

DITERPENOIDS FROM *ISODON FLAVIDUS*

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Key Word Index—*Isodon flavidus*, Labiatae; diterpenoids; flavidusin A and B.

Abstract—Two new diterpenoids of the pimarane type, flavidusin A and B, as well as seven known compounds, glutinosin, *ent*-kauran-16 β ,17-diol, siegesbeckiol, 16-hydroxy feruginol, hinokiol, maslinic acid and 5-hydroxy-7,4'-dimethoxyflavone were isolated from the dried leaves of *Isodon flavidus*. The new diterpenoids were identified as isopimar-8(14)-15,16-diol and 15,16-dihydro-15 β -hydroxy-14 α ,16-epoxyisopimar-8(9)-ene. The absolute configuration of glutinosin is revised to the isopimarane type rather than the *ent*-isopimarane type on the basis of chemical correlation with (+)-isopimara-8(9), 15-diene. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Isodon flavidus (Hand-Mazz) Hara is a perennial herb which is distributed in the northwestern area of Yunnan and Guizhou province, People's Republic of China [1], and has not been previously investigated. From the dried leaves of this herb, collected from Dan Li of Yunnan province, two new diterpenoids of the pimarane type, flavidusin A (2) and B (3), together with seven known compounds were isolated. The structures of the new compounds were elucidated on the basis of spectroscopic analysis (including 2D NMR) and comparison with related compounds. *ent*-Kauranes are characteristic of plants of the genus *Isodon* [2]. However, abietane and pimarane diterpenes, and bicyclic sesquiterpenes have also been isolated from this genus, by Sun, H. D. and his coworkers [3]. It was also found that *ent*-kaurane, abietane and pimarane type diterpenes co-occurred in *I. flavidus* in our research. This paper deals with the structures of these compounds and the inversion of the absolute configuration of glutinosin (1)

RESULTS AND DISCUSSION

Repeated column chromatography and recrystallization of the ethyl acetate extract of dry *I. flavidus* leaves yielded two new constituents (2 and 3), as well as seven known compounds: glutinosin (1) [4], *ent*-kaurane-16 β , 17-diol (4) [7], siegesbeckiol (5) [15], 16-

hydroxy feruginol (6) [16], hinokiol (7) [17], maslinic acid (8) [18] and 5-hydroxy-7,4'-dimethoxyflavone (9) [19]. The absolute configuration of glutinosin (1) was revised to be isopimarane type rather than *ent*-isopimarane type on the basis of chemical correlation with (+)-isopimara-8(9), 15-diene (10).

Glutinosin was assigned the molecular formula (1) C₂₀H₃₄O₂ ([M]⁺, *m/z* = 306). The mass spectral, optical rotation, ¹H and ¹³C NMR data of 1 were in good agreement with those of glutinosin (1a) [4]. The absolute configuration assignment of glutinosin (1a) was established as *ent*-8(9)-isopimarene-15,16-diol based on biogenetic considerations [4]. It is well known that *ent*-pimarane type diterpenoids are the precursors of *ent*-kaurane type diterpenes [5, 6]. However, there is also evidence to show that the pimarane, not *ent*-pimarane diterpenes, co-occurred with *ent*-kaurane diterpenes in the same plant [7]. In order to establish the absolute configuration of glutinosin, the following chemical transformation was performed according to [8] (see Fig. 1). Compound 1 was converted into 10 whose mass spectrum, ¹H and ¹³C NMR and optical rotation were identical with those of (+)-isopimara-8(9), 15-diene [9–11]. Thus, the structure of glutinosin (1) was determined as 8(9)-isopimarene-15,16-diol.

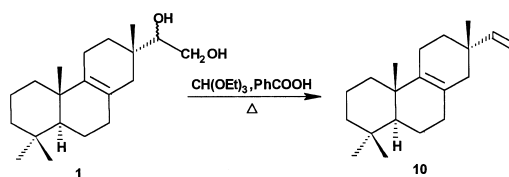


Fig. 1.

