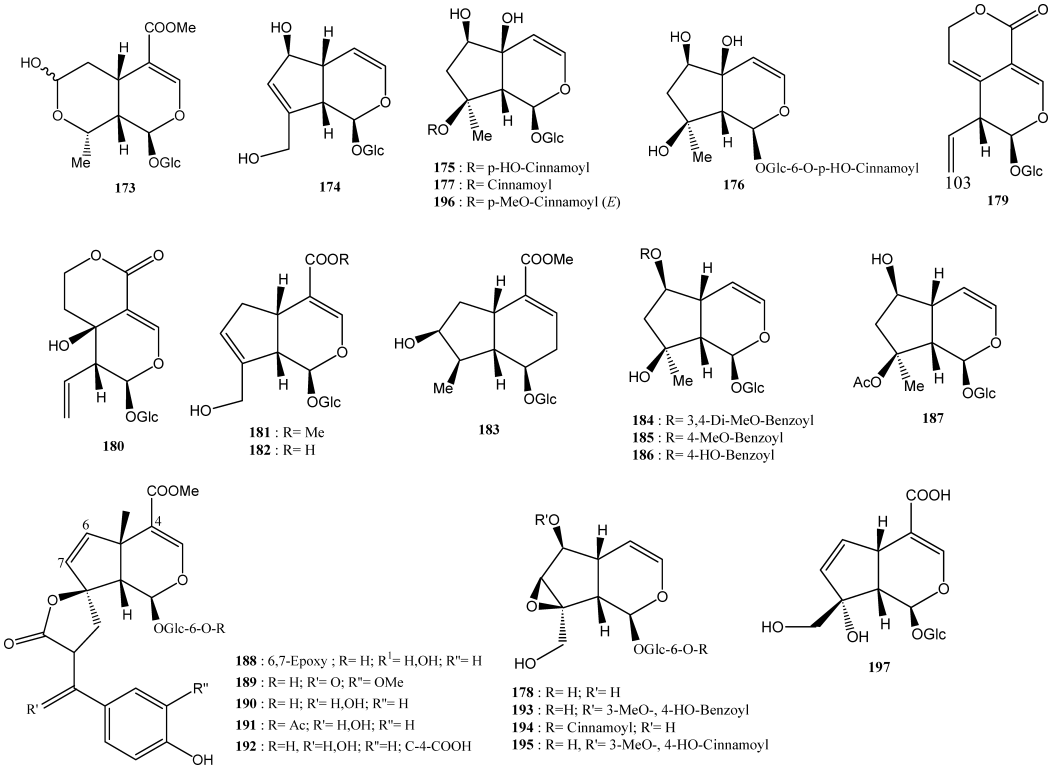


Fig. 2

hypertensive drugs formulations. This fact encouraged for extensive study of different bioactivities of the isolated iridoids, secoiridoids and other phytochemicals from these plant extracts. The biological study on this class of compounds revealed that these compounds exhibit a wide range of bioactivity. In the present review only the pharmacological or biological activities of pure iridoids and secoiridoids published during mid 2005 to 2008 are highlighted.

a. Antibacterial Activity The roots of *Patrinia rupestris* have long been used as Chinese folk medicine for treatment of enteritis, appendicitis and hepatitis.[74] To find out the bioactive principles from the root of this plant, Yang *et al.* isolated several iridoids and evaluated their antibacterial activities. Out of them, two iridoids namely, rupesins C (**160**) and D (**161**) showed significant antibacterial activities against *Bacillus subtilis*, *Escherichia coli* and *Staphylococcus aureus* at a concentration of 100 μg/ml with inhibition zones of 13—20 mm in diameter in cup-plate assay method.[68]

b. Antifungal Activity Iridoid glycoside, 6β-hydroxy-7-epigardoside methyl ester (**114**) isolated from Brazilian Rubiaceae plant, *Alibertia edulis* showed moderate antifungal activity against *Candida albicans* and *C. krusei* with an MIC value of 125 μg/ml in a dilution assay method.[54]

c. Anticancer Activity The leaves of evergreen shrub, *Prismatomeris tetrandra* of temperate areas of Bangladesh and ajoining areas of India have been used in treatment of several ailments like stomachaches and poultices of fresh wounds.[75] Phytochemical investigation afforded several iridoids. Among the isolated iridoids, prismatomerin (**151**) showed remarkable antitumor activity against four mammalian cancer cell lines. L-929 (murine connective tissue),

