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Triterpenes and other Metabolites from *Tibouchina urvilleana*

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Abstract. The chemical study of the leaves and stems of *Tibouchina urvilleana* afforded triterpenes of different types: four oleanane, four ursane, one glutinane, and one taraxerane. Also, two flavonoids and two sterols were isolated. Additionally, the toxicity and topical anti-inflammation activity of the extracts were tested.
Key Words: *Tibouchina urvilleana*, Melastomataceae, triterpenes, flavonoids, sterols.

Resumen. El estudio químico de las hojas y tallos de *Tibouchina urvilleana* permitió aislar triterpenos de diferentes tipos: cuatro oleananos, cuatro ursanos, un glutinano y un taraxerano. También se obtuvieron dos flavonoides y dos esteroles. Adicionalmente, se realizaron pruebas de toxicidad y de actividad tópica anti-inflamatoria de los extractos.
Palabras Clave: *Tibouchina urvilleana*, Melastomataceae, triterpenos, flavonoides, esteroles.

Introduction

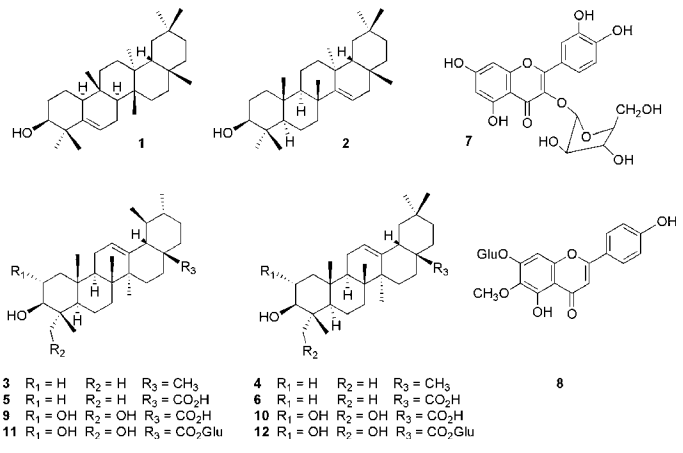
The genus *Tibouchina* Aubl. (Melastomataceae) comprises about 240 species distributed from southern Mexico to northern Argentina [1]. A characteristic of their flowers is the beautiful dark purple color; therefore, several species are currently cultivated as ornamental plants. Also, some species of *Tibouchina* are used in the popular medicine, as *T. grandifolia* whose tea from leaves is utilized to enhance wound healing in Brazil [2]. Although *Tibouchina* is a large genus only eight species have been investigated chemically. The results obtained so far point to phenolic compounds as substances characteristic of this genus. Flavonol glycosides as quercetin 3-*O*-rhamnopyranoside and quercetin 3-*O*-*β*-D-glucopyranoside have been isolated from the leaves of *T. ciliaris* [3], *T. grandifolia* [2], and *T. semidecandra* [4a]. Hydrolysable tannin oligomers, mainly ellegatannins known as nobotanins, were obtained from the stem barks of *T. multiflora* [5] and *T. semidecandra* [4b]. Also, tannins were detected on *T. pulchra* [6]. Additionally and in order to obtain compounds useful as natural food pigments, anthocyanins, the flowers of *T. grandiflora* [7], *T. granulose* [8a,b], *T. semidecandra* [4c], and *T. urvilleana* [9] were analyzed, obtaining malvidin and peonidin derivatives. Since only the chemical constituents of the flowers of *T. urvilleana* have been reported, the present work details the main secondary metabolites from the leaves and stems of this species, and additionally, the study contributes to the knowledge of the genus chemistry.