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CH₂OH fragment. The ¹H-¹H COSY spectrum of **2** also confirmed the presence of the partial structure -CHOH-CH₂OH according to the following facts: the signals at δ 3.85 (1H, *dd*, *J* = 8.8, 2.4 Hz) showed correlation with the signals at δ 3.92 (1H, *dd*, *J* = 10.7, 8.8 Hz) and 4.17 (1H, *dd*, *J* = 10.7, 2.4 Hz), and the two latter signals showed correlation with each other. All the above data suggested **2** possessed a pimarane or isopimarane skeleton with a 1,2-dihydroxyethyl side-chain and a double bond between C-8 and C-14. The chemical shifts of C-8, C-9, C-10, C-11, C-12, C-13, C-14, C-15 and C-16 for **2** were identical with

those observed in some isopimar-8(14)-ene-15,16-diol derivatives [12]. In particular, the observed value for C-8 (δ 137.62) indicated that **2** possessed an isopimar-8(14)-ene skeleton with a 1,2-dihydroxyethyl side chain and was not its C-13 epimer since the latter showed a C-8 carbon resonance at δ 138.6 [13]. Taking into account the co-occurrence of isopimar-8(9)-15,16-diol (**1**), compound **2** possessed an isopimarane skeleton. Therefore, flavidusin A(**2**) is assigned the structure isopimar-8(14)-15,16-diol.

Flavidusin B(**3**) was assigned the molecular formula $C_{20}H_{32}O_2$, ($[M]^+$ m/z at 304), showed very similar spectral data to those of **1**, and exhibited characteristic signals of a diterpene with the isopimar-8(9)-ene skeleton [11] (four methyl group as singlets at δ_H 1.23, 0.80, 0.79 and 0.99; two signals at δ_C 126.06(s) and 141.59(s) attributed to a tetrasubstituted double bond at $\Delta^{8,9}$). In the 1H - 1H COSY of **3**, the signals at δ 4.27 (1H, *dd*, $J = 5.8, 4.1$ Hz) showed correlation with the signals at δ 4.38 (1H, *dd*, $J = 9.0, 5.8$ Hz) and 4.05 (1H, *dd*, $J = 9.0, 4.1$ Hz), and the two latter signals showed correlation with each other, while the signals at δ 4.00 (1H, *br s*) showed no correlation with any protons. The IR spectrum showed the presence of hydroxyl group absorption (3380 cm^{-1}), and the EI mass spectrum showed the $[M]^+$ was two mass units less than that of **1**. All the above evidence suggested that **3** possessed the structure 15,16-dihydro-15-hydroxy-14,16-epoxyisopimar-8(9)-ene, similar to that of premnenol [14]. This conclusion was further confirmed by the COLOC experiment in which the following C-H long-range correlation were observed: the signal at δ 4.00 (1H, *br s*, H-14) showed correlations with the carbon signals at δ 17.47(C-17), 73.82(C-16), 31.20(C-7), 30.11(C-12), 126.06(C-8) and 141.59(C-9); the signal at δ 1.23 (3H, *br s*, H-17) showed correlations with C-14(δ 85.55), C-15(δ 77.07), C-13(δ 42.90) and C-12(δ 30.11). The stereochemistry of **3** was established by a NOE experiment (see Fig. 2). The signals at δ 4.00 (1H, *br s*, H-14) showed correlation with the signals at δ 1.23 (1H, *s*, Me-17) and 2.05 (1H, *m*, H-7 β), which indicated that the configuration of H-14 and Me-17 were β . The signals at δ 1.23 (1H, *s*, Me-17) showed no correlation with the signals at δ 4.27 (1H, *dd*, $J = 5.8, 4.1$ Hz H-15), which revealed the configuration of HO-15 was β . On the other hand, the upfield shift of C-17 (δ 17.47) further confirmed that the configuration of HO-15 was β [15]. Thus, flavidusin B(**3**) was determined as 15,16-dihydro-15 β -hydroxy-14 α ,16-epoxyisopimar-8(9)-ene. The absolute configuration was assumed on the basis of its co-occurrence with **1**.

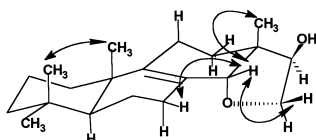


Fig. 2.