KB-3-1 (human cervix carcinoma), A-549 (human lung carcinoma) and SW-480 (human colon adenocarcinoma) with IC_{50} values of 0.21, 0.41, 1.41 and 0.06 μM, respectively in *in vitro* sulforhodamine B (SRB) protein assay method.[66] This compound also showed cell killing effect in solid tumor cell lines like renal cancer (A 498), prostrate cancer (PC-3) and breast cancer (MCF 7) with LC_{50} values in the range of 100 to 0.6 μM.[66]

Morroniside (**173**) a C_{10}-iridoid glucoside isolated from *Lonicera* spp. prevented significantly hydrogen peroxide (H_2O_2) induced apoptosis in human neuroblastoma SH-SY5Y cells at a concentration of 1—100 μM by elevation of cellular glutathione (GSH) levels.[76]

Aucubin (**174**) isolated from the leaves of *Aucuba japonica* inhibited human lung cancer (A-549) cell line by blocking the cell cycle progression in the G(0)/G(1) phase and inducing apoptosis. An enzyme linked imnunosorbent (ELISA) assay showed that the G(0)/G(1) phase arrest was possibly due to p53-mediated induction of p21.[77]

8-*O*-(*p*-Coumaroyl)-harpagide (**175**) of *Harpagophytum procumbens* showed moderate inhibition activity against respiratory raw 264.7 macrophage cell line with an IC_{50} value of about 32 μM in chemiluminescence assay method. Phorbol 12-myristate 13-acetate (PMA) was applied as triggering agent and chemiluminescence was measured with luminal.[11] It may be noted that the dried tubers of the plant are traditionally used as a folk medicine for treatment of skin cancer, allergics, rheumatism and arthritis.[78]

d. Anticardiac Activity The roots of *Scrophularia ningpoensis* have been used as a famous herbal medicine in China for the treatment of hypertension, inflammation, dry cough, pharyngitis and pulmonary tuberculosis.[79] From the 60% ethanol extract of the roots of this plant several iridoid and aromatic glycosides have been isolated and their activity on the regulation of Ca^{2+} ion concentration on rat cardiac myocytes was evaluated. It was observed that iridoid glycosides (**11**, **176**, **177**) significantly inhibited the increase of Ca^{2+} ion induced by KCl at 100 μM. This study indicates that these iridoids might contribute to prophylactic and therapeutic effects on myocardial damage through accumulation of Ca^{2+} ions.[12]

e. Anti-coagulant Activity The iridoid diglycoside (**78**) isolated from the bark of *Adina polycephala* showed potent *in vitro* inhibitory activity against the release of β-glucuronidase in rat polymorphonuclear leukocytes induced by platelet-activating factor (PAF) with an inhibitory rate of 44.8% at a concentration of 10^{-5} M. At the same concentration, the positive control, ginkgolide B gave an inhibition rate of 78.8%. Hence the use of this plant in treatment of inflammatory diseases is justified.[43]

f. Anti-inflammatory Activity The anti-inflammatory potency of seven iridoid glucosides namely, aucubin (**174**), catalpol (**178**), gentiopicroside (**179**), swertiamarin (**180**), geniposide (**181**), geniposidic acid (**182**) and loganin (**183**) was investigated with *in-vitro* testing model systems on inhibition of cyclooxygenase (COX)-1/2 enzymes, the tumor necrosis factor (TNF-α) formation and nitric oxide (NO) production. No single iridoid glucoside exhibited any activities. β-Glucosidase hydrolysis product of the iridoids showed inhibitory activities of different potencies, depending on their chemical structures. The hydrolysed (H)-geniposide and H-loganin exhibited high inhibitory potencies on COX-1 with IC_{50} values of 3.55 and 5.37 μM, respectively. The H-aucubin showed a moderate inhibition on COX-2 with IC_{50} of 8.83 μM but much less inhibition on COX-1 (IC_{50}, 68.9 μM). In addition, H-aucubin only exhibited suppressive activities on both NO production and TNF-α formation with IC_{50} values of 14.1 and 11.2 μM, respectively. Genipin, an aglycone form showed no inhibitory effects on all the testing models, suggesting that possibly the enzymatic hydrolysis of the glycosidic bond of iridoid glycoside is a pre-requisite step to produce various biological activities.[80]

