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DITERPENOIDS FROM *ISODON MELISSOIDES*

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Key Word Index—*Isodon melissoides*; Labiatae; *ent*-kaurane diterpenoids; melissoidesin A–D.

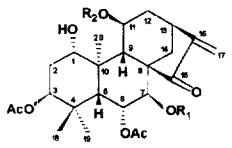
Abstract—Four new *ent*-kaurane diterpenoids, melissoidesin A–D, together with a known diterpenoid, gesneroidin C, were isolated from aerial parts of *Isodon melissoides*. Their structures were elucidated by spectral evidence. The new diterpenoids were identified as *ent*-1β,7α,11α-trihydroxy-3α,6β-diacetoxy-kaur-16-en-15-one; *ent*-1β,11α-dihydroxy-3α,6β,7α-triacetoxy-kaur-16-en-15-one; *ent*-1β,7α,11α,15α-tetrahydroxy-3α,6β-acetoxy-kaur-16-ene; and *ent*-1β,7α,11α-trihydroxy-3α,6β-diacetoxy-16α-ethoxymethyl-kaur-15-one.

INTRODUCTION

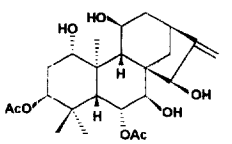
Some plants of genus *Isodon* have been used in Chinese traditional medicine for the treatment of gastrointestinal disorders, and as antitumour and antiphlogist agents [1]. Many *ent*-kaurane diterpenoids with various biological activity have been isolated from the plants of this genus [2]. *I. melissoides* (Benth) Hara, a perennial herb growing naturally in the northwestern area of Yunnan province, People's Republic of China, has not been previously investigated. From the aerial plants of this plant collected from Dan Li of Yunnan province, four new diterpenoids A–D(**1**, **2**, **4**, **5**) together with one known diterpenoid, gesneroidin C(**3**), were isolated. This paper describes the isolation and characterization of the new diterpenoids.

RESULTS AND DISCUSSION

Melissoidesin A(**1**), $C_{24}H_{34}O_8$ ([M]$^+$, m/z = 450), showed the presence of hydroxyl group absorption (3400 cm^{-1}) in its IR spectrum. The ^{1}H and ^{13}C NMR spectral data revealed the presence of three hydroxyl groups, two acetoxyl groups, three methyl groups, four methylene groups (including an exo-methylene group), eight methine groups (including five oxygenated methine), and a ketone group carbon. It was also indicated that the compound contained a five-membered ring with a ketone conjugated to an *exo*-methylene group from the following spectral data: UV λ_{max}^{MeOH} 241(4.72); IR ν_{max}^{KBr}: 1730 and 1650 cm^{-1}; ^{1}H NMR: δ 5.99 and 5.30 (each 1H, *br s*), ^{13}C NMR: δ 214.2(*s*), 156.1(*s*) and 111.7(*t*). These data, coupled with a consideration of the structures of diterpenoids isolated so far from the genus *Isodon* [3], suggested that melissoidesin A(**1**) possessed a structure in which two acetoxyls and three hydroxyl groups were present in an *ent*-kaur-16-en-15-one nucleus. The location of these five functional groups were deduced as follow. In the ^{1}H-^{1}H COSY spectrum of **1**, the following correlations were observed. The signal at δ 4.20 (1H, *dd*, J = 11.4, 4.2 Hz, H-1β) showed correlation with both the signals at δ 2.34 (1H, *ddd*, J = 15.0, 11.4, 2.8 Hz, H-2α) and at δ 2.13 (1H, *ddd*, J = 15.0, 4.2, 2.8 Hz, H-2β), the two latter signals also showed correlation with the signal at δ 4.85 (1H, *t*, J = 2.8 Hz, H-3α). Thus, a hydroxyl group and an acetoxyl group had to be located at C-1 and C-3, respectively. The signal at δ 4.05 (1H, *d*, J = 3.5 Hz, H-7α) showed correlation with the signal at δ 5.63 (1H, *dd*, J = 3.5, 1.8 Hz, H-6β), and the latter showed correlation with the signal



1. R_1=H, R_2=H
2. R_1=Ac, R_2=H
3. R_1=Ac, R_2=Ac



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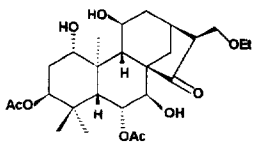

