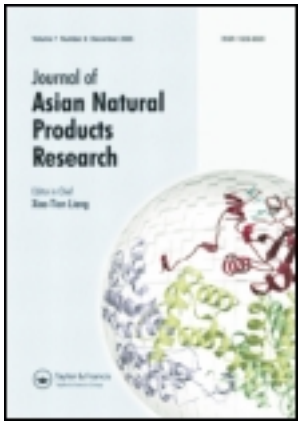

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NON-TAXANE COMPOUNDS FROM THE BARK OF *TAXUS YUNNANENSIS*

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From the bark of *Taxus yunnanensis*, 15 non-taxane compounds were isolated. Through spectroscopic methods such as 1D and 2D NMR and MS experiments, one of them was determined as a new abietane-type diterpenoid named taxayunnin (**1**). The other 14 known compounds were identified as taxamairin C (**2**), taxamairin A (**3**), 3β-hydroxy-sandaracopimaric acid (**4**), (+)-3-hydroxy-isodrimenin (**5**), rubrosterone (**6**), ponasterone A (**7**), ecdysterone (**8**), 20-hydroxy-echysone-20,22-monoacetonide (**9**), 7-oxositosterol (**10**), stigmast-4-en-6β-ol-3-one (**11**), 5α,6β-dihydroxy-daucosterol (**12**), β-sitosterol (**13**), daucosterol (**14**), 1-*O*-β-D-glucopyranosyl-(2*S*, 3*R*, 4*E*, 8*Z*)-2-*N*-(2′-hydroxypalmitoyl)-octadeca-sphinga-4,8-dienine (**15**), respectively. Compounds **4**–**6**, **9**–**12** and **15** were isolated from *Taxus* plants for the first time.

Keywords: Taxaceae; *Taxus yunnanensis*; Bark; Non-taxane compounds

INTRODUCTION

Besides the major and well-known taxane diterpenoids [1], *Taxus* plants also contain abundant non-taxane compounds such as non-taxane diterpenoids, steroids, lignans, flavonoids, sugar derivatives and so on [2,3]. Our previous work on the chemical and biological constituents of the root and bark of *Taxus yunnanensis*, an evergreen tree endemic to Yunnan of China, has led to the isolation of many new and known taxane diterpenoids including paclitaxel [4–14]. In this paper, we report the isolation and structure characterization of a new abietane diterpenoid, taxayunnin (**1**), and fourteen known non-taxane compounds (**2**–**15**) from the bark of this plant.

RESULTS AND DISCUSSION

Taxayunnin (**1**) was obtained as pale yellow needles with mp 215°C. It showed a molecular ion peak at *m/z* 346 [M^+] in its HREI mass spectrum, which in combination with ^1H and ^{13}C

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NMR (including DEPT) spectra suggested a molecular formula $C_{21}H_{30}O_4$. Its ^{1}H NMR spectrum (see Table I) displayed three methyls linked to quaternary carbon atoms, an isopropyl group, and a deshielded aromatic proton at δ 7.62. These evidences indicated **1** was an abietane diterpenoid. Comparison of ^{1}H and ^{13}C NMR spectra (Tables I and II) of **1** with those of **2** revealed that **1** was similar to **2** except for A-ring moiety. The difference could be rationalized to an oxygen bridge, which occurred between C-3 and C-20 in **2**. Further comparison of the ^{1}H NMR data of **1** with those of 3β-hydroxy-demethyl cryptojaponol [15], an abietane diterpenoid isolated from *Salvia pubescens*, suggested that **1** was a mono-methyl ether of 3β-hydroxy-demethyl cryptojaponol. The methoxy group attached to C-12 was supported by the simultaneous HMBC correlations of C-12 with both of 12-OCH_3 and H-15 (Fig. 1). The β-orientation of the hydroxy group at C-3 was established by the NOE correlations of H-3 with H-5 and CH_3-18. Due to the *γ-gauche* deshielding effect of 3β-OH, the chemical shift of C-19 moved upfield obviously (about 3 ppm comparing with that of **2**). Thus the structure of compound **1** was determined as 3,11-dihydroxy-12-methoxy-8,11,13-abietatrien-7-one, and was given the trivial name taxayunnin.