The Brazilian popular tree, *Tabebuia avellanedae* is used as anti-inflammatory medicine in Latin America. Its water extract of the inner bark showed inhibitory activity on NO production in lipopolysaccharide (LPS)-activated J 774.1 macrophage-like cells with an IC_{50} value of 64.7 μg/ml. To find out the bioactive principle from the water extract, fifteen compounds were isolated. Among the isolated compounds, four iridoids (**134**, **184**—**186**) showed potent NO inhibitory activity (IC_{50} values in the range of 13.8—26.1 μg/ml) compared to that of the positive control N^G-monomethyl-L-arginine (L NMMA; IC_{50}, 27.4 μg/ml).[60] This result corroborated the traditional use of this plant as an anti-inflammatory medicine.

g. Antioxidative Activity Secoiridoid, verbenabraside A (**127**) isolated from Japanese wild plant, *Verbena brasiliensis* exhibited stronger radical scavenging effect on 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical than that of standard antioxidant, α-tocopherol at the same concentration of 0.02 mM in 0.1 M acetic acid buffer (pH 5.5) solution in spectrophotometric assay at 517 nm.[57]

Iridoid, ajugoside C (**187**) isolated from *Sideritis perfoliata* L. subsp. *perfoliata* of Greek origin exhibited weak antioxidative effect on DPPH radical in the range of 6.3—23.6% at a concentration of 0.1 μM in spectrophotometric assay method.[81]

h. Anti-protozoal Activity Iridoids, epoxygaertneroside (**188**), methoxygaertneroside (**189**), gaertneroside (**190**), acetylgaertneroside (**191**) and gaertneric acid (**192**) isolated from 80% methanolic extract of *Morinda morindoides* leaves showed significant antiamoebic activity against *Entamoeba histolytica* with IC_{50} values of 1.3, 2.3, 4.3, 5.4 and 7.1 μg/ml, respectively. All these iridoids were devoid of any cytotoxic effect against MT-4 cells at the highest test concentration of 250 μg/ml.[82]

i. Hepatoprotective Activity The Chinese plant, *Neopicrorhiza scrophulariiflora* is used in traditional Chinese medicine for treatment of damp-heat dysentery, jaundice and steaming of bone.[83] The ethanol extract of this plant had been shown to possess hepatoprotective activities against carbon tetrachloride (CCl_4), thioacetamide and acetaminophen-induced liver damage in mice.[84] Bioassay guided analysis of *n*-BuOH portion from the ethanol extract of this plant led to the isolation of thirteen non-glycosidic iridoids and iridoid glycosides. Study of the hepatoprotective activity of these iridoids on CCl_4-induced mice hepatocytes damage *in vitro* indicated that piscroside B (**26**), picroside II (**193**), picroside I (**194**), and picroside III (**195**) exhibited potent hepatoprotective effects with IC_{50} values of 7.3, 4.7, 8.3 and 5.9 μM, respectively. It was also observed that iridoids with a glycosidic linkage at C-1 were less active than those non-glyco-

sidic iridoids. These observations revealed that major iridoid glycosides are probably the pro-drugs and those non-glycosidic iridoids derived from the parent compounds are the pharmacophores.[57)]

j. Neuroprotective Activity Catalpol (**178**) contained richly in the roots of *Rehmannia glutinosa* was found to be of neuroprotection in Mongolian gerbils subjected to transient global cerebral ischemia. Catalpol at a dose of 1 mg/kg body wt intraperitoneally (i.p.) used immediately after reperfusion and repeatedly at 12, 24, 48 and 72 h significantly rescued neurons in hippocampal CA1 subfield and reduced working errors during behavioral testing. The neuroprotective efficacy of catalpol became more evident when the doses were increased to 5 and 10 mg/kg body weight. This neuroprotective efficacy of catalpol became weak when catalpol was given at 6 h after ischemia. This neuroprotection of catalpol was seen in a long post-ischemic period (35 d). All these findings indicated that catalpol might be of therapeutic value for the treatment of global cerebral ischemia.[85)]