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at δ 2.65 (1H, *br s*, H-5B). This suggested that a hydroxyl group and an acetoxyl group were located at C-7 and C-6, respectively. The position of the remaining hydroxyl group was deduced as follows. The signal at δ 6.03 (1H, *d*, J = 3.2 Hz, H-11α) showed correlation with one [δ 2.76 (1H, *m*, H-12α)] of the two methylene protons, H-12α and H-12β [δ (1H, *m*, H-12β)], and the latter showed correlation with the signal at δ 3.05 (1H, *br s*, H-13α). This revealed that the remaining hydroxyl group was located at C-11, and the observation of the abnormal downfield shift (δ 6.03) of H-11α due to intramolecular bonding between H-11α and OH-1α allowed us to assign the configuration of 1α-OH and 11β-OH [4]. The stereochemistry of five functional groups were established as 1α-OH, 3β-OAc, 6α-OAc, 7β-OH, 11β-OH by a NOESY experiment (Fig. 1). Observation of NOEs among H-1β, H-5β and H-9 indicated that the hydroxyl at C-1 was α-orientated. The acetoxyl group at C-3 was judged to be β-orientated due to the observation of NOEs between H-3α with H_3-18 and H_3-19. The NOE effect between H-6 and H_3-18 suggested the acetoxyl at C-6 were α-orientated. Furthermore, the observation of NOEs between H-7α and H-14β, as well as between H_3-20 and H-11α revealed that the configuration of two hydroxyl at C-7 and C-11 were β. Consequently, we established **1** as *ent*-1β,7α,11α-trihydroxy-3α,6β-diacetoxy-kaur-16-en-15-one.

Melissoidesin B(**2**) was assigned the molecular formula $C_{26}H_{36}O_9$ ([M]$^+$, m/z = 492). Its ^{1}H and ^{13}C NMR spectrum were very similar to those of **1**. The only difference between **1** and **2** were that **2** had one more acetoxyl group and one less hydroxyl group than **1**. The downfield shift of the H-7α signal from δ 4.05 (1H, *d*, J = 3.5 Hz) in **1** to δ 5.53 (1H, *d*, J = 3.6 Hz) in **2** indicated the presence of an acetoxyl group at C-7 in **2**. The upfield shift of C-6 (δ 71.0, *d*) and C-7 (δ 71.6, *d*) required placement of the two acetoxyl groups at C-6 and C-7 [4]. Thus, melissoidesin B(**2**) was established as *ent*-1β,11α-dihydroxy-3α,6β,7α-triacetoxy-kaur-16-en-15-one.

Gesneroidin C(**3**), $C_{28}H_{38}O_{10}$ ([M]$^+$ m/z = 534), was identified as gesneroidin C, by direct comparison with an authentic sample and IR, mass, ^{1}H and ^{13}C NMR spectral data reported previously [5].

Melissoidesin C(**4**) was assigned the molecular formula $C_{24}H_{36}O_8$ ([M]$^+$ m/z = 452). Its mass spectrum showed a [M]$^+$ (m/z 452) two amu greater than that of **1**. The ^{1}H and ^{13}C NMR spectra of **4** were very similar to those of **1**, and the only difference between **4** and **1** was that **4** had one more hydroxyl and one less carbonyl group than **1**. After inspection of the ^{1}H and ^{13}C NMR spectral data of **4** and **1**, this hydroxyl group was assigned to the 15β-position on the basis of the following facts. The IR and UV absorption for the α, β-unsaturated ketone of **4** were absent, while the upfield shift of C-9 (δ 53.8) in the spectrum of **4** compared with that of **1** (δ 60.5) was attributed to the γ-gauche steric compression effect between the HO-15β and C-9 [6]. The downfield shift of C-7 (δ 77.5) in **4** was due to the absence of a C-15 ketone group and intramolecular bonding between OH-7β and the C-15 ketone group. Thus, the structure of melissoidesin C(**4**) was *ent*-1β,7α,11α,15α-tetrahydroxy-3α,6β-acetoxy-kaur-16-ene.