Along with the new diterpenoid, fourteen known non-taxane compounds were also obtained. On the basis of the comparison of their spectral data with those reported in the

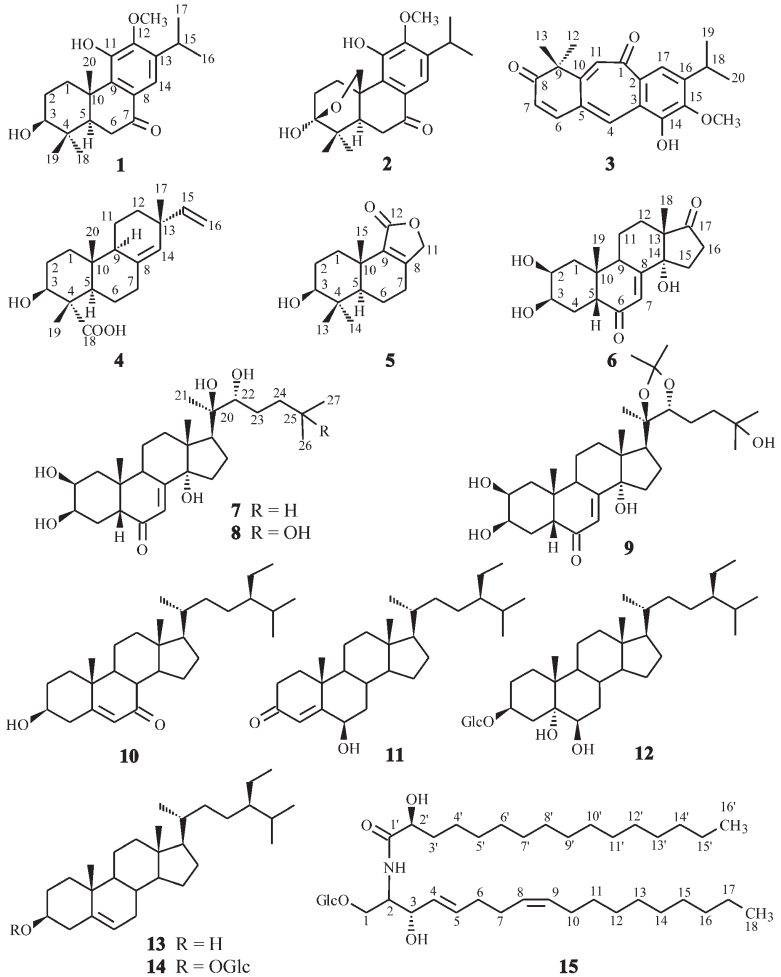

TABLE I ^{1}H NMR data of compounds **1** and **2**

Proton	**1***	**2**†
H-1α	1.58 (1H, m)	1.45 (1H, ddd, 3.0, 12.4, 18.0)
H-1β	3.30 (1H, dt, 3.6, 13.9)	3.43 (1H, ddd, 5.4, 12.6, 18.0)
H-2α	1.81 (2H, m)	1.91 (1H, ddd, 3.7, 12.7, 16.5)
H-2β	–	2.24 (1H, ddd, 5.4, 12.3, 17.9)
H-3	3.35 (1H, dd, 5.2, 6.9)	–
H-5	1.83 (1H, dd, 3.1, 13.9)	2.11 (1H, dd, 2.9, 14.9)
H-6α	2.60 (1H, dd, 14.2, 16.9)	2.53 (1H, dd, 4.0, 14.8)
H-6β	2.68(1H, dd, 3.1, 16.9)	2.64 (1H, t, 14.9)
H-14	7.62 (1H, s)	7.50 (1H, s)
H-15	3.20 (1H, spt, 6.9)	3.18 (1H, spt, 6.8)
CH_3-16	1.24 (3H, d, 6.9)	1.20 (3H, d, 6.8)
CH_3-17	1.26 (3H, d, 6.9)	1.22 (3H, d, 6.8)
CH_3-18	1.07 (3H, s)	1.05 (3H, s)
CH_3-19	0.95 (3H, s)	1.10 (3H, s)
CH_3-20	1.39 (3H, s)	4.75 (1H, dd, 1.4, 8.9, H-20a)
/H_2-20		4.15 (1H, dd, 2.4, 9.0, H-20b)
11-OH	6.12 (1H, s)	6.29 (1H, s)
12-OCH_3	3.81 (3H, s)	3.79 (3H, s)