Catalpol (**178**) also showed significant neuroprotective efficacy in memory damage of mice induced by subcutaneous injection of *d*-galactose (150 mg/kg body weight) for six weeks and application of catalpol in the dose range of 2.5—10 mg/kg body weight for the last two weeks. The brain damage and pathological alternations were measured by hematoxylin and eosin (HE) staining. It was observed that the activities of glutathione *S*-transferase (GSH-ST), glutathione synthetase (GS) and creative kinase (CK) were decreased while the activity of lactate dehydrogenase (LDH) was increased in aging mice brain cortex. This result indicates that catalpol might be useful for the study of neurodegenerative diseases such as Alzheimer's disease and Parkinson's disease.[86)]

Catalpol also exhibited neuroprotective effect on 1-methyl-4-phenylpyridinium (MPP^+)-induced oxidative stress in cultured mesencephalic neurons especially dopaminergic neurons in a dose-dependent manner.[87)]

Catalpol also protected the H_2O_2-injured astrocytes which have critical role in the brain for neurodegenerative disorders. Possibly this iridoid protected them by reducing intracellular ROS formation.[88)]

(*E*)-Harpagoside (**177**) and 8-*O*-(*E*)-*p*-methoxycinnamoyl harpagide (**196**) isolated from *Scrophularia buergeriana* exerted potent cognitive-enhancing activity in scopolamine induced amnestic mice at a dose of 2 mg/kg body weight, *per os* (*p.o.*). Donepezil, an acetylcholinesterase inhibitor and most widely used drug for Alzheimer's disease treatment was employed as positive control. The activity of acetylcholinesterase was inhibited significantly by both (*E*)-harpagoside and 8-*O*-(*E*)-*p*-methoxycinnamoyl harpagide (MCA-Hg) within the cortex and hippocampus to a level similar to that observed in mice treated with donepezil (2 mg/kg body weight, *p.o.*). The treatment with (*E*)-harpagoside or MCA-Hg to scopolamine-induced amnestic mice also significantly decreased TBARS level. Thus this cognitive-enhancing activity of the iridoids was possibly took place through both anti-acetylcholinesterase and anti-oxidant mechanisms.[89)]

k. Antinociceptive Activity Monotropein (**197**) isolated from the roots of *Morinda officinalis* significantly contributed to antinociceptive activity by reducing streching episodes in mice in hot plate and writhing assays at a dose of 20 and 30 mg/kg body weight *p.o.*[90)]

