Chemical Constituents of *Madhuca pasquiery*

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Madhuca pasquiery, 2,4-Dihydroxy Phenylacetic Acid Methyl Ester, Platanic Acid, Triterpenoids, Flavonoids

Four triterpenoids, the scarce nortriterpenoid platanic acid, two flavonoids and 2,4-dihydroxy phenylacetic acid methyl ester, hitherto unknown as a natural product, were isolated from *Madhuca pasquiery*. The structures were established by means of mass and NMR spectroscopy.

Introduction

Madhuca pasquiery (Dub.) Lam., Sapotaceae, is a rare tree with elliptical leaves and yellow flowers growing in Than Hoa province, Ninh Binh province and Vinh Phu province in North Vietnam. The oil of the fruits is used for nutrition (Pham-Hoang Ho, 1993). In Vietnam the decoction of the leaves is used to treat burns (Le The Trung, 1994). The constituents of this plant species have not been investigated until now. In continuation of our phytochemical studies on Vietnamese plants (Anh *et al.*, 1996), we now describe the isolation and structure elucidation of four pentacyclic triterpenoids, a nortriterpenoid, two flavonoids and 2,4-dihydroxy phenylacetic acid methyl ester, the latter one hitherto unknown as a natural product.

Results and Discussion

Leaves and bark of branches of *Madhuca pasquiery* were extracted successively with several solvents of increasing polarity. The extracts were separated by silica gel chromatography. The structures of the isolated compounds were established by mass and NMR spectroscopy.

Triterpene **1**

Compound **1** was isolated from the n-hexane extract of the leaves. It is a triterpene alcohol with friedelane skeleton as revealed by the characteristic fragment at *m/z* 275 in the mass spectrum (Budzikiewicz *et al.*, 1963). The chemical shifts of the carbons of the rings B, C, D and E are consis-

Table I. ^{13}C NMR data of compounds **1–5** (125 MHz).

Carbon	**1** ($CDCl_3$)	**2** (CD_3OD)	**3** ($CDCl_3$)	**4**[a] ($CDCl_3$)	**5**[b] ($CDCl_3$)
1	15.7	42.5[c]	39.0	38.6	37.8
2	35.04	67.2	27.8	27.3	25.2
3	72.6	78.7	78.9	78.9	80.6
4	49.1	42.7[c]	39.6	38.8	38.4
5	37.8[c]	44.2	52.3	55.3	55.4
6	41.7	19.1	21.4	18.2	18.1
7	17.5	33.7	26.7	34.2	34.2
8	53.1	41.1	40.9	40.6	40.7
9	37.1[c]	48.3	148.8	50.3	50.4
10	61.3	39.0[d]	35.9	37.2	37.1
11	35.3	24.7	114.3	20.8	20.8
12	30.6	129.3	36.02	27.2	25.5
13	38.3[d]	140.1	36.8	37.5	38.35
14	39.6[d]	42.2	38.2	42.2	42.2
15	32.3	29.6	29.6	28.3[c]	30.5
16	36.0	26.6	35.97	31.4	32.1
17	30.0	49.3	42.8	56.2	56.4
18	42.8	55.1	52.1	51.2[d]	46.9
19	35.5	73.6	20.2	49.2[d]	49.2
20	28.1	43.1	28.2	212.2	150.4
21	32.8[e]	27.3	59.6	29.7[c]	29.6
22	39.2[e]	39.1[d]	30.8	36.7	37.0
23	11.6	71.3	28.2	28.0	28.0
24	16.3	17.3[e]	15.6	16.1[e]	16.5
25	18.2	17.6[e]	22.11	15.9[e]	16.0
26	20.1	17.6[e]	17.0	15.3[f]	16.2
27	18.6	24.9	15.3	14.7[f]	14.7
28	31.7	182.4	14.0	181.1	181.9
29	34.98	27.1	22.12	30.1	109.7
30	32.0	16.6	23.0	–	19.3

[a] 75 MHz; [b] Shifts of the fatty acid residue are in the experimental part; [c,d,e,f] Assignments interchangeable in each column.