Melissoidesin D(**5**) was assigned the molecular formula $C_{26}H_{40}O_9$ ([M]$^+$ m/z 496). It showed no α, β-unsaturated ketone group absorption in its UV and IR spectral data. Its ^{1}H and ^{13}C NMR spectral data were similar to those of **1** except for the D-ring signals. The *exo*-methylene at C-17 in **1** was replaced by an ethoxyl group δ 0.94 (3H, *t*, CH_3), δ 3.48 (2H, *m*, OCH_2), 4.22 (1H, *dd*, J = 10.2, 7.8 Hz, H-17a) and 4.18 (1H, *dd*, J = 10.2, 3.2 Hz, H-17b) in the ^{1}H NMR spectrum and the signals at δ 69.3 (*t*, OCH_2), 66.3 (*t*, C-17), 57.2 (*d*, C-16) and 15.5 (*q*, CH_3) in the ^{13}C NMR spectrum. The β-configuration of the ethoxymethyl group in **5** was deduced from the abnormal upfield shift of C-12 (δ 34.07) [7]. Therefore, the structure was represented as *ent*-1β,7α,11α-trihydroxy-3α,6β-diacetoxy-16α-ethoxymethyl-kaur-15-one. This compound may be an artefact formed from compound **1**.

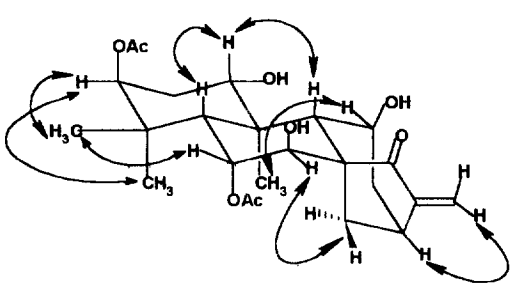

Fig. 1. NOE effects observed in melissoidesin A.

EXPERIMENTAL

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

Plant material. Plant material was collected in Dan Li county, Yunnan province, People's Republic of China, in Sept. 1993, and identified as *I. melissoides* (Benth.) Hara by Prof. Xi-Wen Li. A voucher specimen (KIB 93-09-01, Lin) is deposited in the herbarium of the Department of Taxonomy, Kunming Institute of Botany.

Extraction and isolation. Dried aerial parts (5.9 kg) of *I. melissoides* were extracted with EtOH (6 l × 3) under reflux. The combined EtOH extract was concd *in vacuo* to give a residue (500 g), which was dissolved in 90% EtOH (1000 ml) and partitioned with petrol. The 90% EtOH layer was concd *in vacuo*. The residue was suspended in H_2O (1500 ml) and the suspension was extraction with EtOAc (1000 ml × 3). After being washed with H_2O, the EtOAc extract was evapd *in vacuo* to give a residue (200 g) which was chro-

matographed over 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 further purified by silica gel CC and recrystallization, yielding compound **1**(24 g), **2**(108 mg), **3**(800 mg), **4**(150 mg) and **5**(200 mg).

Melissoidesin A(**1**). Amorphous powder, $C_{24}H_{34}O_8$, mp 245–246°; $[\alpha]_D^{22}$ −24.4°C ($CHCl_3$, *c* 0.44); UV λ_{max}^{MeOH} nm (log ε): 241(4.72); IR ν_{max}^{KBr} cm^{-1}: 3400, 1730, 1650, 1350, 1250, 1032, 4.22; EIMS *m/z* (rel. int.): 450 $[M]^+$ (5), 390 $[M\text{-}HOAc]^+$ (24), 372 $[M\text{-}HOAc\text{-}CO]^+$ (20), 312 $[M\text{-}2\times HOAc\text{-}H_2O]^+$ (100); ^1H NMR(pyridine-d_5) δ: 6.62, 6.45, 6.35 (each 1H, 3 × OH, lost on D_2O exchange), 4.20 (1H, *dd*, *J* = 11.4, 4.2 Hz, H-1β), 2.34 (1H, *dd*, *J* = 15.0, 11.4, 4.2 Hz, H-2α), 2.13 (1H, *ddd*, *J* = 15.0, 4.2, 2.8 Hz, H-2β), 4.85 (1H, *t*, *J* = 2.8 Hz, H-3α), 2.65 (1H, *br s*, H-5β), 5.63 (1H, *dd*, *J* = 3.5, 1.8 Hz, H-6β), 4.05 (1H, *d*, *J* = 3.5 Hz, H-7α), 3.00 (1H, *br s*, H-9β), 6.03 (1H, *br s*, *J* = 3.2 Hz, H-11α), 2.76 (1H, *m*, H-12α), 2.23 (1H, *m*, H-12β), 3.05 (1H, *br s*, H-13α), 2.80 (1H, *d*, *J* = 12.1 Hz, H-14-α), 1.42 (1H, *dd*, *J* = 12.1, 2.5 Hz, H-14β), 5.99 (1H, *br s*, H-17a), 5.30 (1H, *br s*, H-17b), 1.08 (3H, *s*, Me-18), 1.14 (3H, *s*, Me-19), 1.72 (3H, *s*, Me-20), 2.18, 1.89 (each 3H, *s*, 2 × Ac); ^{13}C NMR(DEPT): Table 1.