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References

1) Dinda B., Debnath S., Harigaya Y., *Chem. Pharm. Bull.*, **55**, 159—222 (2007).
2) Dinda B., Debnath S., Harigaya Y., *Chem. Pharm. Bull.*, **55**, 689—728 (2007).
3) El-Naggar L. J., Beal J. L., *J. Nat. Prod.*, **43**, 649—707 (1980).
4) Boros C. A., Stermitz F. R., *J. Nat. Prod.*, **53**, 1055—1147 (1990).
5) Boros C. A., Stermitz F. R., *J. Nat. Prod.*, **54**, 1173—1246 (1991).
6) Al-Hazimi H. M. G., Alkhathlan H. Z., *J. Chem. Soc. Pakisthan*, **18**, 336—357 (1996).
7) Es-Safi N. E., Khlifi S., Kollman A., Kerhoas L., Abbouyi A. E., Ducrot P. H., *Chem. Pharm. Bull.*, **54**, 85—88 (2006).
8) Takashima J., Ikeda Y., Komiyama K., Hayashi M., Kishida A., Ohsaki A., *Chem. Pharm. Bull.*, **55**, 343—345 (2007).
9) Manguro L. O. A., Ogur J. A., Okora D. M., Wagai S. O., Lemmen P., *J. Asian Nat. Prod. Res.*, **9**, 617—629 (2007).
10) Al-Rehaily A. J., Abdel-Kader M. S., Ahmad M. S., Mossa J. S., *Phytochemistry*, **67**, 429—432 (2006).
11) Qi J., Chen J. J., Cheng Z. H., Zhou J. H., Yu B. Y., Qiu S. X., *Phytochemistry*, **67**, 1372—1377 (2006).
12) Chen B., Liu Y., Liu H. W., Wang N. L., Yang B. F., Yao X. S., *Chem. Biodiv.*, **5**, 1723—1735 (2008).
13) Kanchanapoom T., Chumsri P., Kasai R., Otsuka H., Yamasaki K., *J. Asian Nat. Prod. Res.*, **7**, 269—272 (2005).
14) Ahmad V. U., Kousar F., Zubair M., Khan A., Shaiq Ali M., Iqbal Choudhary M., Sener B., *Fitoterapia*, **77**, 12—14 (2006).
15) Arot Manguro L. O., Wagai S. O., Lemmen P., *Phytochemistry*, **67**, 830—837 (2006).
16) Yu H. W., Li B. G., Li G. Y., Li C. S., Fang D. M., Zhang G. L., *Chem. Pharm. Bull.*, **55**, 1744—1747 (2007).
17) Murata T., Endo Y., Miyase T., Yoshizaki F., *J. Nat. Prod.*, **71**, 1768—1770 (2008).
18) Huang S. X., Zhou Y., Nie Q. J., Ding L. S., Peng S. L., *J. Asian Nat. Prod. Res.*, **8**, 259—263 (2006).
19) Wang H., Wu F.-H., Xiong F., Wu J.-J., Zhang L.-Y., Ye W.-C., Li P., Zhao S. X., *Chem. Pharm. Bull.*, **54**, 1144—1149 (2006).
20) Dominguez M., Marin J. C., Esquivel B., Cespedes C. L., *Phytochemistry*, **68**, 1762—1766 (2007).
21) Tiwari N., Yadav A. K., Srivastava P., Shanker K., Verma R. K., Gupta M. M., *Phytochemistry*, **69**, 2387—2390 (2008).
22) Guo Y., Xu J., Li Y., Watanabe R., Oshima Y., Yamakuni T., Ohizumi Y., *Chem. Pharm. Bull.*, **54**, 123—125 (2006).
23) Kanemoto M., Matsunami K., Otsuka H., Shinzato T., Ishigaki C., Takeda Y., *Phytochemistry*, **69**, 2517—2522 (2008).
24) Teng J., Zhang F. G., Zhang Y. W., Takaishi Y., Duan H. Q., *Chinese Chem. Lett.*, **19**, 450—452 (2008).
25) Xie H., Morikawa T., Matsuda H., Nakamura S., Muraoka O., Yoshikawa M., *Chem. Pharm. Bull.*, **54**, 669—675 (2006).
26) Kanchanapoom T., Noiarsa P., Otsuka H., Ruchirawat S., *Phytochemistry*, **67**, 516—520 (2006).
27) Kim I. H., Uchiyama N., Kawahara N., Goda Y., *Phytochemistry*, **67**, 2691—2696 (2006).
28) Gousiadou C., Karioti A., Heilmann J., Skaltsa H., *Phytochemistry*, **68**, 1799—1804 (2007).
29) Chang W. L., Wang H. Y., Shi L. S., Lai J. H., Lin H. C., *J. Nat. Prod.*, **68**, 1683—1685 (2005).
30) Turner A., Chen S. N., Nikolic D., van Breemen R., Farnsworth N. R., Pauli G. F., *J. Nat. Prod.*, **70**, 253—258 (2007).
31) Huang X. Z., Wang Y. H., Yu S. S., Fu G. M., Hu Y. C., Liu Y., Fan L. H., *J. Nat. Prod.*, **68**, 1646—1650 (2005).
32) Jiang W., Kuang L. S., Hou A. J., Qian M., Li J. Z., *Helv. Chim. Acta*, **90**, 1296—1301 (2007).
33) Tao S. H., Wu J., Qi S. H., Zhang S., Li M. Y., Li Q. X., *Helv. Chim. Acta*, **90**, 1718—1722 (2007).
34) Sun Y., Ouyang J., Deng Z., Li Q., Lin W., *Magn. Reson. Chem.*, **46**,