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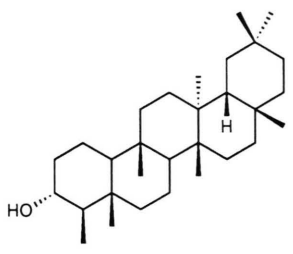

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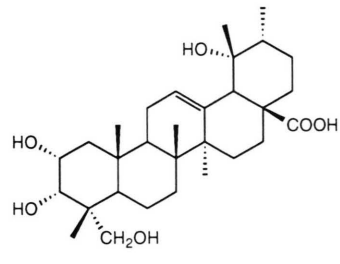

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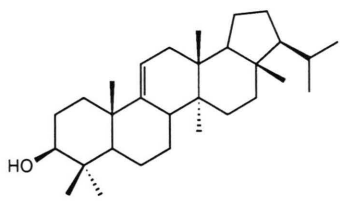

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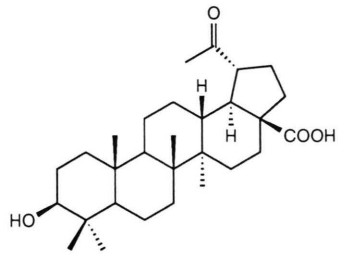

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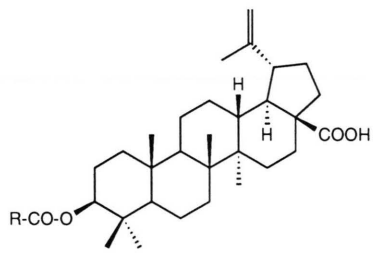

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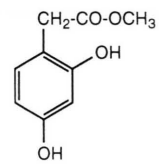
R = CH_3-$(CH_2)_n$-



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tent with those of friedelin (Prakash *et al.*, 1987). The differences in ring A result from the transformation of the keto into a hydroxy group. The proton H-3 appears in the ^{1}H NMR spectrum as a broad singlet at δ 3.74 ppm, which reflects the α-orientation of the hydroxy group by the missing $^3J_{aa}$ coupling corresponding to the structure of α-friedelinol.

Triterpene acid **2**

The mass spectrum of this compound obtained from the EtOAc extract of the leaves shows the $[M]^+$ at *m/z* 504 corresponding to the molecular formula $C_{30}H_{48}O_6$ of a tetrahydroxy triterpene acid. The fragment at *m/z* 264 is characteristic for the retro-Diels Alder product of a Δ^{12}-oleanoic or -ursanoic acid derivative (Budzikiewicz *et al.*, 1963). Analysis of the CH long-range correlations from the HMBC experiment locates the hydroxy groups at C-2, C-3, C-19 and C-23/24. The 2α,3α-dihydroxy configuration is revealed by the splitting of the H-2 signal at δ 3.88, which shows one $^3J_{aa}$ coupling of 10.7 Hz with H-1^a. One known compound with all these features is myrianthic acid (2α,3α,19α,24-tetrahydroxyurs-12-en-28-oic acid). The carbon shifts of myrianthic acid in

C_5D_5N (Seto et al., 1984) are mainly in agreement with those of compound **2** which are taken in CD_3OD and thus show some expectable solvent-dependent differences of 1-2 ppm at C-2, C-12, C-17 and C-28. This compound is not very common. It has been found for example in *Myrianthus arboreus* (Ojinnaka *et al.*, 1984) and in *Rosa laevigata* (Gao *et al.*, 1993).

Triterpene **3**

Compound **3** was obtained from the n-hexane extract of the leaves. The carbon shifts in the rings B, C, D and E are in agreement with those of arborinol with a 3α-hydroxy group (Chakravarty *et al.*, 1994). The differences in ring A are caused by the β-orientation of the substituent which is proved by the $^3J_{aa}$ coupling of 11.6 Hz between H-3 and H^a-2. The resulting structure of isoarborinol is confirmed by comparison of the proton shifts with reference data (Gonzalez *et al.*, 1990).