EXPERIMENTAL

General. Mps: uncorr; UV: MeOH; IR: KBr; EIMS: 70 eV; 1H and ^{13}C NMR: 400 MHz and 100 MHz, respectively, with TMS as int. standard, the chemical shift values were reported in δ (ppm) units with reference to the solvent (pyridine- d_5), coupling constant in Hz.

Plant material. Plant material was collected in Dan Li county, Yunnan province, People's Republic of China, in Sept. 1993, and identified as *I. flavidus* (Hand-Mazz) Hara by Prof. Xi-Wen Li. A voucher specimen (KIB 93-09-02, Lin) is deposited in the herbarium of the Department of Taxonomy, Kunming Institute of Botany.

Extraction and isolation. Dried leaves (2.35 kg) of *I. flavidus* were extracted with EtOH ($3l \times 3$) under reflux. The extract was concd *in vacuo* to give a residue (210 g) which was dissolved in 90% EtOH (1000 ml) and the soln was partitioned with petrol. The 90% EtOH layer was concd *in vacuo*. The residue was suspended in H_2O (1000 ml) and the suspension was extracted with EtOAc (1000 ml \times 3). After being washed with H_2O , the EtOAc extract was evapd *in vacuo* to give a residue (110 g) which was sepd by CC on silica gel (200–300 mesh, 1.5 kg). The column was eluted with $CHCl_3$, $CHCl_3$ - Me_2CO (9.5:0.5, 9:1, 4:1, 7:3, 3:2) and Me_2CO . The eluates were collected as 500 ml frs. All components were purified by silica gel CC with $CHCl_3$ -cyclohexane-isopropanol repeatedly and recrystallization, yielding **1** (40 g), **2** (100 mg), **3** (46 mg), **4** (500 mg), **5** (100 mg), **6** (1.0 g), **7** (80 mg), **8** (30 mg) and **9** (57 mg).

Glutinosin (1). $C_{20}H_{34}O_2$, colourless needles (from MeOH), mp 89 – 90° ; $[\alpha]_D^{22} + 57.60^\circ$ ($CHCl_3$, c 1.03); UV λ_{max}^{MeOH} nm: end absorption; IR ν_{max}^{KBr} cm^{-1} : 3500, 1620; EIMS m/z (rel. int.): 306 $[M]^+$ (75), 291 $[M-Me]^+$ (85), 273 $[M-Me-H_2O]^+$ (80), 245 $[M-CHOHCH_2OH]^+$ (100); 1H NMR (pyridine- d_5) δ : 6.06 and 5.08 (each 1H, *br s*, $2 \times OH$), 3.94–4.13 (3H, *m*, H-15, H-16), 1.05 (3H, *s*, Me-17), 0.98 (3H, *s*, Me-20), 0.84 (3H, *s*, Me-19), 0.81 (3H, *s*, Me-18); ^{13}C NMR: Table 1.

(+)-**Isopimara-8(9),15-diene (10)** $C_{20}H_{32}$, colourless crystals (from MeOH), mp 50 – 52° ; $[\alpha]_D^{22} + 99.9^\circ$ ($CHCl_3$, c 0.95), was prepd from glutinosin (**1**) according to the method of ref [8]: glutinosin (**1**, 712 mg, 2 mmol), ethyl orthoformate (1200 mg, 11.2 mmol), and benzoic acid (50 mg) were heated at 90 – 100° for 2 hr. After concn *in vacuo*, benzoic acid (100 mg) was added and the mixt. was heated at 160 – 170° for 1 hr. After cooling, CH_2Cl_2 (20 ml) was added, and the soln was washed with satd Na_2CO_3 . The CH_2Cl_2 layer was sepd, and dried with K_2CO_3 . The soln was concd and purified by CC on silica gel with the petrol-EtOAc (4:1) to give **10** (243 mg) (yield 40%). EIMS m/z (rel. int.): 272 $[M]^+$ (79), 257 $[M-Me]^+$ (100); 1H NMR (pyridine- d_5) δ : 5.73 (1H, *dd*, $J = 17.6, 10.8$ Hz, H-15), 4.86 (1H, *dd*, $J = 10.8, 1.5$ Hz, H-16a), 4.81 (1H, *dd*, $J = 17.6, 1.5$ Hz, H-16b), 0.94 (3H, *s*, Me-17), 0.93