* 500 MHz, $CDCl_3$, *J* in Hz, δ in ppm.
† 400 MHz, $CDCl_3$, *J* in Hz, δ in ppm.

TABLE II ^{13}C NMR data of compounds **1–4**

Carbon	**1***	**2**†	**3**†	**4**†
C-1	34.7 t	29.9 t	188.1 s	36.9 t
C-2	27.9 t	35.9 t	120.9 s	27.0 t
C-3	78.0 d	98.1 s	146.1 s	75.6 d
C-4	39.2 s	40.8 s	133.7 d	53.4 s
C-5	49.7 d	47.2 d	130.2 s	49.7 d
C-6	35.3 t	35.9 t	147.8 d	24.5 t
C-7	198.5 s	198.3 s	123.8 d	35.3 t
C-8	128.6 s	130.1 s	200.8 s	136.0 s
C-9	137.3s	127.2 s	50.5 s	50.4 d
C-10	39.9 s	37.0 s	151.4 s	37.7 s
C-11	146.5 s	147.6 s	131.4 d	18.8 t
C-12	149.3 s	149.1 s	26.8 q	34.5 t
C-13	139.4 s	140.5 s	27.5 q	37.5 s
C-14	117.5 d	117.2 d	146.6 s	129.6 d
C-15	26.8 d	26.7 d	148.3 s	148.7 d
C-16	23.4 q	23.4 q	136.6 s	110.3 t
C-17	23.5 q	23.4 q	119.4 d	26.1 q
C-18	28.0 q	26.7 q	27.5 d	182.5 s
C-19	15.3 q	18.2 q	23.4 q	11.0 q
C-20	18.0 q	65.3 t	23.4 q	12.9 q
OCH_3	61.8 q	61.9 q	62.0 q	

* 125 MHz, $CDCl_3$, δ in ppm.
† 100 MHz, $CDCl_3$, δ in ppm.

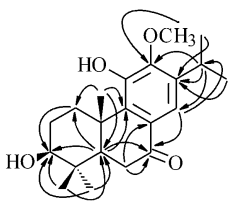

FIGURE 1 Selected HMBC correlations of compound **1** (from H to C).

literatures, these compounds were identified as an abietane-type diterpenoid, taxamairin C (**2**) [16]; a deformed abietane-type diterpenoid, taxamairin A (**3**) [16]; an isopimarane-type diterpenoid, 3β-hydroxysandaracopimaric acid (**4**) [17]; a drimane-type sesquiterpenoid, (+)-3-hydroxy-isodrimenin (**5**) [18]; nine steroids, namely rubrosterone (**6**) [19], ponasterone A (**7**) [20], ecdysterone (**8**) [20], 20-hydroxy-echysone-20,22-monoacetonide (**9**) [21], 7-oxositosterol (**10**) [22], stigmast-4-en-6β-ol-3-one (**11**) [22], 5α,6β-dihydroxy-daucosterol (**12**) [23], β-sitosterol (**13**) [22], daucosterol (**14**) [24]; and a cerebroside, 1-*O*-β-D-gluco-pyranosyl-(2*S*, 3*R*, 4*E*, 8*Z*)-2-*N*-(2′-hydroxypalmitoyl)-octadeca-sphinga-4,8-dienine (**15**) [25] respectively. The structures of compounds **4**–**7**, **9**, **12** and **15** were further confirmed by 2D NMR experiments. Full assignments of compound **7** were also achieved. Among these known compounds, **4**–**6**, **9**–**12** and **15** were isolated from *Taxus* plants for the first time.