Melissoidesin B(**2**). Amorphous powder, $C_{26}H_{36}O_9$ mp 231–232°; $[\alpha]_D^{22}$ −11.9° ($CHCl_3$, *c* 0.13); UV λ_{max}^{MeOH} nm (log ε): 231(5.69); IR ν_{max}^{KBr} cm^{-1}: 3450, 1725, 1649, 1370, 1250, 1030; EIMS *m/z* (rel. int.): 492 $[M]^+$ (10), 432 $[M\text{-}HOAc]^+$ (18), 390 $[M\text{-}HOAc\text{-}COCH_2]^+$ (100), 312 $[M\text{-}3\times HOAc]^+$ (80); ^1H NMR (pyridine-d_5) δ: 4.12 (1H, *dd*, *J* = 11.6, 4.4 Hz, H-1β), 2.30 (1H, *ddd*, *J* = 15.0, 11.4, 3.5 Hz, H-2α), 2.10 (1H, *ddd*, *J* = 15.0, 4.4, 3.5 Hz, H-2β) 4.85 (1H, *t*, *J* = 3.5 Hz, H-3α), 2.35 (1H, *br s*, H-5β), 5.40 (1H, *dd*, *J* = 3.6, 1.8 Hz, H-6β), 5.53 (1H, *d*, *J* = 3.6 Hz, H-7α), 2.98 (1H, *br s*, H-9β), 6.01 (1H, *br d*, *J* = 3.4, H-11α), 2.37 (1H, *m*, H-12α), 2.15 (1H, *m*, H-12β). 3.00 (1H, *br s*, H-13α), 2.79 (1H, *d*, *J* = 12.0 Hz, H-14α), 1.42 (1H, *dd*, *J* = 12.0, 2.4 Hz, H-14β), 5.89 (1H, *br s*, H-17a), 5.18 (1H, *br s*, H-17b), 0.96 (3H, *s*, Me-18), 1.12 (3H, *s*, Me-19), 1.72 (3H, *s*, Me-20), 2.28, 2.18, 2.01 (each 3H, *s*, 3 × Ac); ^{13}C NMR(DEPT): Table 1.

Gesneroidin C(**3**). Amorphous powder, $C_{28}H_{38}O_{10}$, mp 240–242°; $[\alpha]_D^{22}$ −58.6° ($CHCl_3$, *c* 0.5); UV λ_{max}^{MeOH} nm (log ε): 240(5.56); IR ν_{max}^{KBr} cm^{-1}: 3485, 1725, 1649, 1370, 1249, 1030; EIMs *m/z* (rel. int.): 534 $[M]^+$ (5), 474 $[M\text{-}HOAc]^+$ (10), 432 $[M\text{-}HOAc\text{-}COCH_2]^+$ (25), 390 $[M\text{-}HOAc\text{-}COCH_2\text{-}H_2O]^+$ (45), 312 $[M\text{-}3\times HOAc\text{-}COCH_2]^+$ (95), 294 $[M\text{-}HOAc\text{-}COCH_2\text{-}H_2O]^+$ (100); ^1H NMR(pyridine-d_5) δ: 6.83 (1H, *br s*, OH, lost on D_2O exchange) 4.24 (1H, *dd*, *J* = 11.4, 4.3 Hz, H-1β), 2.30 (1H, *ddd*, *J* = 15, 11.4, 3.5 Hz, H-

Table 1. ^{13}C NMR data of compounds **1**–**5** (pyridine-d_5)