Table 1. ^{13}C NMR data of compounds **1–3** and **10** (100 MHz, δ in ppm with reference to the signal of pyridine- d_5)

C	1	2	3	10
1	40.9 <i>t</i>	40.0 <i>t</i>	37.3 <i>t</i>	37.0 <i>t</i>
2	19.3 <i>t</i>	19.0 <i>t</i>	19.0 <i>t</i>	19.0 <i>t</i>
3	42.1 <i>t</i>	42.4 <i>t</i>	41.9 <i>t</i>	41.9 <i>t</i>
4	32.5 <i>s</i>	33.4 <i>s</i>	33.5 <i>s</i>	33.3 <i>s</i>
5	51.8 <i>d</i>	51.3 <i>d</i>	51.3 <i>d</i>	51.9 <i>d</i>
6	20.5 <i>t</i>	22.9 <i>t</i>	20.4 <i>t</i>	21.2 <i>t</i>
7	33.4 <i>t</i>	36.6 <i>t</i>	31.2 <i>t</i>	32.6 <i>t</i>
8	124.5 <i>s</i>	137.6 <i>s</i>	126.1 <i>s</i>	124.4 <i>s</i>
9	137.4 <i>s</i>	54.4 <i>d</i>	141.6 <i>s</i>	137.2 <i>s</i>
10	37.7 <i>s</i>	38.5 <i>s</i>	37.9 <i>s</i>	37.6 <i>s</i>
11	19.4 <i>t</i>	19.4 <i>t</i>	19.3 <i>t</i>	19.1 <i>t</i>
12	33.0 <i>t</i>	31.1 <i>t</i>	30.1 <i>t</i>	35.1 <i>t</i>
13	32.5 <i>s</i>	38.4 <i>s</i>	42.9 <i>s</i>	35.1 <i>s</i>
14	37.2 <i>t</i>	129.1 <i>d</i>	85.6 <i>d</i>	32.6 <i>t</i>
15	76.1 <i>d</i>	79.8 <i>d</i>	77.1 <i>d</i>	146.5 <i>d</i>
16	63.8 <i>t</i>	63.5 <i>t</i>	73.8 <i>t</i>	110.6 <i>t</i>
17	21.3 <i>q</i>	22.3 <i>q</i>	17.5 <i>q</i>	27.8 <i>q</i>
18	33.5 <i>q</i>	33.9 <i>q</i>	33.2 <i>q</i>	33.4 <i>q</i>
19	21.9 <i>q</i>	23.3 <i>q</i>	21.8 <i>q</i>	21.9 <i>q</i>
20	19.4 <i>q</i>	15.1 <i>q</i>	20.4 <i>q</i>	19.7 <i>q</i>

Table 2. ^{13}C NMR data of compounds **4–7** (100 MHz, δ in ppm with reference to the signal of pyridine- d_5)