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were obtained on a XRC-1 micro melting point apparatus and are uncorrected. 1D and 2D NMR experiments were performed either on a Bruker AM-400 or DRX-500 spectrometer. Unless otherwise indicated, chemical shifts (δ) were expressed in ppm with reference to the solvent signals. FABMS and HRFABMS were taken on a VG Auto Spec-3000 or on a Finnigan MAT 90 instrument. IR spectra were recorded on a Bio-Rad FTS-135 spectrometer with KBr pellets. UV spectral data were obtained on a UV 210A spectrometer. Optical rotations were carried out on a HORIBA SEPA-300 High Sensitive Polarimeter or Perkin–Elmer model 241 Polarimeter. Column chromatography was performed either on Si gel (200–300 mesh, Qingdao Marine Chemical Incorporation, China), Si gel H (10–40 μ, Qingdao Marine Chemical Incorporation, China), Lichroprep Rp_{18} gel (40–63 μm, Merck, Darmstadt, Germany), or on MCI gel (70–150 μ, Mitsubishi Chemical Corporation, Tokyo, Japan). Fractions were monitored by TLC and spots were visualized by heating Si gel plates sprayed with 10% H_2SO_4 in EtOH.

Plant Material

The barks of *T. yunnanensis* Cheng et L. K. Fu (Taxaceae) were collected in Lijiang Prefecture of Yunnan Province of People's Republic of China in January, 1997. The plant material was identified by Prof Xi-Wen Li at Kunming Institute of Botany. A voucher specimen (No. YAF-97-18) has been deposited at the Yunnan Academy of Forestry, Kunming, Yunnan, People's Republic of China.

Extraction and Isolation

Dried bark (50 kg) was milled and extracted by maceration in EtOH for one week, the extract was concentrated *in vacuo* to a syrup, diluted with H_2O and partitioned with $CHCl_3$. The $CHCl_3$ layer was evaporated *in vacuo* to afford 500 g of a residue, which was absorbed on 800 g of Si gel and chromatographed on a pre-packed (2 kg) Si gel column. Gradient elution was accomplished with $CHCl_3$–Me_2CO (1:0, 9:1, 8:2, 7:3, 0:1). 102 mg of compound **7** was crystallized from the Me_2CO fraction. The $CHCl_3$ fraction was rechromatographed on Si gel eluting with petroleum ether–Me_2CO and petroleum ether–*i*–PrOH to afford compounds **1** (15 mg), **3** (400 mg), **5** (10 mg), **10** (20 mg) and **13** (24 mg), respectively. Part of the 9:1 $CHCl_3$–Me_2CO fraction was subjected to repeated chromatography on Si gel sequentially eluting with $CHCl_3$–Me_2CO, petroleum ether–EtOAc, petroleum ether–Me_2CO and cyclohexane–EtOAc to yield compounds **2** (24 mg), **4** (12 mg) and **11** (5 mg), respectively.

Part of the Me_2CO fraction was further chromatographed on Si gel using $CHCl_3$–MeOH and $CHCl_3$–*i*–PrOH as eluents, and on RP_{18} and MCI gel using MeOH–H_2O and acetonitrile–H_2O as eluents to provide compounds **6** (20 mg), **8** (8 mg), **9** (22 mg), **12** (4 mg), **14** (15 mg) and **15** (30 mg), respectively.