638—642 (2008).
35) Dinda B., Debnath S., Arima S., Sato N., Harigaya Y., *Chem. Pharm. Bull.*, **54**, 1030—1033 (2006).
36) Yang X. W., Ma Y. L., He H. P., Wang Y. H., Di Y. T., Zhou H., Li L., Hao X. J., *J. Nat. Prod.*, **69**, 971—974 (2006).
37) Feng Y., Li X. M., Duan X. J., Wang B. G., *Chem. Biodiv.*, **3**, 799—806 (2006).
38) Li M., Jia Z., Zhang R., Hu Z., Tian X., *Carbohydr. Res.*, **343**, 561—565 (2008).
39) Calis I., Guvenc A., Armagan M., Koyuncu M., Gotfredsen C. H., Jensen S. R., *Helv. Chim. Acta*, **90**, 1461—1466 (2007).
40) Fu X. M., Chou G. X., Wang Z. T., *Helv. Chim Acta*, **91**, 646—652 (2008).
41) Ono M., Ueno M., Masuoka C., Ikeda T., Nohara T., *Chem. Pharm. Bull.*, **53**, 1342—1344 (2005).
42) Zhou X. Q., Bi Z. M., Li P., Tang D., Cai H. X., *Chin. Chem. Lett.*, **18**, 1221—1223 (2007).
43) Zhang Y., Gan M., Lin S., Liu M., Song W., Zi J., Wang S., Li S., Yang Y., Shi J., *J. Nat. Prod.*, **71**, 905—909 (2008).
44) Martin F., Hay A. E., Corno L., Gupta M. P., Hostettmann K., *Phytochemistry*, **68**, 1307—1311 (2007).
45) Takamura C., Hirata T., Ueda T., Ono M., Miyashita H., Ikeda T., Nohara T., *J. Nat. Prod.*, **70**, 1312—1316 (2007).
46) Zhao J. F., Yuan Q. M., Yang X. D., Zhang H. B., Li L., *Helv. Chim. Acta*, **88**, 2532—2536 (2005).
47) Bai H., Hu L., *Helv. Chim. Acta*, **89**, 884—894 (2006).
48) Kikuchi M., Kakuda R., Kikuchi M., Yaoita Y., *Chem. Pharm. Bull.*, **56**, 610—611 (2008).
49) Xu M., Wang D., Zhang Y. J., Yang C. R., *J. Asian Nat. Prod. Res.*, **10**, 491—498 (2008).
50) Tan J. J., Tan C. H., Li M., Jiang S. H., Zhu D. Y., *Helv. Chim. Acta*, **90**, 143—148 (2007).
51) Dinda B., Majumder S., Arima S., Sato N., Harigaya Y., *J. Nat. Med.*, **62**, 447—451 (2008).
52) Yalcm F. N., Ersoz T., Avci K., Gotfredsen C. H., Jensen S. R., Calis I., *Helv. Chim. Acta*, **90**, 332—336 (2007).
53) Schripsema J., Caprini G. P., van der Heijden R., Bino R., de Vos R., Dagnino D., *J. Nat. Prod.*, **70**, 1495—1498 (2007).
54) da Silva V. C., Giannini M. J. S. M., Carbone V., Piacente S., Pizza C., Bolzani V. da S., Lopes M. N., *Helv. Chim. Acta*, **91**, 1355—1362 (2008).
55) Mohamed M. A., Marzouk M. S. A., Moharram F. A., El-Sayed M. M., Baiuomy A. R., *Phytochemistry*, **66**, 2780—2786 (2005).
56) Kong N. C., He H. P., Wang Y. H., Gao S., Di Y. T., Hao X. J., *Helv. Chim. Acta*, **90**, 972—976 (2007).
57) Ono M., Oishi K., Abe H., Masuoka C., Okawa M., Ikeda T., Nohara T., *Chem. Pharm. Bull.*, **54**, 1421—1424 (2006)
58) Tian X. Y., Wang Y. H., Liu H. Y., Yu S. S., Fang W. S., *Chem. Pharm. Bull.*, **55**, 1677—1681 (2007).
59) Thomas P. S., Kanaujia A., Ghosh D., Duggar R., Katiyar C. K., *Indian J. Chem.*, **47B**, 1298—1302 (2008).
60) Awale S., Kawakami T., Tezuka Y., Ueda J. Y., Tanaka K., Kadota S., *Chem. Pharm. Bull.*, **53**, 710—713 (2005).
61) Dinda B., Debnath S., Majumder S., Arima S., Sato N., Harigaya Y., *Indian J. Chem.*, **44B**, 2362—2366 (2005).
62) Kamiya K., Tanaka Y., Endang H., Umar M., Satake T., *Chem. Pharm. Bull.*, **53**, 1597—1599 (2005).
63) Valladares M. G., Rios M. Y., *J. Nat. Prod.*, **70**, 100—102 (2007).