C	4	5	6	7
1	42.3 <i>t</i>	52.3 <i>t</i>	39.8 <i>t</i>	37.8 <i>t</i>
2	18.7 <i>t</i>	64.1 <i>d</i>	20.0 <i>t</i>	28.9 <i>t</i>
3	42.6 <i>t</i>	50.5 <i>t</i>	42.4 <i>t</i>	78.9 <i>d</i>
4	33.6 <i>s</i>	34.9 <i>s</i>	37.3 <i>s</i>	39.7 <i>s</i>
5	56.3 <i>d</i>	56.1 <i>d</i>	51.1 <i>d</i>	50.6 <i>d</i>
6	20.5 <i>t</i>	20.7 <i>t</i>	20.1 <i>t</i>	19.8 <i>t</i>
7	37.8 <i>t</i>	38.0 <i>t</i>	30.4 <i>t</i>	30.7 <i>t</i>
8	44.9 <i>s</i>	44.9 <i>s</i>	130.0 <i>s</i>	133.2 <i>s</i>
9	57.2 <i>d</i>	57.2 <i>d</i>	149.3 <i>s</i>	148.4 <i>s</i>
10	40.5 <i>s</i>	41.3 <i>s</i>	38.1 <i>s</i>	39.7 <i>s</i>
11	18.9 <i>t</i>	18.9 <i>t</i>	112.3 <i>d</i>	111.7 <i>d</i>
12	26.9 <i>t</i>	26.9 <i>t</i>	154.7 <i>s</i>	154.0 <i>s</i>
13	46.1 <i>d</i>	46.2 <i>d</i>	126.1 <i>s</i>	125.9 <i>s</i>
14	40.5 <i>t</i>	42.5 <i>t</i>	128.9 <i>d</i>	127.1 <i>d</i>
15	54.0 <i>t</i>	54.1 <i>t</i>	37.3 <i>d</i>	27.5 <i>d</i>
16	81.7 <i>s</i>	81.6 <i>s</i>	68.2 <i>t</i>	23.4 <i>q</i>
17	66.5 <i>t</i>	66.5 <i>t</i>	25.4 <i>q</i>	23.4 <i>q</i>
18	33.7 <i>q</i>	34.0 <i>q</i>	33.9 <i>q</i>	28.9 <i>q</i>
19	21.7 <i>q</i>	22.7 <i>q</i>	22.2 <i>q</i>	23.2 <i>q</i>
20	18.0 <i>q</i>	19.2 <i>q</i>	17.6 <i>q</i>	16.4 <i>q</i>

(3H, *s*, Me-20), 0.89 (3H, *s*, Me-19), 0.87 (3H, *s*, Me-18); ^{13}C NMR: Table 1.

Flavidusin A (2). $\text{C}_{20}\text{H}_{34}\text{O}_2$, colourless crystals (from MeOH), mp 85–86°; $[\alpha]_{\text{D}}^{22} + 31.82^\circ$ (CHCl_3 , *c* 0.55); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: end absorption; IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3300, 2910, 1360, 1405; EIMS *m/z* (rel. int.): 306 $[\text{M}]^+$ (21), 291 $[\text{M}-\text{Me}]^+$ (25), 273 $[\text{M}-\text{Me}-\text{H}_2\text{O}]^+$ (18), 245 $[\text{M}-\text{CHOHCH}_2\text{OH}]^+$ (100); ^1H NMR (pyridine- d_5) δ : 5.67 (1H, *br s*, H-14), 3.85 (1H, *dd*, *J* = 8.8, 2.4 Hz, H-15), 4.17 (1H, *dd*, *J* = 10.7, 2.4 Hz, H-16a), 3.92 (1H, *dd*, *J* = 10.7, 8.8 Hz, H-16b), 1.24 (3H, *s*, Me-17), 0.82 (3H, *s*, Me-20), 0.82 (3H, *s*, Me-19), 0.78 (3H, *s*, Me-18); ^{13}C NMR: Table 1.

Flavidusin B (3). $\text{C}_{20}\text{H}_{32}\text{O}_2$, colourless crystals (from MeOH), mp 79–80°; $[\alpha]_{\text{D}}^{22} + 109.0^\circ$ (CHCl_3 , *c* 0.65); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: end absorption; IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3380, 2910, 1410, 1000; EIMS *m/z* (rel. int.): 304 $[\text{M}]^+$ (42), 289 $[\text{M}-\text{Me}]^+$ (34), 271 $[\text{M}-\text{Me}-\text{H}_2\text{O}]^+$ (70), 243 $[\text{M}-\text{CHOHCH}_2\text{OH}]^+$ (100); ^1H NMR (pyridine- d_5) δ : 4.05 (1H, *br s*, H-14), 4.27 (1H, *dd*, *J* = 5.8, 4.1 Hz, H-15), 4.38 (1H, *dd*, *J* = 9.0, 5.8 Hz, H-16a), 4.00 (1H, *dd*, *J* = 9.0, 4.1 Hz, H-16b), 1.23 (3H, *s*, Me-17), 0.80 (3H, *s*, Me-20), 0.79 (3H, *s*, Me-19), 0.99 (3H, *s*, Me-18); ^{13}C NMR: Table 1.