Taxayunnin (1)

$C_{21}H_{30}O_4$, pale yellow needles, mp 215°C; $[\alpha]_D^{16.4}$ + 7.33° (*c* 0.75, CH_3OH); UV (MeOH) λ_{max} (log ε): 312 (3.7), 296.5 (3.5), 269 (4.3) nm; IR ν_{max} (KBr): 3443, 2972, 2944, 2876, 1734, 1700, 1675, 1671, 1636, 1598, 1560, 1507, 1450, 1419, 1363, 1321, 1212, 1172, 1140, 1085, 1049, 1014, 996, 948, 760, 659, 627 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) data see Table I, ^{13}C NMR (125 MHz, $CDCl_3$) data see Table II; EIMS *m/z* (%): 346 $[M]^+$ (100), 331 (20), 313 (51), 304 (5), 287 (20), 271 (15), 259 (18), 245 (64), 233 (20), 219 (18), 203 (17), 193 (16), 173 (10), 157 (7), 145 (8), 128 (9), 115 (10), 91 (11), 77 (7), 69 (9), 57 (14); HREIMS *m/z* 346.2134 $[M]^+$, Calcd 346.2144.

Taxamairin C (2)

$C_{21}H_{28}O_5$, colorless needles; IR ν_{max} (KBr): 3490, 2967, 2931, 2873, 1679, 1608, 1561, 1474, 1423, 1398, 1366, 1325, 1253, 1226, 1176, 1102, 1055, 1039, 995, 918, 887, 748, 551 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) data see Table I; ^{13}C NMR (100 MHz, $CDCl_3$) data see Table II; Positive FABMS *m/z* (%): 361 $[M + H]^+$ (100), 343 $[M - H_2O + H]^+$ (17), 304 (6), 245 (2), 85 (3), 60 (11).

Taxamairin A (3)

$C_{21}H_{22}O_4$, yellow needles; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (1H, s, H-4), 7.28 (1H, d, $J = 9.9$ Hz, H-6), 6.08 (1H, d, $J = 9.8$ Hz, H-7), 6.92 (1H, s, H-11), 1.43 (3H, s, CH_3-12), 1.43 (3H, s, CH_3-13), 6.64(1H, br s, 14-OH), 7.91 (1H, s, H-17), 3.32 (1H, heptet, $J = 6.8$ Hz, H-18), 1.29 (3H, d, $J = 7.0$ Hz, CH_3-19), 1.29 (3H, d, $J = 7.0$ Hz, CH_3-20), 3.87 (3H, s, 15-OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) data see Table II; EIMS *m/z* (%): 338 $[M]^+$ (87), 323 $[M - CH_3]^-$ (6), 267 $[M - (CH_3)_2CH–CO]^-$ (55), 252 (10), 237 (13), 165 (16), 115 (7).

3β-Hydroxysandaracopimaric Acids (4)

$C_{20}H_{30}O_3$, colorless needles; ^1H NMR (400 MHz, $CDCl_3$) δ 1.81 (1H, dd, $J = 2.3$, 12.1 Hz, H-1a), 1.27 (1H, overlap, H-1b), 1.70 (1H, m, H-2a), 1.58 (1H, m, H-2b), 4.10 (1H, dd, $J = 4.0$, 11.7 Hz, H-3), 1.78 (1H, dd, $J = 2.3$, 12.2 Hz, H-5), 1.54 (1H, m, H-6a), 1.27 (1H, overlap, H-6b), 2.23 (1H, dd, $J = 3.1$, 14.5 Hz, H-7a), 2.09 (1H, m, H-7b), 1.74 (1H, br d, $J = 8.5$ Hz, H-9), 1.63 (1H, m, H-11a), 1.52 (1H, m, H-11b), 1.46 (1H, m, H-12a), 1.37 (1H, m, H-12b), 5.23 (1H, br s, H-14), 5.76 (1H, dd, $J = 10.6$, 17.4 Hz, H-15), 4.90 (1H, dd, $J = 1.3$, 17.4 Hz, H-16a), 4.88 (1H, dd, $J = 1.3$, 10.6, H-16b), 1.04 (3H, s, H-17), 1.16 (3H, s, H-19), 0.83 (3H, s, H-20), 1.17 (1H, br s, 3′-OH); ^{13}C NMR (100 MHz, $CDCl_3$) data see Table II; Negative FABMS *m/z* (%): 317 $[M - H]^-$ (100), 301 (2), 97 (1); FABMS *m/z* (%): 318 $[M]^+$ (5), 301 (54), 283 (15), 249 (9), 219 (16), 191 (49), 177 (11), 157 (100), 139 (12), 122 (6), 106 (3), 92 (1), 79 (3).