Nortriterpene acid **4**

This compound was isolated from the n-BuOH extract of the barks of branches. The MS shows the molecular ion at *m/z* 458 corresponding to the molecular formula $C_{29}H_{46}O_4$ and the base peak at *m/z* 189, which is characteristic for saturated pentacyclic triterpenoids. The ^{13}C NMR spectrum exhibits one keto group at δ 212.2, an acid function at δ 181.1 and an oxygen-substituted carbon at δ 78.9. Platanic acid possesses all the above mentioned features and its carbon shifts in C_5D_5N (Fujioka *et al.*, 1994) are in agreement with those of the isolated compound in $CDCl_3$ under consideration of the solvent effects, which cause some deviations of 1-3 ppm for the carbons 3, 20, 28 and 29. The proton shifts taken in the same solvent are identical. Platanic acid is a very scarce nortriterpene acid. Until now it was only isolated from *Platanus spp.* (Platanaceae) (Aplin *et al.*, 1963) and from *Syzigium claviforum* (Myrtaceae) (Fujioka *et al.*, 1994). It exhibits anti-HIV activity (Fujioka *et al.*, 1994).

Triterpene acid ester **5**

This sample was isolated from the *n*-hexane extract of the leaves. The base peak in the mass spectrum at *m/z* 438 together with the prominent peak at *m/z* 189 characterizes a pentacyclic triterpene acid derivative. The carbon shifts agree with those of betulinic acid (Siddiqui *et al.*, 1988). Additional signals (one carboxy signal at δ 173.7 and several signals at nearly 30 ppm) suggest the presence of a fatty acid residue. The mass spectrum shows several molecular ions indicating the different chain lengths of the fatty acid moieties. The molecular ion peak with the highest intensity at *m/z* 694 (4.4.%) represents the compound 3-O-palmitoyl betulinic acid with the molecular formular $C_{46}H_{78}O_4$. The peak with the second highest intensity at *m/z* 666 (3.2%) identifies the homologous myristoyl derivative. Also homologues with even-numbered chain lengths between 18 and 30 carbons are present in the sample but in low concentrations (rel. int. 0.1–1%). *Madhuca* species are known to contain fatty acid esters of triterpenes (Hegnauer, 1973). The main component of the isolated sample, 3-O-palmitoyl betulinic acid, is known from *Madhuca butyraceae* (Awasthi *et al.*, 1968), but has not been found in other plant species.

Compound **6**

The mass spectrum of this compound isolated from the MeOH extract of the leaves shows the $[M]^+$ peak at *m/z* 182.0585 corresponding to $C_9H_{10}O_4$. The base peak at *m/z* 123 represents a dihydroxy benzylium ion, which was formed by loss of a carboxymethyl group ($\Delta m/z = 59$) from a dihydroxy phenyl acetic acid methyl ester. The easy loss of MeOH to yield the corresponding lacton at *m/z* 150 locates one hydroxy group in ortho-position to the acetic acid substituent. The ^1H NMR spectrum shows an 1,2,4-trisubstituted benzene ring. These data are consistent with 2,4- or 2,5-dihydroxy phenylacetic acid methyl ester. The 2,5-dihydroxy derivative is known from *Entada phaseoloides* (Leguminosae) (Dai *et al.*, 1991), but its carbon shifts are not consistent with those of the isolated compound. Calculation of the ^1H and ^{13}C shifts for the 2,4-dihydroxy compound with substituent increments shows good agreement with the values of the isolated compound. This structure and also the free acid are not known as natural products. The methyl ester is only mentioned once in the literature in a patent about skin whitening cosmetics (Oreal, 1993). The acid is a

part of the spider toxin clavamine, from which it can be gained by hydrolysis (Yoshioka *et al.*, 1990).