ent-Kaurane-16 β ,17-diol (4). $\text{C}_{20}\text{H}_{34}\text{O}_2$, colourless needles (from MeOH), mp 188–189°; $[\alpha]_{\text{D}}^{22} - 35.7^\circ$ (CHCl_3 , *c* 0.68); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): end absorption; IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3480, 2910, 1410, 1351, 1050; EIMS *m/z* (rel. int.): 306 $[\text{M}]^+$ (42), 289 $[\text{M}-\text{Me}]^+$ (15), 275 $[\text{M}-\text{CH}_2\text{OH}]^+$ (100), 257, 243; ^1H NMR (pyridine- d_5) δ : 4.05, 4.13 (each 1H, *ABd*, *J* = 10.9 Hz, H-17), 0.95 (3H, *s*, Me-20), 0.81 (3H, *s*, Me-19), 0.78 (3H, *s*, Me-18); ^{13}C NMR: Table 2.

Siegesbeckiol (5). $\text{C}_{20}\text{H}_{34}\text{O}_3$, colourless needles (from MeOH), mp 268–269°; $[\alpha]_{\text{D}}^{22} - 26.7^\circ$ (CHCl_3 , *c*

0.74); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: end absorption; IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3300, 2910, 1440, 1040; EIMS *m/z* (rel. int.): 304 $[\text{M}-\text{H}_2\text{O}]^+$ (6), 291 $[\text{M}-\text{CH}_2\text{OH}]^+$ (95), 273 $[\text{M}-\text{CH}_2\text{OH}-\text{H}_2\text{O}]^+$ (100), 255, 231; ^1H NMR (pyridine- d_5) δ : 4.25 (1H, *tt*, *J* = 11.5, 3.1 Hz, H-2 α), 4.03, 4.10 (each 1H, *ABd*, *J* = 10.7 Hz, H-17), 1.04 (3H, *s*, Me-17), 0.90 (3H, *s*, Me-19), 0.80 (3H, *s*, Me-20); ^{13}C NMR: Table 2.

16-Hydroxy ferruginol (6). $\text{C}_{20}\text{H}_{30}\text{O}_2$, colourless crystals (from MeOH), mp 83–85°; $[\alpha]_{\text{D}}^{22} + 55.9^\circ$ (CHCl_3 , *c* 0.54); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 220(5.73), 283 (5.55); IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3300, 2920, 1605, 1680, 1305, 1405, 1020; EIMS *m/z* (rel. int.): 302 $[\text{M}]^+$ (90), 287 $[\text{M}-\text{Me}]^+$ (65), 284 $[\text{M}-\text{H}_2\text{O}]^+$ (50), 271 $[\text{M}-\text{Me}-\text{H}_2\text{O}]^+$ (100), 187(75); ^1H NMR (pyridine- d_5) δ : 7.14 (1H, *br s*, H-11), 7.12 (1H, *br s*, H-14), 4.24 (1H, *dd*, *J* = 10.2, 5.8 Hz, H-16a), 4.08 (1H, *dd*, *J* = 14.0, 6.5 Hz, H-16b), 3.80 (1H, *dd*, *J* = 13.1, 6.5 Hz, H-7 β), 2.79 (1H, *m*, H-7 α), 2.93 (1H, *dd*, *J* = 16.4, 6.5 Hz, H-6 α), 1.61 (3H, *d*, *J* = 7.0 Hz, Me-17), 1.23, 0.94, 0.90 (each 3H, *s*, Me-18, Me-19, Me-20); ^{13}C NMR: Table 2.