(+)-3-Hydroxyisodrimenin (5)

$C_{15}H_{22}O_3$, white needles; ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.7 (t, C-1), 27.4 (t, C-2), 78.7 (d, C-3), 38.9 (s, C-4), 51.7 (d, C-5), 18.1 (t, C-6), 25.5 (t, C-7), 158.9 (s, C-8), 135.4 (s, C-9), 34.7 (s, C-10), 70.6 (t, C-11), 172.5 (s, C-12), 15.4 (q, C-13), 28.3 (q, C-14), 20.1 (q, C-15); EIMS *m/z* (%): 250 $[M]^+$ (61), 232 (18), 217 (56), 207 (100), 194 (51), 189 (45), 175 (10), 163 (31), 151 (57), 138 (21), 125 (16), 119 (26), 105 (41), 91 (63), 77 (46), 69 (66), 55 (37).

Rubrosterone (6)

$C_{19}H_{26}O_5$, amorphous solid; ^{13}C NMR (100 MHz, CD_3OD) δ 37.4 (t, C-1), 68.5 (d, C-2), 68.7 (d, C-3), 32.9 (t, C-4), 52.0 (d, C-5), 205.9 (s, C-6), 122.5 (d, C-7), 164.6 (s, C-8), 35.9 (d, C-9), 39.4 (s, C-10), 20.8 (t, C-11), 25.0 (t, C-12), 54.1 (s, C-13), 80.5 (s, C-14), 29.1 (t, C-15), 34.0 (t, C-16), 220.2 (s, C-17), 17.6 (q, CH_3-18), 24.6 (q, CH_3-19); Negative FABMS *m/z* (%): 333 $[M - H]^-$ (100), 316 (55), 172 (1)., 155 (2), 125 (4), 111 (6), 97 (17), 80 (16).

Ponasterone A (7)

$C_{27}H_{44}O_6$, white needles; IR ν_{max} (KBr): 3387, 2958, 2873, 1645, 1381, 1051, 874 cm^{-1}; ^1H NMR (400 MHz, Pyridine-d_5) δ 2.13–2.26 (1H, m, H-1a), 1.87–1.97 (1H, m, H-1b), 4.18 (1H, br dd, $J = 3.7$, 11.5 Hz, H-2), 4.23 (1H, br s, H-3), 2.02–2.10 (1H, m, H-4a), 1.69–1.86 (1H, m, H-4b), 3.02 (1H, dd, $J = 3.6$, 13.0 Hz, H-5), 6.27 (1H, d, $J = 2.0$ Hz, H-7), 3.60 (1H, br t, $J = 8.4$ Hz, H-9), 1.69–1.86 (1H, m, H-11a), 1.87–1.97 (1H, m, H-11b), 2.02–2.10 (1H, m, H-12a), 2.62 (1H, ddd, $J = 4.0$, 8.5, 12.5 Hz, H-12b), 1.87–1.97 (1H, m, H-15a), 2.13–2.26 (1H, m, H-15b), 2.02–2.10 (1H, m, H-16a), 2.46 (1H, ddd, $J = 3.9$, 9.9, 13.7 Hz, H-16b), 2.93 (1H, t, $J = 9.2$ Hz, H-17), 1.23 (3H, s, CH_3-18), 1.06 (3H, s, CH_3-19), 1.58 (3H, s, CH_3-21), 3.81 (1H, d, $J = 10.1$ Hz, H-22), 1.54 (1H, d, $J = 9.9$ Hz, H-23a), 1.69–1.86 (1H, m, H-23b), 1.37–1.46 (1H, m, H-24a), 1.69–1.86 (1H, m, H-24b), 1.46–1.53 (1H, m, H-25), 0.81 (3H, d, $J = 4.5$ Hz, CH_3-26), 0.80 (1H, d, $J = 4.5$ Hz, CH_3-27); ^{13}C NMR (100 MHz, Pyridine-d_5) δ 38.0 (t, C-1), 68.1 (d, C-2), 68.1 (d, C-3), 32.5 (t, C-4), 51.4 (d, C-5), 203.4 (s, C-6), 121.8 (d, C-7), 166.0 (s, C-8), 34.5 (d, C-9), 38.7 (s, C-10), 21.2 (t, C-11), 32.1 (t, C-12), 48.2 (s, C-13), 84.3 (s, C-14), 31.8 (t, C-15), 21.5 (t, C-16), 50.1 (d, C-17), 17.9 (q, CH_3-18), 24.5 (q, CH_3-19), 76.8 (s, C-20), 21.6 (q, CH_3-21), 76.8 (d, C-22), 30.3 (t, C-23), 37.2 (t, C-24), 28.2 (d, C-25), 22.4 (q, CH_3-26), 23.3 (q, CH_3-27); Positive FABMS *m/z* (%): 465 $[M + H]^+$ (29), 385 (77), 343 (39), 283 (19), 85 (59).