Results and Discussion

The leaves and stems of *T. urvilleana* were extracted successively with hexane, EtOAc, and MeOH. Purification of the hexane extract permitted the isolation of glutinol (**1**) [10], taraxerol (**2**) [11], a mixture of *α*- and *β*-amyrins (**3**, **4**) [11b, 12], *β*-sitosterol, and ursolic (**5**) [13] and oleanolic (**6**) [14] acids as a mixture. From EtOAc extract only *β*-sitosterol was obtained. The purification of MeOH extract afforded *β*-sitosteryl *β*-D-glucopyranoside, the flavonoids avicularin (**7**) [4a, 15] and hispidulin 7-*O*-*β*-D-glucopyranoside (**8**) [16], and two mixtures, one constituted of asiatic and arjunolic acids (**9** and **10**) [11b,17] and the other one of quadranoside IV (**11**) and arjunglucoside II (**12**) [17b]. Inorganic compound NH_4Cl [18] was also obtained.

Compounds *β*-sitosterol and *β*-sitosteryl *β*-D-glucopyranoside were identified by directly comparison of their NMR and physical data, including the Rf, with those of authentic samples. The structures of the triterpenes **1**-**6** and **9**-**12** and of the flavonoids **7** and **8** were elucidated by analysis of their spectroscopic features, which were identical with their data described in the literature.

Additionally, the extracts were tested on the 12-*O*-tetradecanoylphorbol 13-acetate (TPA) model of induced ear edema in mice [19], but the anti-inflammatory answer was not significant. Also, in the *in-vitro* cytotoxicity assay on the human cancer cell lines U-251, PC-3, K-562, HCT-15, MCF-7, and SKLU-1 [20], the extracts proved, unfortunately, to be moderate to poor (63.8 - 1%) in the inhibition of the cancer cells growth. Nevertheless, diverse biological activities have been reported for some of the metabolites obtained in the present work. Thus, anti-inflammatory, antioxidant, antiglicative, and antibacterial activities have been reported for ursolic and



oleanolic acids (**5**, **6**) [21]. Antioxidant, antifungal, antibacterial, anticholinesterase, antitumoral, and antiasthmatic activities as well as beneficial therapeutics in the treatment of diabetes and the capacity of inhibition of the insect growth have been described for the arjunolic acid (**10**) [22]. In the case of asiatic acid (**9**), dermatological activities related to its ability to stimulate collagen synthesis and its anti-inflammatory activity were reported [23]. For taraxerol (**2**), its antidiabetic potential activity was published [24]. *β*-amyrin (**4**) was reported as a candidate for alleviating oxalate toxicity, an important urinary stone-forming constituent [25]. *α*- and β-amiryns (**3**, **4**) showed to have a potent irritant potential on mouse skin [26]. For glutinol (**1**), its cytotoxicity against four human cancer cell lines and its moderate anti-inflammatory activity have been reported [27]. For the flavonoid avicularin (**7**), its inhibitory activity of rat aldose reductase and cytotoxicity against Ehrlich ascitis carcinoma cells were described [28].

In conclusion, the chemical study of the leaves and stems of *T. urvilleana* afforded ten triterpenes (**1**-**6**, **9**-**12**), two flavonoids (**7**, **8**), two sterols, and NH_4Cl. Moreover, triterpenic compounds are described for the first time in the genus *Tibouchina*.

General Experimental Procedures

Melting points were determined on a Fisher-Johns melting points apparatus and are uncorrected. IR spectra were recorded on a Bruker Tensor 27 or on a Perkin Elmer 400 spectrophotometer. NMR spectra were obtained on an Eclipse Jeol 300 MHz, a Varian-Unity 300 MHz, a Bruker Avance 300 MHz, a Varian Inova 500 MHz, or a Bruker Avance III 400 MHz spectrometer with TMS as internal standard. EIMS (70 eV) spectra were obtained on a Jeol JMS-AX505HA mass spectrometer and ESIMS spectra were performed in positive mode on an ESI Ion Trap Bruker Esquire 600. Vacuum column chromatography (VCC) was carried out with silica gel G 60 (Merck, Darmstadt, Germany). Flash column chromatography (FCC) was performed with silica gel 60 (230-400 mesh, Macherey-Nagel). Preparative TLC was carried out on precoated Sil G-100UV_{254} plates (Macherey-Nagel). All solvents were routinely distilled prior to use.

