Pergamon

PII: S0031-9422(97)00608-0

Phytochemistry, Vol. 48, No. 6, pp. 1025–1029, 1998

Printed in Great Britain
0031-9422/98 $19.00+0.00

DITERPENOIDS FROM *ISODON FLAVIDUS*

QIN-SHI ZHAO, JUN TIAN, JIAN-MIN YUE, SHAO-NONG CHEN, ZHONG-WEN LIN and HAN-DONG SUN*

Laboratory of Phytochemistry, Kunming Institute of Botany, Academia Sinica, Kunming 650204, Yunnan, People's Republic of China

(*Received in revised form* 2 *June* 1997)

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-16β,17-diol, siegesbeckiol, 16-hydroxy feruginol, hinokiol, maslinnic 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-15β-hydroxy-14α,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.

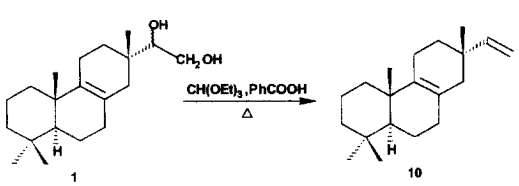
INTRODUCTION

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-16β, 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**).

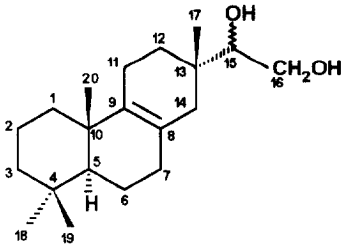
Glutinosin was assigned the molecular formula (**1**) $C_{20}H_{34}O_2$ ($[M]^+$, $m/z = 306$). The mass spectral, optical rotation, ^1H and ^{13}C NMR data of **1** were in good agreement with those of glutinosin (**1a**) [4]. The absolute configuration assignment of glutinosin (**1a**) was established 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 ^{13}C 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.



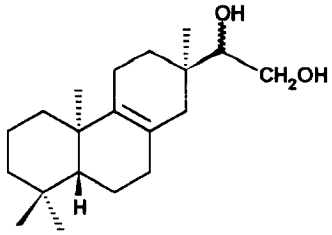
1 10

Fig. 1.

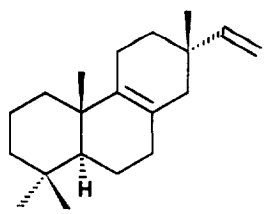
*Author to whom the correspondence should be addressed.



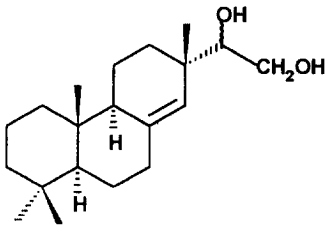
1



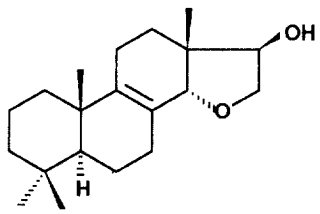
1a



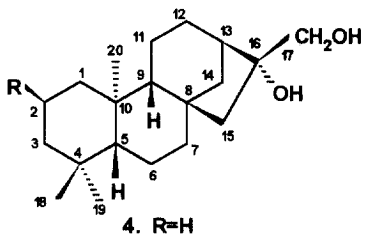
10



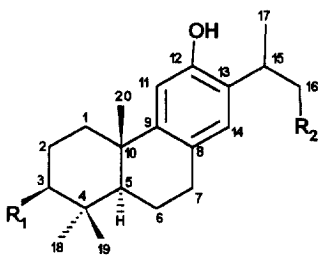
2



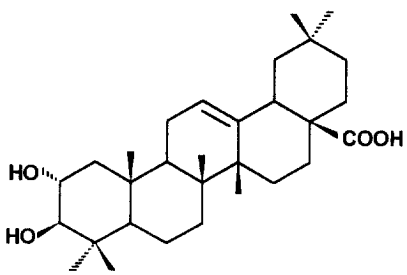
3



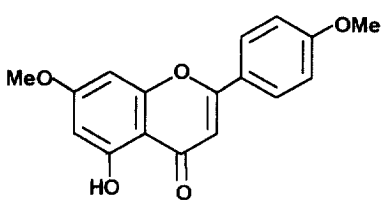
4. R=H
5. R=OH



6. R_1=H, R_2=OH
7. R_1=OH, R_2=H



8



9

Flavidusin A (**2**) was assigned the molecular formula $C_{20}H_{34}O_2$ ($[M]^+$ m/z = 306), showed hydroxyl (3300 cm^{-1}) and olefinic (1620 cm^{-1}) absorptions in its IR spectrum. Its ^1H NMR spectrum showed the signal for one olefinic proton without a vicinal hydrogen atom at δ 5.67 (1H, *br s*), the signals for three ABX system protons geminal to a hydroxyl group at δ 3.85 (1H, *dd*, J = 8.8, 2.4 Hz), 3.92 (1H, *dd*, J = 10.7, 8.8 Hz) and 4.17 (1H, *dd*, J = 10.7, 2.4 Hz), and four tertiary methyl singlets (δ 1.24, 0.83, 0.82 and 0.78). Furthermore, its mass spectrum showed a fragment ion at m/z 245 corresponding to the loss of a -CHOH-CH_2OH fragment. The ^1H-^1H COSY spectrum of **2** also confirmed the presence of the partial structure -CHOH-CH_2OH 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 ^{1}H-^{1}H 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-7β), 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-15β-hydroxy-14α,16-epoxyisopimar-8(9)-ene. The absolute configuration was assumed on the basis of its co-occurrence with **1**.