Flavanol **7**

This compound was obtained from the MeOH extract of the leaves. The mass spectrum, the carbon shifts and the optical rotation are in agreement with those of (2*R*,3*R*)-3,4',5,7-tetrahydroxyflavan), which is known as (-)-epiafzelechin (Waterman P. G. *et al.*, 1979).

Flavonoid glycoside **8**

The mass spectrum of this compound isolated from the EtOAc extract of the leaves, shows a very small molecular ion peak at *m/z* 478. Loss of the sugar moiety yields the aglycon as base peak at *m/z* 322 which agrees with the molecular formula $C_{22}H_{22}O_{12}$ for a pentahydroxy methoxy flavone. The location of the hydroxy and methoxy groups was deduced from the CH long-range correlations in the HMBC experiment. Analysis of the ^1H NMR signals belonging to the sugar moiety reveals an α-rhamnoside. The resulting structure 3,3',5,5',7-pentahydroxy-4'-methoxyflavon-3α-O-rhamnoside is known as mearnsitrin (MacKenzie, 1969).

Additionally, the following common compounds were identified: Epicatechin was isolated from the MeOH extract of the leaves and identified by analysis of the mass and ^1H NMR spectrum. Betulinic acid was found in the EtOAc extract of the bark of branches and identified by comparison of the R_f value and of the MS spectrum with an authentic sample. Ursolic acid is present in the n-hexane extract of the leaves and in the EtOAc extract of the bark of branches. The mass and ^{13}C NMR spectra of the isolated samples were in agreement with those of an authentic sample. Friedelin was isolated from the n-hexane extract of the leaves and identified by comparison of the ^{13}C shifts of the isolated compound with reference data (Prakash *et al.*, 1987). Two samples, which contained mixtures of steroids with the same R_f-value, were isolated from the *n*-hexane extract of the leaves and from the *n*-hexane extract of the bark of branches. The main components of both samples were spinasterol and dihydrospinasterol, which were identified by GC-MS after acetylation of the mixture in the usual manner. α- and β-Amyrin were identified in the same way from the *n*-hexane extract of the bark of branches.

The plant also contains many triterpene acid esters esterified with mixtures of homologous fatty acids like in sample **5**, which were not investigated further.

Experimental

Melting points are uncorrected. EI-MS: AMD 402, 70 eV. NMR: Varian Unity 500 and Gemini 300. CC: silica gel 60, 70–200 and 230–400 mesh ASTM (Merck); TLC: precoated silica gel plates 60 F_{254} (Merck), detection: UV-light, spray reagent: vanillin in H_2SO_4.

Plant material

Leaves of *Madhuca pasquiery* were collected in the National Park Cuc Phuong (Ninh Binh province) in September 1993. Branches were collecctd in the same place in October 1994. The species was identified by Dr. Tran Dinh Dai. A voucher specimen (No. 56114 HN) is deposited in the Institute of Ecology and Natural Resources, National Centre for Scientific Research and Technology, Hanoi, Vietnam.

Extraction and isolation

The dried leaves (1.2 kg) were extracted (three times overnight) with *n*-hexane, EtOAc, MeOH and water, successively. After removal of the solvent under reduced pressure, 41 g *n*-hexane extract, 46 g EtOAc extract, 188 g MeOH extract and 113 g water extract were obtained. The *n*-hexane extract (15 g) was separated on silica gel 60 (120 g, 70-200 mesh) with increasing amounts of EtOAc in *n*-hexane (0-100% EtOAc, 124 fractions, each 50 ml). Fractions 12-29 (3.43 g) were further purified by CC on silica gel 60 (120 g, 230-400 mesh) using *n*-hexane-EtOAc (8:2) to yield 49 mg **3**. From fractions 36-48 (3.38 g) 43 mg **1** and 20 mg **5** were obtained by CC on silica gel 60 (150 g, 230-400 mesh) with *n*-hexane-EtOAc (8:2).