Plant Material

Leaves and stems of *Tibouchina urvilleana* (DC.) Cogn. were collected in Puebla, State of Puebla, Mexico, in July 2009. A voucher specimen (MEXU 174618) was deposited at the Herbarium Nacional, Instituto de Biología, UNAM.

Extraction and Isolation

Air-dried stems and leaves were ground in a Laboratory mill (Model 4, Thomas Scientific, USA). After, the material (679 g) was put in a glass column (10 × 60 cm), and with assistance of vacuum it was extracted successively with hexane, EtOAc, and MeOH. The evaporation of solvents under reduced pressure in a Rotavapor (R-114, Büchi Labortechnik AG, Switzerland) gave the respective extracts. Hexane extract (9 g) was purified by VCC (90 g of silica gel) using as eluent hexane-EtOAc mixtures of increasing polarity to afford four main fractions (A-D). Fraction A eluted with hexane-EtOAc 97:3 presented white solids which were crystallized on $CHCl_3$-MeOH to yield 183.4 mg of glutinol (**1**), mp 211-213 °C. [10]. Crystallization of fraction B (obtained with hexane-EtOAc 97:3) on $CHCl_3$-MeOH produced 8.0 mg of taraxerol (**2**), mp 272-275 °C) [11]. The mother liqueurs were recrystallized on MeOH to afford 93.0 g of *α*- and *β*-amyrins as a mixture (**3** and **4**) [11b, 12]. Fraction C, eluted with hexane-EtOAc 94:6, produced by crystallization on EtOH 238.0 mg of *β*-sitosterol, mp 138-139 °C (Lit. [29] mp 135-136 °C). Fraction D (485.0 mg), obtained with hexane-EtOAc 80:20, was purified by VCC (10 g of silica gel) using as eluent hexane-Me_2CO 85:15 to produce 24.5 mg of white crystals constituted of a mixture of ursolic and oleanolic acids (**5** and **6**) [13,14]. The purification of EtOAc extract (14.9 g) by VCC (160 g of silica gel) eluted with a hexane-Me_2CO polarity gradient only afforded *β*-sitosterol (22.4 mg). MeOH extract (68 g) was submitted to a VCC (600 g of silica gel) using as eluent CH_2Cl_2-MeOH mixtures of increasing polarity to yield five fractions (E-I). Fraction F (1.68 g, obtained with CH_2Cl_2-MeOH 93:7) was purified by two consecutive VCC eluted the first one with CH_2Cl_2-MeOH 95:5 and the second one with CH_2Cl_2-Me_2CO 75:25 to produce 7.9 mg of asiatic and arjunolic acids (**9** and **10**) as a mixture [11b,17], and 52.1 mg of *β*-sitosteryl *β*-D-glucopyranoside, mp 290-295 °C (desc.) (Lit. [29] mp 290-294 °C). Fraction G (2.5 g) eluted with CH_2Cl_2-MeOH 93:7 was submitted to a VCC (27 g of silica gel) using as eluent CH_2Cl_2-MeOH mixtures of increasing polarity to yield 81.1 mg of avicularin (**7**) [4a, 15] from CH_2Cl_2-MeOH 93:7 eluates as yellow crystals of mp 206-209 °C (MeOH). Fraction H (5.6 g, obtained with CH_2Cl_2-MeOH 90:10) was subfractioned into H1-H3 by a VCC (60 g of silica gel) eluted with CH_2Cl_2-MeOH 90:10. Subfraction H1 was submitted to a Sephadex LH-20 column using as eluent MeOH to afford 17.0 mg of hispidulin 7-*O*-*β*-D-glucopyranoside (**8**) as yellow crystals, mp 257-259 °C [16], and 61.0 mg of **7**. Subfraction H2 produced 57.9 mg of **8** after a Sephadex LH-20 column eluted with MeOH. 5.1 mg of a mixture of quadranoside IV and arjunglucoside II (**11** and **12**) [17b] was obtained after the purification of subfraction H3 by a Sephadex LH-20 column (MeOH) followed by a preparative TLC (CH_2Cl_2-*i*PrOH 4:1, 4×) and a FCC (CH_2Cl_2-*i*PrOH 77:23). Fraction I (34.7 g), obtained with CH_2Cl_2-MeOH 85:15, was submitted to a VCC (350 g of silica gel) using as eluent CH_2Cl_2-MeOH mixtures of increasing polarity. From eluates of CH_2Cl_2-MeOH 85:15 were obtained 559.5 mg of NH_4Cl as white crystals (sublimate at 315 °C) [18]. The mother liqueurs (250 mg) were purified by a VCC (3 g de silica gel) eluted with a CH_2Cl_2-MeOH polarity gradient to produce 89.9 mg of NH_4Cl from CH_2Cl_2-MeOH 75:25 eluates.