64) Elsasser B., Krohn K., Akhtar M. N., Florke U., Kouam S. F., Kuigoua M. G., Ngadjui B. T., Abegaz B. M., Antus S., Kurtan T., *Chem. Biodiv.*, **2**, 799—808 (2005).
65) Stephens P. J., Pan J. J., Krohn K., *J. Org. Chem.*, **72**, 7641—7649 (2007).
66) Krohn K., Gehle D., Dey S. K., Nahar N., Mosihuzzaman M., Sultana N., Sohrab M. H., Stephens P. J., Pan J. J., Sasse F., *J. Nat. Prod.*, **70**, 1339—1343 (2007).
67) Wang R., Xiao D., Bian Y. H., Zhang X. Y., Li B. J., Ding L. S., Peng S. L., *J. Nat. Prod.*, **71**, 1254—1257 (2008).
68) Yang X. P., Li E. W., Zhang Q., Yuan C. S., Jia Z. J., *Chem. Biodiv.*, **3**, 762—770 (2006).
69) Yu L., Huang R., Han C., Lv Y., Zhao Y., Chen Y., *Helv. Chim. Acta*, **88**, 1059—1062 (2005).
70) Zou X., Peng S., Liu X., Bai B., Ding L., *Fitoterapia*, **77**, 374—377 (2006).
71) Itoh A., Tanaka Y., Nagakura N., Akita T., Nishi T., Tanahashi T., *Phytochemistry*, **69**, 1208—1214 (2008).
72) Dinda B., Debnath S., Majumder S., Arima S., Sato N., Harigaya Y., *Chinese Chem. Lett.*, **17**, 1331—1334 (2006).
73) Tian X. Y., Wang Y. H., Yu S. S., Fang W. S., *Org. Lett.*, **8**, 2179—2182 (2006).
74) Jiangsu New Medical College, "Chinese Medicine Dictionary," Shanghai People's Publishing House, Shanghai, 1986, pp. 1347—1349.
75) Ambasta S. P., "The Useful Plants of India, Raw Materials, Publication and Information Directorate," CSIR, New Delhi, 1992, p. 491.
76) Wang W., Huang W., Li L., Ai H., Sun F., Liu C., An Y., *Cell. Mol. Neurobiol.*, **28**, 293—305 (2008).
77) Hung J. Y., Yang C. J., Tsai Y. M., Huang H. W., Huang M. S., *Clin. Exp. Pharmacol. Physiol.*, **35**, 995—1001 (2008).
78) Stewart K. M., Cole D., *J. Ethnopharmacol.*, **100**, 225—236 (2005).
79) Jiangsu New Medical College, "Dictionary of Chinese Medical Material," Shanghai Scientific and Technical Publisher, Shanghai, 1997.
80) Park K. S., Kim B. H., Chang I. M., *Evid. Based Complement Alternat. Med.*, July 27, 2007 (Epub ahead of print); DOI: 10.1093/ecam/nem 129.
81) Charami M. T., Lazari D., Karioti A., Skaltsa H., Hadjipavlou-Litina D., Souleles C., *Phytother. Res.*, **22**, 450—454 (2008).
82) Cimanga K., Kambu K., Tona L., Hermans N., Apers S., Totte J., Pieters L., Vlietinek A. J., *Planta Med.*, **72**, 751—753 (2006).
83) State Pharmacopeia Commission of P. R. China, "Pharmacopeia of the P.R. China," Vol. 1, People's Health Publishing House & Chemical Industry Publishing House, Beijing, 2005, pp. 167—168.
84) Liu J., Liu B. L., Zhang J. Q., Zhang N., *Chin. J. New Drugs*, **11**, 459—461 (2002).
85) Li D. Q., Li Y., Liu Y., Bao Y. M., Hu B., An L. J., *Toxicon*, **46**, 845—851 (2005).
86) Zhang X. L., An L. J., Bao Y. M., Wang J. Y., Jiang B., *Food Chem. Toxicol.*, **46**, 2888—2894 (2008).
87) Tian Y. Y., Jiang B., An L. J., Bao Y. M., *Eur. J. Pharmacol.*, **568**, 142—148 (2007).
88) Bi J., Jiang B., Liu J. H., Lei C., Zhang X. L., An L. J., *Neurosci. Lett.*, **442**, 224—227 (2008).
89) Jeong E. J., Lee K. Y., Kim S. H., Sung S. H., Kim Y. C., *Eur. J. Pharmacol.*, **588**, 78—84 (2008).
90) Choi J., Lee K. T., Choi M. Y., Nam J. H., Jung H. J., Park S. K., Park H. J., *Biol. Pharm. Bull.*, **28**, 1915—1918 (2005).