Ecdysterone (β-edysone) (8)

$C_{27}H_{44}O_7$, colorless block crystals; Positive FABMS *m/z* (%): 481 $[M + H]^+$ (100), 463 (35), 445 (40), 427 (180), 347 (16), 303 (14), 250 (11), 143 (23), 69 (340).

20-Hydroxyechysone 20,22-monoacetonide (9)

$C_{30}H_{48}O_7$, white powders; Negative FABMS *m/z* (%): 519 $[M - H]^-$ (100), 503 (48), 443 (7), 318 (2), 249 (3), 125 (5).

7-Oxositosterol (10)

$C_{29}H_{48}O_2$, white needles; EIMS *m/z* (%): 428 $[M]^+$ (100), 414 (14), 395 (9), 287 (14), 247 (10), 205 (10), 192 (21), 161 (18), 135 (16), 95 (18), 81 (22), 69 (29).

Stigmast-4-en-6β-ol-3-one (11)

$C_{29}H_{48}O_2$, white needles; Positive FABMS *m/z* (%): 429 $[M + H]^+$ (19), 373 (100), 355 (180), 263 (28), 235 (38), 206 (56), 171 (69), 157 (81), 133 (66), 115 (44), 101 (36), 79 (42), 65 (14).

5α,6β-Dihydroxydaucosterol (12)

$C_{35}H_{62}O_8$, pale yellow needles; ^{1}H NMR (400 MHz, pyridine-d_5) δ 5.02 (1H, m, H-3), 2.83 (1H, t, $J = 11.7$ Hz, H-4a), 2.50 (1H, dd, $J = 4.6$, 12.5 Hz, H-4b), 4.14 (1H, br s, H-6), 0.71 (3H, s, CH_3-18), 1.53 (3H, s, CH_3-19), 0.97 (3H, d, $J = 6.4$ Hz, CH_3-21), 0.85 (3H, d, $J = 6.8$ Hz, CH_3-26), 0.86 (3H, d, $J = 6.8$ Hz, CH_3-27), 0.88 (3H, t, $J = 7.4$ Hz, CH_3-29), 4.95 (1H, d, $J = 7.6$ Hz, H-1′), 4.05 (1H, t, $J = 8.2$ Hz, H-2′), 4.19 (1H, t, $J = 8.9$ Hz, H-3′), 4.28 (1H, t, $J = 9.0$ Hz, H-4′), 3.75 (1H, m, H-5′), 4.49 (1H, dd, $J = 2.2$, 11.9 Hz, H-6′a), 4.38 (1H, dd, $J = 5.0$, 11.8, H-6′b); ^{13}C NMR (100 MHz, pyridine-d_5) δ 33.1 (t, C-1), 29.6 (t, C-2), 75.4 (d, C-3), 38.7 (t, C-4), 75.9 (s, C-5), 76.4 (d, C-6), 35.7 (t, C-7), 31.3 (d, C-8), 45.9 (d, C-9), 39.2 (s, C-10), 21.8 (t, C-11), 40.7 (t, C-12), 44.2 (s, C-13), 56.7 (d, C-14), 24.7 (t, C-15), 28.7 (t, C-16), 56.7 (d, C-17), 12.4 (q, CH_3-18), 17.0 (q, CH_3-19), 36.6 (d, C-20), 19.1 (q, CH_3-21), 34.4 (t, C-22), 27.0 (t, C-23), 46.2 (d, C-24), 29.6 (d, C-25), 19.3 (q, CH_3-26), 20.0 (q, CH_3-27), 23.8 (t, C-28), 12.2 (q, CH_3-29), 102.4 (d, C-1′), 75.4 (d, C-2′), 78.6 (d, C-3′), 71.8 (d, C-4′), 78.3 (d, C-5′), 62.9 (t, C-6′); Negative FABMS *m/z* (%): 609 $[M - H]^-$ (87), 571 (32), 519 (31), 505 (56), 479 (100), 463 (23), 421 (30), 325 (75), 311 (52), 294 (38), 245 (12), 159 (22), 119 (37), 99 (11), 80 (28).