Glutinol (1). White crystals: mp 211-213 °C (Lit. [10] mp 210-213 °C, 210-212 °C); $[\alpha]_D^{25}$ +57.6 (*c* 0.25, $CHCl_3$); IR (KBr) ν_{max} 3441, 2925, 2866, 1454, 1383, 1034 cm^{-1}; ^1H NMR

($CDCl_3$, 300 MHz) δ 5.63 (1H, br d, *J* = 6.0 Hz, H-6), 3.47 (1H, dd, *J* = 3.3, 2.4 Hz, H-3), 1.16 (3H, s, H-28), 1.14 (3H, s, H-23), 1.09 (3H, s H-26), 1.04 (3H, s, H-24), 1.00 (3H, s, H-27), 0.99 (3H, s, H-30), 0.95 (3H, s, H-29), 0.85 (3H, s, H-25); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.6 (C-5), 122.1 (C-6), 76.3 (C-3), 49.7 (C-10), 47.4 (C-18), 43.0 (C-8), 40.8 (C-14), 39.3 (C-4), 38.9 (C-22), 37.8 (C-13), 36.0 (C-16), 35.1 (C-19), 34.8 (C-9), 34.6 (C-11), 34.5 (C-30), 33.1 (C-21), 32.4 (C-28), 32.1 (C-15), 32.0 (C-29), 30.3 (C-12), 30.1 (C-17), 28.9 (C-23), 28.2 (C-20), 27.8 (C-7), 25.5 (C-24), 23.6 (C-1), 19.6 (C-27), 18.4 (C-26), 18.2 (C-2), 16.2 (C-25); EIMS *m/z* (rel. int.): 426 $[M]^+$ (7), 411 (4), 408 (3), 393 (3), 274 (100), 259 (80), 205 (30), 134 (36), 109 (29), 95 (37), 71 (24), 69 (26), 55 (21).

Taraxerol (2). White crystals: mp 272-275 °C (Lit. [11a] mp 278-279 °C); $[\alpha]_D^{25}$ +0.18 (*c* 0.11, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3400, 2929, 2857, 1457, 1377 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.53 (1H, dd, *J* = 8.1, 3.3 Hz, H-15), 3.20 (1H, dd, *J* = 10.5, 4.8 Hz, H-3), 2.03 (1H, dt, *J* = 12.0, 3.0 Hz, H-7a), 1.92 (1H, dd, *J* = 14.7, 3.0 Hz, H-16a), 1.09 (3H, s, H-26), 0.98 (3H, s, H-23), 0.95 (3H, s, H-29), 0.93 (3H, s, H-25), 0.91 (6H, s, H-27, H-30), 0.82 (3H, s, H-28), 0.80 (3H, s, H-24); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.1 (C-14), 116.9 (C-15), 79.1 (C-3), 55.5 (C-5), 49.3 (C-18), 48.8 (C-9), 41.3 (C-19), 39.0 (C-4), 38.8 (C-8), 38.0 (C-17), 37.74 (C-1), 37.72 (C-13), 37.6 (C-10), 36.7 (C-16), 35.1 (C-7, C-12), 33.7 (C-21), 33.4 (C-29), 33.1 (C-22), 29.9 (C-28), 29.8 (C-26), 28.8 (C-20), 28.0 (C-23), 27.2 (C-2), 25.9 (C-27), 21.3 (C-30), 18.8 (C-6), 17.5 (C-11), 15.5 (C-24, C-25); EIMS *m/z* (rel. int.): 426 $[M]^+$ (27), 411 (24), 302 (57), 287 (37), 218 (29), 204 (100), 189 (19), 135 (31), 95 (19), 69 (27), 55 (28).