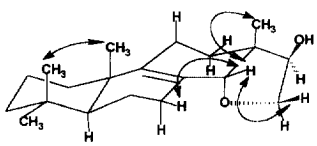


Fig. 2.

EXPERIMENTAL

General. Mps: uncorr; UV: MeOH; IR: KBr; EIMS: 70 eV; ^{1}H 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 × 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 × 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° ($CHCl_3$, *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); ^{1}H NMR (pyridine-d_5) δ: 6.06 and 5.08 (each 1H, *br s*, 2 × 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° ($CHCl_3$, *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); ^{1}H 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 *t*	40.0 *t*	37.3 *t*	37.0 *t*
2	19.3 *t*	19.0 *t*	19.0 *t*	19.0 *t*
3	42.1 *t*	42.4 *t*	41.9 *t*	41.9 *t*
4	32.5 *s*	33.4 *s*	33.5 *s*	33.3 *s*
5	51.8 *d*	51.3 *d*	51.3 *d*	51.9 *d*
6	20.5 *t*	22.9 *t*	20.4 *t*	21.2 *t*
7	33.4 *t*	36.6 *t*	31.2 *t*	32.6 *t*
8	124.5 *s*	137.6 *s*	126.1 *s*	124.4 *s*
9	137.4 *s*	54.4 *d*	141.6 *s*	137.2 *s*
10	37.7 *s*	38.5 *s*	37.9 *s*	37.6 *s*
11	19.4 *t*	19.4 *t*	19.3 *t*	19.1 *t*
12	33.0 *t*	31.1 *t*	30.1 *t*	35.1 *t*
13	32.5 *s*	38.4 *s*	42.9 *s*	35.1 *s*
14	37.2 *t*	129.1 *d*	85.6 *d*	32.6 *t*
15	76.1 *d*	79.8 *d*	77.1 *d*	146.5 *d*
16	63.8 *t*	63.5 *t*	73.8 *t*	110.6 *t*
17	21.3 *q*	22.3*q*	17.5 *q*	27.8 *q*
18	33.5 *q*	33.9 *q*	33.2 *q*	33.4 *q*
19	21.9 *q*	23.3 *q*	21.8 *q*	21.9 *q*
20	19.4 *q*	15.1 *q*	20.4 *q*	19.7 *q*