C	1	2	3	4	5
1	77.3 *d*	77.3 *d*	77.0 *d*	77.5 *d*	77.3 *d*
2	34.0 *t*	33.6 *t*	33.7 *t*	35.4 *t*	34.0 *t*
3	79.6 *d*	79.4 *d*	79.1 *d*	79.6 *d*	79.6 *d*
4	37.1 *s*	37.1 *s*	37.0 *s*	37.3 *s*	37.1 *s*
5	41.5 *d*	42.5 *d*	42.4 *d*	41.4 *d*	41.3 *d*
6	72.5 *d*	71.0 *d*	71.1 *d*	74.1 *d*	73.4 *d*
7	73.6 *d*	71.6 *d*	71.5 *d*	77.5 *d*	72.5 *d*
8	50.0 *s*	50.5 *s*	48.9 *s*	46.8 *s*	50.7 *s*
9	60.5 *d*	60.3 *d*	56.1 *d*	53.8 *d*	59.1 *d*
10	44.5 *s*	44.4 *s*	44.2 *s*	43.7 *s*	44.7 *s*
11	67.1 *d*	67.0 *d*	70.5 *d*	66.4 *d*	66.3 *d*
12	41.5 *t*	41.2 *t*	38.2 *t*	43.3 *t*	34.0 *t*
13	37.1 *d*	37.9 *d*	37.2 *d*	40.5 *d*	30.3 *d*
14	36.2 *t*	36.4 *t*	35.8 *t*	34.5 *t*	33.9 *t*
15	214.2 *s*	205.7 *s*	205.1 *s*	83.0 *d*	224.1 *s*
16	156.1 *s*	151.0 *s*	150.9 *s*	157.2 *s*	57.2 *d*
17	111.7 *t*	110.5 *t*	112.3 *t*	105.8 *t*	66.3 *t*
18	28.0 *q*	28.0 *q*	28.0 *q*	28.1 *q*	27.9 *q*
19	23.8 *q*	23.5 *q*	23.5 *q*	23.9 *q*	23.7 *q*
20	15.5 *q*	15.2 *q*	15.2 *q*	15.1 *q*	15.6 *q*
OAc	170.3 *s*	170.1 *s*	170.1 *s*	170.3 *s*	170.3 *s*
	170.0 *s*	169.7 *s*	169.9 *s*	170.2 *s*	170.0 *s*
	21.5 *q*	169.5 *s*	169.6 *s*	21.5 *q*	21.5 *q*
	20.9 *q*	21.4 *q*	169.4 *s*	21.0 *q*	20.9 *q*
		20.6 *q*	21.3 *q*		69.3 *t* (OCH_2)
			21.3 *q*		15.5 *q* (Me)
			20.8 *q*		
			20.8 *q*		

2α), 2.12 (1H, *ddd*, J = 15, 4.3, 3.5 Hz, H-2β), 4.89 (1H, *t*, J = 3.5 Hz, H-3α), 2.37 (1H, *br s*, H-5β), 5.38 (1H, *dd*, J = 3.5, 1.8 Hz, H-6β), 5.48 (1H, *d*, J = 3.5 Hz, H-7α), 2.65 (1H, *br s*, H-9β), 6.43 (1H, *br d*, J = 3.2 Hz, H-11α), 2.19 (1H, *m*, H-12α), 2.04 (1H, *m*, H-12β), 2.92 (1H, *br s*, H-13α), 2.66 (1H, *d*, J = 12.3 Hz, H-14α), 1.44 (1H, *dd*, J = 12.3, 2.5 Hz, H-14β), 5.92 (1H, *br s*, H-17a), 5.19 (1H, *br s*, H-17b), 0.97 (3H, *s*, Me-18), 1.09 (3H, *br s*, Me-19), 1.67 (3H, *s*, Me-20), 2.23, 2.18, 2.02, 1.74 (each 3H, *s*, 4 × Ac); ^{13}C NMR(DEPT): Table 1.