α- and β- Amyrins (3, 4). IR (KBr) ν_{max} 3285, 2918, 2850, 1460, 1381, 1362, 1033, 995 cm^{-1}; compound **3**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.13 (1H, dd, *J* = 3.6, 3.3 Hz, H-12), 3.23 (1H, dd, *J* = 10.5, 5.4 Hz, H-3), 1.07 (3H, s, H-27), 1.01 (3H, s, H-26), 1.00 (3H, s, H-23), 0.96 (3H, s, H-25), 0.92 (3H, d, *J* = 7.5 Hz, H-30), 0.80 (3H, s, H-28), 0.79 (3H, d, *J* = 6.0 Hz, H-29), 0.79 (3H, s, H-24); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.6 (C-13), 124.4 (C-12), 79.0 (C-3), 59.0 (C-18), 55.1 (C-5), 47.7 (C-9), 42.0 (C-14), 41.5 (C-22), 39.6 (C-19, C-20), 38.8 (C-1, C-4, C-8), 36.9 (C-10), 33.7 (C-17), 32.9 (C-7), 31.2 (C-21), 29.7 (C-16), 28.7 (C-28), 28.1 (C-23), 27.2 (C-2), 26.6 (C-15), 23.3 (C-11, C-27), 21.4 (C-30), 18.4 (C-6), 17.5 (C-29), 16.8 (C-26), 15.6 (C-24, C-25); compound **4**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.18 (1H, dd, *J* = 3.6, 3.3 Hz, H-12), 3.24 (1H, dd, *J* = 10.2, 5.1 Hz, H-3), 1.13 (3H, s, H-27), 1.00 (3H, s, H-26), 0.97 (3H, s, H-28), 0.94 (3H, s, H-25), 0.87 (6H, s, H-29, H-30), 0.83 (3H, s, H-23), 0.79 (3H, s, H-24); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.2 (C-13), 121.7 (C-12), 79.0 (C-3), 55.1 (C-5), 47.6 (C-9), 47.2 (C-18), 46.8 (C-19), 41.7 (C-14), 39.8 (C-8), 38.8 (C-4), 38.6 (C-1), 37.4 (C-22), 36.9 (C-10), 34.7 (C-21), 33.3 (C-29), 32.6 (C-7), 31.1 (C-20), 28.4 (C-28), 28.1 (C-15, C-23), 27.0 (C-27), 26.1 (C-2, C-16), 23.7 (C-30), 23.5 (C-11), 18.4 (C-6), 16.8 (C-26), 15.7 (C-25), 15.5 (C-24).