20 g of the EtOAc extract were chromatographed on silica gel 60 (70-200 mesh) and eluted with solvents of increasing polarity (2-100% EtOAc in n-hexane followed by 5-100% MeOH in EtOAc, 128 fractions with 100 ml). Fractions 110-114 (2.00 g), were purified with 100% EtOAc and 5% MeOH in EtOAc to yield 38 mg **2** and 44 mg **8**.

27 g MeOH extract were separated by chromatography on silica gel (270 g) eluting with increasing amounts of MeOH in $CHCl_3$ (5% MeOH –

100% MeOH, 66 fractions with 150 ml). Fractions 16-19 (403 mg) were further purified over silica gel using $CHCl_3$-MeOH (8:2) to yield 10 mg **7**. Fractions 30-38 (0.35 g) gave 10 mg **6** after chromatography with $CHCl_3$-MeOH (75:25)

The dried barks of branches (1 kg) were extracted three times with 80% aqueous methanol at room temp.; the organic solvent was removed under reduced pressure. The aqueous residue was extracted three times with *n*-hexane, EtOAc and water-saturated *n*-BuOH giving 2.01 g *n*-hexane extract, 54.51 g EtOAc extract and 167.94 g *n*-BuOH extract. The *n*-BuOH extract was separated by chromatography on silica gel (200 g, 70-200 mesh) with increasing amounts of MeOH in $CHCl_3$ as eluent (0% – 100% EtOAc, 79 fractions, each 100 ml). Fractions 13-25 (211 mg) afforded 15 mg **4** after purification with $CHCl_3$-MeOH (8:2).

3α-Friedelanol (**1**). White solid, m.p. 288–289 °C. MS *m/z* (rel. int.): 428 $[M]^+$ (46), 413 $[M\text{-}Me]^+$ (69), 395$[M\text{-}Me\text{-}H_2O]^+$ (16), 304 (8), 289 (7), 275 (80), 263 (22), 261 (22), 257 (30), 248 (28), 234 (57), 233 (51), 231 (59), 220 (58), 206 (52), 177 (47), 165 (100). ^1H NMR ($CDCl_3$, 500 MHz) δ: 3.74 (1 H, br s, H-3), 1.90 (1 H, dt, *J* = 10.1 and 2.6 Hz), 1.74 (1 H, dt, *J* = 12.7 and 3.1 Hz), 1.17 (3 H, s, Me), 1.006 (3 H, s, Me), 0.996 (3 H, s, Me), 0.990 (3 H, s, Me), 0.97 (3 H, s, Me), 0.95 (3 H, s, Me), 0.94 (3 H, d, *J* = 7.3 Hz, Me, H-23), 0.86 (3 H, s, Me). ^{13}C NMR see Table I.

Myrianthic acid (**2**). White solid. m.p. 241–244 °C. $[\alpha]_D^{32}$ +23.9°, (MeOH, c 0.23). UV λ_{max}^{MeOH} nm (log ε): 282 (3.06), 205 (3.80). IR ν_{max}^{KBr} (cm^{-1}): 3432, 2928, 1688, 1461, 1451, 1383, 1268, 1234, 1159, 1045, 934. MS *m/z* (rel. int.): 504 $[M]^+$ (4), 458 (13), 264 (15), 246 (26), 231 (11), 218 (19), 201 (41), 173 (54), 146 (100), 205 (100). HRMS 504.3495 $[M]^+$ ($C_{30}H_{48}O_6$ requires 504.3451). ^1H NMR (CD_3OD, 500 MHz) δ: 5.30 (1 H, t, *J* < 1 Hz, H-12), 3.88 (1 H, dm, *J* = 10.7 Hz, H-2), 3.61 (1 H, d, *J* = 2.1 Hz, H-3), 3.54 (1 H, d, *J* = 10.8 Hz, H^B-23), 3.39 (1 H, d, *J* = 10.8 Hz, H^A-23), 2.57 (1 H, td, *J* = 13.1 and 4.3 Hz), 1.35 (3 H, s, Me), 1.20 (3 H, s, Me), 1.02 (3 H, s, Me), 0.93 (3 H, d, *J* = 6.7 Hz, H-30), 0.80 (3 H, s, Me), 0.79 (3 H, s, Me). ^{13}C NMR see Table I.