Hinokiol (7). $\text{C}_{20}\text{H}_{30}\text{O}_2$, colourless crystals (from MeOH), mp 233–235°; $[\alpha]_{\text{D}}^{22} + 72.5^\circ$ (CHCl_3 , *c* 0.46); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 220(5.83), 283(5.57); IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3510, 3280, 2930, 1600, 1410, 1450, 1500, 1210; EIMS *m/z* (rel. int.): 302 $[\text{M}]^+$ (100), 287 $[\text{M}-\text{Me}]^+$ (65), 269 $[\text{M}-\text{Me}-\text{H}_2\text{O}]^+$ (95), 227(64), 215(60); ^1H NMR (pyridine- d_5) δ : 7.14 (1H, *br s*, H-11), 7.10 (1H, *s*, H-14), 3.70 (1H, *dd*, *J* = 14.0, 6.8 Hz, H-3 α), 3.50 (1H, *dd*, *J* = 10.8, 5.6 Hz, H-7 β), 2.85 (1H, *m*, H-7 α), 2.94 (1H, *dd*, *J* = 16.8, 6.0 Hz, H-6 α), 1.40 (3H, *d*, *J* = 7.2 Hz, Me-17), 1.33, 1.27, 1.10 (each 3H, *s*, Me-20, Me-18 and Me-19); ^{13}C NMR: Table 2.

Maslinic acid (8). $\text{C}_{30}\text{H}_{48}\text{O}_4$, white powder. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3505, 3280, 2925, 2830, 1600, 1410, 1445, 1500;

EIMS m/z (rel. int.): 472 $[M-Me]^+$ (15), 457 $[M-Me]^+$ (5), 426 $[M-COOH]^+$ (20), 248(100), 203(92), 133(60); 1H NMR (pyridine- d_5) δ : 4.08 (1H, ddd , $J = 10.2, 9.4, 4.2$ Hz, H-2 β), 3.37 (1H, d , $J = 9.4$ Hz, H-3 α), 5.46 (1H, t , $J = 3.2$ Hz, H-12), 1.20, 1.19, 1.11, 1.03, 0.98, 0.96, 0.93 (each 3H, s , $7 \times Me$); ^{13}C NMR (DEPT) δ : 47.81 (t , C-1), 68.66 (d , C-2), 83.91 (d , C-3), 39.87 (s , C-4), 56.01 (d , C-5), 18.93 (t , C-6), 33.29 (t , C-7), 39.94 (s , C-8), 48.25 (d , C-9), 38.64 (s , C-10), 23.81 (t , C-11), 122.25 (d , C-12), 144.94 (s , C-13), 42.3 (s , C-14), 28.36 (t , C-15), 24.00 (t , C-16), 46.74 (s , C-17), 42.09 (d , C-18), 46.56 (t , C-19), 31.00 (s , C-20), 34.34 (t , C-21), 33.29 (t , C-22), 29.38 (q , C-23), 16.89 (q , C-24), 17.55 (q , C-25), 16.89 (q , C-26), 26.23 (q , C-27), 180.17 (s , C-28), 17.65 (q , C-29), 23.81 (q , C-30).

5-Hydroxy-7,4'-dimethoxyflavone (9). $C_{17}H_{14}O_5$, yellow needles (from MeOH). UV λ_{max}^{MeOH} nm (log ϵ): 210(6.54), 269(6.32); IR ν_{max}^{KBr} cm^{-1} : 3400, 1650, 1600, 1500, 1430, 1350, 1340, 1260, 1110, 1020, 8020; EIMS m/z (rel. int.): 300 $[M+2]^+$ (80), 284(51), 267(100), 257(52), 240(35), 226(24), 212(38), 166(53); 1H NMR (pyridine- d_5) δ : 6.51 (1H, s , H-3), 6.41 (1H, d , $J = 2.4$ Hz, H-6), 6.30 (1H, d , $J = 2.4$ Hz, H-8), 7.78 (2H, dd , $J = 7.2, 2.4$, H-2' and H-6'), 6.96 (2H, dd , $J = 7.2, 2.8$ Hz, H-3' and H-5'), 3.83, 3.84 (each 3H, s , $2 \times OMe$); ^{13}C NMR (DEPT) δ : 163.25 (s , C-2), 104.30 (d , C-3), 180.36 (s , C-4), 162.61 (s , C-5), 98.02 (d , C-6), 165.44 (s , C-7), 92.56 (s , C-8), 157.67 (s , C-9), 105.54 (s , C-10), 123.58 (s , C-1'), 127.96 (d , C-2' and C-6'), 114.48 (d , C-3' and C-5'), 162.22 (s , C-4'), 55.72 (q , OMe), 55.48 (q , OMe).

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