Ursolic (5) and oleanolic (6) acids. IR (KBr) ν_{max} 3412, 2925, 2858, 1688, 1455, 1382, 1030, 996 cm^{-1}; compound **5**: ^{1}H NMR ($CDCl_3$ + DMSO-d_6, 300 MHz) δ 5.24 (1H, t, *J* = 3.6 Hz, H-11), 3.18 (1H, dd, *J* = 8.3, 6.4 Hz, H-3), 2.20 (1H, brd, *J* = 11.1 Hz, H-18), 1.14 (3H, s, H-27), 1.08 (6H, s, H-23, H-26), 0.99 (3H, s, H-24), 0.93 (3H, d, *J* = 7.5 Hz, H-29), 0.85 (3H, d, *J* = 6.3 Hz, H-30), 0.78 (3H, s, H-25); ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 75 MHz) δ 179.6 (C-28), 138.0 (C-13), 125.0 (C-12), 78.3 (C-3), 55.0 (C-5), 52.5 (C-18), 47.3 (C-9, C-17), 41.8 (C-14), 40.1 (C-8), 39.3 (C-4), 38.8 (C-19), 38.6 (C-20), 38.5 (C-10), 38.4 (C-1), 36.5 (C-22), 32.7 (C-7), 32.2 (C-21), 30.4 (C-15), 27.9 (C-23), 27.0 (C-2), 23.9 (C-16), 23.2 (C-27), 23.0 (C-11), 20.9 (C-30), 18.1 (C-6), 16.8 (C-26, C-29), 16.7 (C-24, C-25); compound **6**: ^{1}H NMR ($CDCl_3$ + DMSO-d_6, 300 MHz) δ 5.27 (1H, t, *J* = 3.6 Hz, H-11), 3.18 (1H, dd, *J* = 9.0, 5.7 Hz, H-3), 2.84 (1H, dd, *J* = 14.4, 4.5 Hz, H-18), 1.14 (3H, s, H-27), 1.08 (3H, s, H-23), 0.99 (3H, s, H-24), 0.92 (3H, s, H-30), 0.91 (3H, s, H-29), 0.89 (3H, s, H-25), 0.80 (3H, s, H-26); ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 75 MHz) δ 179.8 (C-28), 143.8 (C-13), 121.8 (C-12), 78.3 (C-3), 55.0 (C-5), 47.3 (C-9), 45.8 (C-17, C-19), 40.9 (C-18), 40.6 (C-14), 40.4 (C-8), 40.1 (C-4), 38.2 (C-1), 36.7 (C-10), 33.7 (C-7), 32.7 (C-29), 32.5 (C-21, C-22), 29.3 (C-20), 27.9 (C-23), 27.8 (C-15), 27.4 (C-2), 25.6 (C-27), 23.1 (C-16), 22.8 (C-11), 23.3 (C-30), 18.1 (C-6), 16.7 (C-26), 15.5 (C-24, C-25).

Avicularin (7). Yellow crystals: mp 206-209 °C (Lit. [4b, 15b] mp 170-175 °C, mp 216-217 °C); $[\alpha]_D^{25}$ -184.5 (*c* 0.35, MeOH); IR (Nujol) ν_{max} 3284, 1654, 1605, 1559, 1364, 1270, 1199, 1114 cm^{-1}; ^{1}H NMR (MeOH-d_4, 300 MHz) δ 7.52 (1H, d, *J* = 2.1 Hz, H-2'), 7.48 (1H, dd, *J* = 8.4, 2.1 Hz, H-6'), 6.89 (1H, d, *J* = 8.4 Hz, H-5'), 6.38 (1H, d, *J* = 2.1 Hz, H-8), 6.15 (1H, d, *J* = 2.1 Hz, H-6), 5.46 (1H, d, *J* = 1.0 Hz, H-1''), 4.32 (1H, dd, *J* = 3.0, 1.0 Hz, H-2''), 3.91 (1H, dd, *J* = 5.1, 3.0 Hz, H-3''), 3.87 (1H, ddd, *J* = 6.0, 5.1, 3.9 Hz, H-4''), 3.5 (2H, m, H-5''); ^{13}C NMR (MeOH-d_4, 75 MHz) δ 180.0 (C-4), 166.1 (C-7), 163.1 (C-5), 159.3 (C-2), 158.6 (C-9), 149.8 (C-4'), 146.4 (C-3'), 134.9 (C-3), 123.1 (C-1'), 123.0 (C-6'), 116.9 (C-2'), 116.5 (C-5'), 109.6 (C-1''), 105.6 (C-10), 99.9 (C-6), 94.8 (C-8), 88.1 (C-4''), 83.3 (C-2''), 78.7 (C-3''), 62.6 (C-5''); ESIMS *m/z* 457 $[M + Na]^+$.