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

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

Flavidusin A(**2**). $C_{20}H_{34}O_2$, colourless crystals (from MeOH), mp 85–86°; $[\alpha]_D^{22}+31.82°$ ($CHCl_3$, *c* 0.55); UV λ_{max}^{MeOH} nm: end absorption; IR ν_{max}^{KBr} cm^{-1}: 3300, 2910, 1360, 1405; EIMS *m/z* (rel. int.): 306 $[M]^+$ (21), 291 $[M-Me]^+$ (25), 273 $[M-Me-H_2O]^-$ (18), 245 $[M-CHOHCH_2OH]^+$ (100); ^1H NMR (pyridine-d_5) δ: 5.67 (1H, *br s*, H-14), 3.85 (1H5, *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**). $C_{20}H_{32}O_2$, colourless crystals (from MeOH), mp 79–80°; $[\alpha]_D^{22}+109.0°$ ($CHCl_3$, *c* 0.65); UV λ_{max}^{MeOH} nm: end absorption; IR ν_{max}^{KBr} cm^{-1}: 3380, 2910, 1410, 1000; EIMS *m/z* (rel. int.): 304 $[M]^+$ (42), 289 $[M-Me]^+$ (34), 271 $[M-Me-H_2O]^+$ (70), 243 $[M-CHOHCH_2OH]^+$ (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*-16β,17-*diol* (**4**). $C_{20}H_{34}O_2$, colourless needles (from MeOH), mp 188–189°; $[\alpha]_D^{22}-35.7°$ ($CHCl_3$, *c* 0.68); UV λ_{max}^{MeOH} nm (log ε): end absorption; IR ν_{max}^{KBr} cm^{-1}: 3480, 2910, 1410, 1351, 1050; EIMS *m/z* (rel. int.): 306 $[M]^+$ (42), 289 $[M-Me]^+$ (15), 275 $[M-CH_2OH]^+$ (100), 257, 243; ^1H NMR (pyridine-d_5) δ: 4.05, 4.13 (each 1H, AB*d*, 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**). $C_{20}H_{34}O_3$, colourless needles (from MeOH), mp 268–269°; $[\alpha]_D^{22}-26.7°$ ($CHCl_3$, *c* 0.74); UV λ_{max}^{MeOH} nm: end absorption; IR ν_{max}^{KBr} cm^{-1}: 3300, 2910, 1440, 1040; EIMS *m/z* (rel. int.): 304 $[M-H_2O]^+$ (6), 291 $[M-CH_2OH]^+$ (95), 273 $[M-CH_2OH-H_2O]^+$ (100), 255, 231; ^1H NMR (pyridine-d_5) δ: 4.25 (1H, *tt*, J = 11.5, 3.1 Hz, H-2α), 4.03, 4.10 (each 1H, AB*d*, 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**). $C_{20}H_{30}O_2$, colourless crystals (from MeOH), mp 83–85°; $[\alpha]_D^{22}+55.9°$ ($CHCl_3$, *c* 0.54); UV λ_{max}^{MeOH} nm (log ε): 220(5.73), 283 (5.55); IR ν_{max}^{KBr} cm^{-1}: 3300, 2920, 1605, 1680, 1305, 1405, 1020; EIMS *m/z* (rel. int.): 302 $[M]^+$ (90), 287 $[M-Me]^+$ (65), 284 $[M-H_2O]^+$ (50), 271 $[M-Me-H_2O]^+$ (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-7β), 2.79 (1H, *m*, H-7α), 2.93 (1H, *dd*, J = 16.4, 6.5 Hz, H-6α), 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**). $C_{20}H_{30}O_2$, colourless crystals (from MeOH), mp 233–235°; $[\alpha]_D^{22}+72.5°$ ($CHCl_3$, *c* 0.46); UV λ_{max}^{MeOH} nm (log ε): 220(5.83), 283(5.57); IR ν_{max}^{KBr} cm^{-1} 3510, 3280, 2930, 1600, 1410, 1450, 1500, 1210; EIMS *m/z* (rel. int.): 302 $[M]^+$ (100), 287 $[M-Me]^+$ (65), 269$[M-Me-H_2O]^-$ (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-3α), 3.50 (1H, *dd*, J = 10.8, 5.6 Hz, H-7β), 2.85 (1H, *m*, H-7α), 2.94 (1H, *dd*, J = 16.8, 6.0 Hz, H-6α), 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**). $C_{30}H_{48}O_4$, white powder. IR ν_{max}^{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-2β), 3.37 (1H, *d*, J = 9.4 Hz, H-3α), 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 × 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*, 21, 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 × 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).

REFERENCES

1. Wu, C. Y. and Li, H. W., *Flora Republicae Popularris Sinicae*. Vol. 66. Beijing Academic Press, Beijing, 1979, p. 492.
2. Fujita, E. and Node, M., *Progress in the Chemistry of Organic Natural Products*, 1984, **46**, 144.
3. Wu, S. H., Zhang, H. J., Lin, Z. W. and Sun, H. D., *Phytochemistry*, 1992, **34**, 1176.
4. Sun, H.-D., Lin, Z.-W., Sen, P.-Q., *Acta Botannic Yunnica*, 1987, **9**, 247.
5. Robert, M. C. and Ken, H.-Y., *Journal of Organic Chemistry*, 1987, **52**, 2065.
6. Tsichritzis, F. and Jakupovic, J., *Phytochemistry*, 1990, **29**, 3173.
7. Junichi, K., Testsuya, K. and Toshio, K., *Chemical and Pharmaceutical Bulletin*, 1982, **10**, 3912.
8. Hiyama, T. and Nozaki, H., *Bulletin of the Chemical Society of Japan*, 1973, **46**, 2248.
9. Zinkel, D. F. and Conner, A. H., *Phytochemistry*, 1973, **12**, 983.
10. Audier, H. E., Bory, S., Fetion, M. and Anh, N. T., *Bulletin de la Societe Chimique de France*, 1966, 4002.
11. Wenkert, E. and Buckwalter, B. L., *Journal of the American Chemical Society*, 1972, **94**, 4367.
12. Richard, C. C., *Journal of Organic Chemistry*, 1975, **40**, 3789.
13. Bansal, R. K., Maria, C. G., Krishna, C. J., Benjamin, R. and Renuka, P., *Phytochemistry*, 1980, **19**, 1979.
14. Bheemasankara, C. R., Gopalakrishna, P. and Suseela, K., *Indian Journal of Chemistry*, 1985, 403.
15. Xiong, J., Ma, Y.-B. and Xu, Y.-L., *Phytochemistry*, 1992, **31**, 917.
16. Ozaki, N., Hasegawa, S. and Hirose, Y., *Phytochemistry*, 1983, **22**, 1771.
17. Ytagai, M., *Phytochemistry*, 1980, **19**, 1149.
18. Seo, S., Tomita, Y. and Tori, K., *Tetrahedron Letter*, 1975, **1**, 7.
19. Rangaswami, S. and Iyer, R. T., *Indian Journal of Chemistry*, 1969, **7**, 526.