Melissoidesin C(**4**). Amorphous powder, $C_{24}H_{36}O_8$ mp 236–238°, $[\alpha]_D^{22}$ +16.36° (MeOH, *c* 0.38); UV λ_{max}^{MeOH} nm (log ε): end absorption; IR ν_{max}^{KBr} cm^{-1}: 3350, 1725, 1375, 1208, 1030; EIMs *m/z* (rel. int.): 452 $[M]^+$ (5), 434 $[M\text{-}H_2O]^+$ (8), 374 $[M\text{-}HOAc\text{-}H_2O]^+$ (40), 356 $[M\text{-}HOAc\text{-}2\times H_2O]^+$ (35), 296 $[M\text{-}2\times HOAc\text{-}2\times H_2O]^+$ (95), 270 $[M\text{-}2\times HOAc\text{-}4\times H_2O]^+$ (100); ^{1}H NMR(pyridine-d_5) δ: 6.42, 6.33, 6.18 (each 1H, *br s*, OH lost on D_2O exchange), 4.40 (1H, *dd*, J = 11.6, 4.0 Hz, H-1β), 2.36 (1H, *ddd*, J = 15.0, 11.6, 2.6 Hz, H-2α), 2.17 (1H, *ddd*, J = 15.0, 4.0, 2.6 Hz, H-2β), 4.91 (1H, *t*, J = 2.6 Hz, H-3α), 2.62 (1H, *br s*, H-5β), 5.56 (1H, *br s*, H-6β), 3.83 (1H, *d*, J = 3.2 Hz, H-7α), 2.90 (1H, *br s*, H-9β), 6.09 (1H, *br d*, J = 4.5 Hz H-11α), 2.42 (1H, *m*, H-12α), 2.22 (1H, *m*, H-12β), 2.66 (1H, *br s*, H-13α), 2.39 (1H, *d*, J = 12.0 Hz, H-14α), 1.10 (1H, *dd*, J = 12.0, 2.8 Hz, H-14β); 4.56 (1H, *d*, J = 5.4 Hz, H-15α, D_2O exchange, *br s*), 5.35 (1H, *br s*, H-17a), 5.03 (1H, *br s*, H-17b), 1.04 (3H, *s*, Me-18), 1.13 (3H, *s*, Me-19), 1.70 (3H, *s*, Me-20), 2.18, 1.92 (each 3H, *s*, 2 × Ac); ^{13}C NMR(DEPT): Table 1.

Melissoidesin D(**5**). Amorphous powder, $C_{26}H_{40}O_9$, mp 215–216°; $[\alpha]_D^{22}$ −4.20° (MeOH, *c* 0.50); UV λ_{max}^{MeOH} (log ε): end absorption; IR ν_{max}^{KBr} cm^{-1}: 3410, 1720, 1370, 1230, 1030; EIMS *m/z* (rel. int.): 496 $[M]^+$ (17), 488 $[M\text{-}H_2O]^+$ (15), 358 $[M\text{-}2\times HOAc\text{-}H_2O]^+$ (100); ^{1}H NMR(pyridine-d_5) δ: 6.45, 6.48 (each 1H, *br s*, OH, lost on D_2O exchange), 4.08 (1H, *dd*, J = 11.3, 4.32 Hz, H-1β), 2.34 (1H, *ddd*, J = 15.0, 11.3, 2.6 Hz, H-2α), 2.17 (1H, *ddd*, J = 15.0, 4.2, 2.6 Hz, H-2β), 4.83 (1H, *t*, J = 2.6 Hz, H-3α), 2.58 (1H, *br s*, H-5β), 5.56 (1H, *dd*, J = 3.4, 1.8 Hz, H-6β), 4.02 (1H, *d*, J = 3.4 Hz, H-7α), 2.98 (1H, *br s*, H-9β), 5.95 (1H, *d*, J = 4.2 Hz, H-11α), 2.31 (1H, *m*, H-12α), 2.19 (1H, *m*, H-12β), 2.75 (1H, *br s*, H-13α), 2.78 (1H, *d*, J = 12.3 Hz, H-14α), 1.49 (1H, *dd*, J = 12.3, 2.8 Hz, H-14β), 4.22 (1H, *dd*, J = 10.2, 7.8 Hz, H-17a), 4.18 (1H, *dd*, J = 10.2, 3.2 Hz, H-17b), 1.02 (3H, *s*, Me-18), 1.14 (3H, *s*, Me-19), 1.85 (3H, *s*, Me-20), 2.29, 2.01 (each 3H, *s*, 2 × Ac), 3.48 (2H, *m*, $-OCH_2CH_3$), 0.94 (3H, *t*, $-OCH_2CH_3$); ^{13}C NMR(DEPT): Table 1.

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