Hispidulin 7-*O*-*β*-D-glucopyranoside (8). Yellow crystals: mp 257-259 °C (Lit. [16a] mp 256-258 °C); $[\alpha]_D^{25}$ -45.5 (*c* 0.24, MeOH); IR (Nujol) ν_{max} 3308, 1644, 1597, 1564, 1460, 1376, 1357, 1249, 1102 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.94 (2H, d, *J* = 9.0 Hz, H-2', H-6'), 7.01 (1H, s, H-8), 6.93 (2H, d, *J* = 9.0 Hz, H-3', H-5'), 6.84 (1H, s, H-3), 5.10 (1H, d, *J* = 7.0 Hz, H-1''), 3.76 (3H, s, OCH_3), 3.74 (1H, m, H-6a''), 3.48 (1H, m, H-6b''), 3.45 (1H, m, H-4''), 3.33 (1H, m, H-3''), 3.31 (1H, m, H-2''), 3.20 (1H, dd, *J* = 9.0, 8.0 Hz, H-5''); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 182.3 (C-4), 164.3 (C-2), 161.3 (C-4'), 156.5 (C-7), 152.4 (C-9), 152.1 (C-5), 132.5 (C-6), 128.6 (C-2', C-6'), 121.1 (C-1'), 116.0 (C-3', C-5'), 105.7 (C-10), 102.7 (C-3), 100.2 (C-1''), 94.4 (C-8), 77.3 (C-4''), 76.7 (C-2''), 73.2 (C-3''), 69.6 (C-5''), 60.6 (C-6''), 60.3 (OCH_3); ESIMS *m/z* 485 $[M + Na]^+$.

Asiatic (9) and arjunolic (10) acids. IR (KBr) ν_{max} 3319, 2921, 2853, 1690, 1457, 1382, 1035 cm^{-1}; compound **9**: ^{1}H NMR (pyridine-d_5, 300 MHz) δ 5.49 (1H, t, *J* = 3.6 Hz, H-12), 4.3-4.2 (4H, m, H-2, H-3, H-23), 2.63 (1H, d, *J* = 9.6

Hz, H-18), 1.22 (3H, s, H-26), 1.09 (6H, s, H-25, H-27), 1.07 (3H, s, H-24), 0.98 (3H, d, J = 7.0 Hz, H-29), 0.93 (3H, d, J = 7.0 Hz, H-30); ^{13}C NMR (pyridine-d_5, 75 MHz) δ 180.2 (C-28), 139.3 (C-13), 125.6 (C-12), 78.3 (C-3), 68.9 (C-2), 66.6 (C-23), 53.6 (C-18), 48.0 (C-5, C-17), 47.9 (C-9), 47.8 (C-1), 43.7 (C-4), 42.2 (C-14), 40.1 (C-8), 39.5 (C-19), 39.4 (C-20), 38.3 (C-10), 37.5 (C-22), 32.9 (C-7), 31.1 (C-21), 28.7 (C-15), 24.9 (C-16), 23.9 (C-27), 23.7 (C-11), 21.4 (C-30), 18.6 (C-6), 17.6 (C-26), 17.4 (C-25, C-29), 14.4 (C-24); compound **10**: ^{1}H NMR (pyridine-d_5, 300 MHz) δ 5.49 (1H, t, J = 3.6 Hz, H-12), 4.3-4.2 (4H, m, H-2, H-3, H-23), 3.30 (1H, dd, J = 13.6, 4.4 Hz, H-18), 1.22 (3H, s, H-26), 1.16 (3H, s, H-27), 1.09 (3H, s, H-25), 1.07 (3H, s, H-24), 1.01 (3H, s, H-30), 0.93 (3H, s, H-29); ^{13}C NMR (pyridine-d_5, 75 MHz) δ 179.9 (C-28), 144.9 (C-13), 125.5 (C-12), 78.3 (C-3), 68.9 (C-2), 66.6 (C-23), 48.1 (C-9), 47.9 (C-5), 47.8 (C-1), 46.7 (C-17), 46.4 (C-19), 42.0 (C-18), 43.7 (C-4), 42.2 (C-14), 39.9 (C-8), 38.5 (C-10), 34.2 (C-21), 33.2 (C-22, C-29), 32.9 (C-7), 31.0 (C-20), 28.3 (C-15), 26.2 (C-27), 24.0 (C-16), 23.8 (C-30), 23.7 (C-11), 18.6 (C-6), 17.6 (C-25), 17.5 (C-26), 14.4 (C-24).