1-O-β-D-Glucopyranosyl-(2S, 3R, 4E, 8Z)-2-N-(2′-hydroxypalmitoyl)-octadecasphinga-4,8,-dienine (15)

$C_{40}H_{75}NO_9$, white powders; ^{1}H NMR (400 MHz, CD_3OD) δ 5.72 (1H, dt, $J = 15.4$, 5.8 Hz, H-5), 5.48 (1H, dd, $J = 7.4$, 15.5 Hz, H-4), 5.37 (2H, m, H-8 and H-9), 4.26 (1H, d, $J = 7.8$ Hz, H-1″), 0.90 (6H, t, $J = 7.0$ Hz, CH_3-18 and CH_3-16′); ^{1}H NMR (400 MHz, Pyridine-d_5) δ 4.70 (1H, dd, $J = 5.8$, 10.3 Hz, H-1a), 4.21 (1H, overlap, H-1b), 4.76 (1H, m, H-2), 4.57 (1H, br t, $J = 4.3$ Hz, H-3), 5.95 (2H, m, H-4 and H-5), 5.48 (2H, m, H-8 and H-9), 0.86 (6H, t, $J = 6.8$ Hz, CH_3-18 and CH_3-16′), 8.36 (1H, d, $J = 8.6$ Hz, 2-NH). 4.76 (1H, overlap, H-2′), 4.90 (1H, d, $J = 7.7$ Hz, H-1″), 4.03 (1H, br t, $J = 6.4$ Hz, H-2″), 4.21 (2H, m, H-3″ and H-4″), 3.09 (1H, m, H-5″), 4.50 (1H, d, $J = 10.1$ Hz, H-6″a), 4.34 (1H, dd, $J = 5.2$, 11.7 Hz, H-6″b); ^{13}C NMR (100 MHz, Pyridine-d_5, values may be interchanged) δ 70.1 (t, C-1), 54.7 (d, C-2), 72.6 (d, C-3), 132.1 (2C, d, C-4 and C-5), 32.9 (t, C-6), 27.6 and 27.4 (each t, C-7 and C-10), 130.7 and 129.5 (each d, C-8 and C-9), 14.3 (2C, q, CH_3-18 and CH_3-16′), 175.7 (s, C-1′), 72.4 (d, C-2′), 105.6 (d, C-1″), 75.1 (d, C-2″), 78.5 (2C, d, C-3″ and C-5″), 71.7 (d, C-4″), 62.8 (t, C-6″); Positive FABMS *m/z* (%): 715 (53), 697 (67), 534 (78), 262 (92); HRFABMS *m/z* 714.5497, calcd. 714.550.

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