Isoarborinol (**3**). White solid, m.p. 298 °C. MS *m/z* (rel. int.): 426 $[M]^+$ (62), 411 $[M\text{-}Me]^+$ (100), 393 $[M\text{-}Me\text{-}H_2O]^+$ (22), 273 (16), 259 (59), 241 (19). ^1H NMR ($CDCl_3$, 500 MHz) δ: 5.23 (1 H, dm, *J* = 4.1 Hz, H-11), 3.22 (1 H, dd, *J* = 11.6 and 4.3 Hz, H-3), 2.03 (1 H, dm, *J* = 12.8 and 1.5 Hz), 1.03 (3 H, s, Me), 0.98 (3 H, s, Me), 0.89 (3 H, d, *J* = 6.6 Hz, Me), 0.83 (3 H, d, *J* = 6.6 Hz, Me), 0.82 (3 H, s, Me), 0.81 (3 H, s, Me), 0.77 (3 H, s, Me), 0.76 (3 H, s, Me). ^{13}C NMR see Table I.

Platanic acid (**4**). White solid. m.p. 270–287 °C. $[\alpha]_D^{24}$ -27.5, ($CHCl_3$, c 0.08). MS *m/z* (rel. int.): 458 $[M]^+$ (20), 440 $[M\text{-}H_2O]^+$ (63), 425 $[M\text{-}Me\text{-}H_2O]^+$ (24), 412 (11), 397 (25), 223 (21), 207 (51), 191 (24), 190 (45), 189 (100), 147 (42), 135 (44), 121 (37), 107 (36), 95 (46), 81 (49), 69 (38). HRMS 458.3417 $[M]^+$ ($C_{29}H_{46}O_4$ requires 458.3396). ^1H NMR ($CDCl_3$, 300 MHz) δ: 3.25 (1 H, td, *J* =10.0 and 4.7 Hz, H-19), 3.20 (1 H, dd, *J* = 11.0 and 5.0 Hz, H-3), 2.19 (3 H, s, H-29), 1.01 (3 H, s, Me), 0.97 (3 H, s, Me), 0.91 (3 H, s, Me), 0.82 (3 H, s, Me), 0.75 (3 H, s, Me). ^{13}C NMR see Table I.

Fatty acid esters of betulinic acid (**5**). MS *m/z* (rel. int): 694 (4.4), 680 (1.3), 679 (2.2), 667 (1.7), 666 (3.2), 651 (1.4), 649 (1.8), 648 (2.8), 620 (1.8), 439 (58), 438 (100), 423 (26), 395 (33), 189 (42). ^{13}C NMR of the fatty acid residues ($CDCl_3$, 125 MHz) δ: 173.5 (C-1'), 34.8 (C-2'), 31.9, 26.69*, 29.58, 29.46, 29.36, 29.25, 29.17, 28.0, 23.7, 22.7, 14.1 (Me), (*this signal possesses nearly the tenfold intensity) (shifts of the triterpene moiety in Table I).