Quadranoside IV (11) and arjunglucoside II (12). IR (Nujol) ν_{max} 3369, 1732, 1637 cm^{-1}; compound **11**: ^{1}H NMR (pyridine-d_5, 500 MHz) δ 6.25 (1H, d, J = 8.5 Hz, H-1'), 5.41 (1H, brs, H-12), 4.3-4.23 (2H, m, H-2, H-3), 4.45-4.19 (5H, m, H-2', H-3', H-4', H-6', H-23a), 4.03 (1H, m, H-5'), 3.70 (1H, d, J = 10.0 Hz, H-23b), 2.50 (1H, brd, J = 11.0 Hz, H-18), 1.18 (3H, s, H-26), 1.10 (3H, s, H-25), 1.09 (3H, s, H-27), 1.06 (3H, s, H-24), 0.90 (3H, d, J = 6.0 Hz, H-29), 0.86 (3H, s, H-30); ^{13}C NMR (pyridine-d_5, 125 MHz) δ 181.3 (C-28), 137.0 (C-13), 124.0 (C-12), 95.7 (C-1'), 79.2 (C-5'), 78.9 (C-3'), 74.0 (C-2'), 71.2 (C-3, C-4'), 68.9 (C-2), 66.5 (C-23), 62.2 (C-6'), 53.3 (C-18), 48.2 (C-17), 48.0 (C-5), 47.9 (C-9), 47.8 (C-1), 43.6 (C-4), 42.2 (C-14), 40.2 (C-8), 39.2 (C-19), 39.1 (C-20), 38.3 (C-10), 36.8 (C-21, C-22), 32.8 (C-7), 28.6 (C-15), 24.6 (C-16), 23.7 (C-11), 23.6 (C-27), 21.2 (C-30), 18.5 (C-6), 17.6 (C-26), 17.4 (C-25), 17.3 (C-29), 14.4 (C-24); compound **12**: ^{1}H NMR (pyridine-d_5, 500 MHz) δ 6.32 (1H, d, J = 8.0 Hz, H-1'), 5.43 (1H, brs, H-12), 4.3-4.23 (2H, m, H-2, H-3), 4.45-4.19 (5H, m, H-2', H-3', H-4', H-6', H-23a), 4.03 (1H, m, H-5'), 3.70 (1H, d, J = 10.0 Hz, H-23b), 3.17 (1H, dd, J = 14.0, 4.0 Hz, H-18), 1.15 (6H, s, H-26, H-27), 1.09 (3H, s, H-25), 1.06 (3H, s, H-24), 0.86 (6H, s, H-29, H-30); ^{13}C NMR (pyridine-d_5, 125 MHz) δ 181.3 (C-28), 143.5 (C-13), 124.0 (C-12), 95.7 (C-1'), 79.3 (C-5'), 78.9 (C-3'), 74.1 (C-2'), 71.2 (C-3), 71.1 (C-4'), 68.9 (C-2), 66.5 (C-23), 62.3 (C-6'), 48.1 (C-5), 47.9 (C-1), 47.8 (C-9), 47.0 (C-17), 46.1 (C-19), 43.6 (C-4), 41.7 (C-14, C-18), 40.0 (C-8), 38.4 (C-10), 33.9 (C-21), 33.2 (C-7), 33.0 (C-29), 32.5 (C-22), 30.7 (C-20), 28.2 (C-15), 26.0 (C-27), 23.8 (C-11), 23.7 (C-30), 23.4 (C-16), 18.4 (C-6), 17.7 (C-26), 17.6 (C-25), 14.4 (C-24).

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