2,4-Dihydroxy phenylacetic acid methyl ester (**6**). Amorphous solid. UV λ_{max}^{MeOH} nm (log ε): 280 (3.60), 213 (3.99). IR ν_{max}^{KBr} (cm^{-1}): 3385, 2955, 1715, 1622, 1523, 1461, 1216, 1172, 1104, 1086, 979, 843, 796. MS *m/z* (rel. int.): 182 $[M]^+$ (68), 150 (77), 123 (100), 122 (34), 95 (9), 94 (12). HRMS 182.0585 $[M]^+$ ($C_9H_{10}O_4$ requires 182.0579). ^1H NMR (CD_3OD, 500 MHz) δ: 6.88 (1 H, d, *J* = 8.2 Hz, H-6), 6.29 (1 H, d, *J* = 2.4 Hz, H-3), 6.24 (1 H, dd, *J* = 8.2 and 2.4 Hz, H-5), 3.65 (3 H, s, OMe), 3.49 (2 H, s, H-7). ^{13}C NMR (CD_3OD, 125 MHz) δ: 175.2 (C-8), 158.7 (C-2), 157.6 (C-4), 132.4 (C-6), 113.7 (C-1), 107.4 (C-5), 103.3 (C-3), 52.2 (OMe), 35.7 (C-7).

(-)-Epiafzelechin (**7**). Amorphous solid. $[\alpha]_D^{32}$ -37.9°, (MeOH, c 0.20). MS *m/z* (rel. int.): 274 $[M]^+$ (22), 167 (8), 139 (100), 136 (35), 107 (36), 106 (27). ^1H NMR (CD_3OD, 500 MHz) δ: 7.31 (2 H, d, *J* = 8.4 Hz, H-2'/6'), 6.77 (2 H, d, *J* = 8.4 Hz, H-3'/5'), 5.94* (1 H, d, *J* = 2.1 Hz, H-6), 5.90* (1 H, d, *J* = 2.1 Hz, H-8), 4.18 (1 H, ddd, *J* = 4.6, 2.9 and 1.5 Hz, H-3), 2.74 (1 H, dd, *J* = 16.8 and 2.9 Hz, H-4), (H-2 is hidden under the HDO signal). ^{13}C NMR (CD_3OD, 125 MHz) δ: 158.0, 157.9, 157.7 and 157.4 (C-5,7,9 and 4'), 131.6 (C-1'), 129.1 (C-2'/6'), 115.7 (C-3'/5'), 100.0 (C-10), 96.4* (C-6), 95.9* (C-8), 79.9 (C-2), 67.5 (C-3), 29.4 (C-4), (*assignment interchangeable).

Mearnsitrin (**8**). amorphous, yellow solid. $[\alpha]_D^{32}$ -119°, (MeOH, c 0.16). MS *m/z* (rel. int.): 478 $[M]^+$ (<1), 332 $[aglycon]^+$ (100), 317 $[332\text{-}Me]^+$

(97), 303 (6), 289 (15), 261 (18). ^{1}H NMR ($CDCl_3$+CD_3OD, 500 MHz) δ: 6.96 (2 H, s, H-2'/6'), 6.39 (1 H, d, J = 2.1 Hz, H-8), 6.27 (1 H, d, J = 2.1 Hz, H-6), 5.32 (1 H, d, J = 1.5 Hz, H-1"), 4.28 (1 H, dd, J = 3.2 and 1.7 Hz, H-2"), 3.92 (3 H, s, 4'-OMe), 3.80 (3 H, dd, J = 8.9 and 3.1 Hz, H-3"), 3.39–3.34 (2 H, overlapped, H-4", H-5"), 0.96 (3 H, d, J = 5.8 Hz, H-6"). ^{13}C NMR ($CDCl_3$+CD_3OD, 125 MHz) δ: 177.7 (C-4), 164.0 (C-7), 161.1 (C-5), 156.9* (C-9), 156.5* (C-2), 149.7 (C-3'/5'), 137.3 (C-4'), 134.8 (C-3), 125.0 (C-1'), 108.0 (C-2'/6'), 104.2 (C-10), 101.6 (C-1"), 98.1 (C-6), 93.0 (C-8), 71.3 (C-4"), 70.1* (C-2"), 69.9* (C-3"), 69.8 (C-5"), 59.2 (4-OMe), 15.9 (C-6"), (*assignment interchangeable).

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