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Nor-lignan and sesquiterpenes from *Cremanthodium ellisii*

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Abstract

A nor-lignan and two sesquiterpenes, along with six known compounds, have been isolated from the medicinal plant *Cremanthodium ellisii*. Their structures were determined on the basis of spectral evidence, especially 2D NMR (^{1}H–^{1}H COSY, HMQC, HMBC).

Keywords: Cremanthodium ellisii; Compositae; Nor-lignan; Sesquiterpene

1. Introduction

About 47 species of the genus *Cremanthodium* (Compositae) are distributed in China, especially in the northwest and southwest regions (most of the genus *Cremanthodium* grow at an elevation of 3500–5000 m) (Northwestern Plant Institute of Botany, 1985). Some *Cremanthodium* plants like the title species have been used in traditional Tibetan medicine for anti-inflammation, detoxication and relief of pain since ancient times (Northwestern Plateau Institute of Biology, 1991).

Up to now, only the chemical constituents of *Cremanthodium ellisii* kitam collected in Zhang County, Gansu province of China have been reported (Chen, Zhu, Shen & Jia, 1996). In this paper, we report the isolation and structural elucidation of three new compounds, (−)-4′-*O*-methyl-nyasol (**1**), 2β,3β-epoxy-4-acetyl-5α,8,10,-triisobutyryl-1,11-dihydroxy bisabolene (**2**) and 4α-acetyl-2β,5α,8-triisobutyryl-1β,3α,10,11-tetrahydroxybisabolene (**3**), as well as six known compounds, 4α-acetyl-2β-angeloyl-5α,8-diisobutyryl-1β,3α,10,11-tetrahydroxybisabolene (**4**), 4α-acetyl-2β-angeloyl-5α,10-diisobutyryl-1β,3α,8,11-tetrahydroxybisabolene (**5**), sitosterol (**6**), 7α-hydroxysitosterol (**7**), apigenin 7-α-L-rhamnosyl-(1‴ → 6″)-β-D-glucopyranoside (**8**), and luteolin 7-α-L-rhamnosyl-(1‴ → 6″)-β-D-glucopyranoside (**9**), which have been isolated by silica gel column chromatography, polyamide column chromatography, PTLC and HPLC from the MeOH extracts of *C. ellisii* collected from a different region of China (Huzhu County, Qinghai province).

2. Results and discussion

4α-acetyl-2β-angeloyl-5α,8-diisobutyryl-1β,3α,10,11-tetrahydroxybisabolene (**4**) (Chen et al., 1996), 4α-acetyl-2β-angeloyl-5α,10-diisobutyryl-1β,3α,8,11-tetrahydroxybisabolene (**5**) (Chen et al., 1996), sitosterol (**6**) (Greca, Monaco & Previtera, 1990), 7α-hydroxy sitosterol (**7**) (Greca et al., 1990), apigenin 7-α-L-rhamnosyl-(1‴ → 6″)-β-D-glucopyranoside (**8**) (Kikuchi & Yamauchi, 1985) and luteolin 7-α-L-rhamnosyl-(1‴ → 6″)-β-D-glucopyranoside (**9**) (Imperato, 1994) were identified by comparison of their spectral data (EI and FAB mass spectra, ^{1}H, ^{13}C NMR and DEPT) with those published in the literature.

Compound **1** was obtained as a colorless gum; its HR-EIMS *m*/*z* 266.1284) indicated a molecular formula of $C_{18}H_{18}O_2$. The ^{1}H NMR spectrum of compound **1** showed the presence of two *p*-substituted aromatic rings at δ 6.76 (2H, *d*, *J* = 8.4 Hz, H-3″, H-

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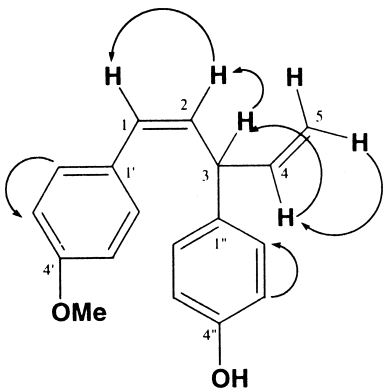
5″), 6.89 (2H, *d*, *J* = 8.5 Hz, H-3′, H-5′), 7.04 (2H, *d*, *J* = 8.5 Hz, H-2″, H-6″), 7.23 (2H, *d*, *J* = 8.5 Hz, H-2′, H-6′), two pairs of double bonds at δ 6.50 (1H, *d*, *J* = 11.4 Hz, H-1), 5.70 (1H, *t*, *J* = 11.4 Hz, H-2), 6.00 (1H, *ddd*, *J* = 17.6, 11.4, 6.0 Hz, H-4), 5.15-5.19 (2H, *m*, H-5), a methine proton signal at δ 4.48 (1H, *m*, H-3) and a methoxy group at δ 3.77 (3H, *s*, MeO). The above results were confirmed by ^{13}C NMR and DEPT spectral data: two *p*-substituted aromatic rings (δ 129.8, C-1′, 129.8, C-2′, C-6′, 113.6, C-3′, C-5′, 158.5, C-4′; 135.6, C-1″, 128.8, C-2″, C-6″, 115.3, C-3″, C-5″, 154.0, C-4″), two pairs of double bonds (δ 128.6, C-1, 131.6, C-2; 140.7, C-4, 115.0, C-5), a methoxy at δ 55.2 and a methine signal at δ 46.8. DEPT spectrum indicated that C-5 was a methylene carbon, consequently C-4 and C-5 was a terminal double bond. The ^{1}H NMR signal of H-1 was a doublet, indicating that C-1 was connected with an aromatic carbon. From the above results, the skeleton of **1** was as shown, confirmed by ^{1}H–^{1}H COSY spectral analysis (Scheme 1).

The ^{13}C NMR signal of C-1′ was overlapped by other carbon signals when $CDCl_3$ was used as a solvent (δ 129.8, C-1′, C-2′, C-6′); however, it was separated when CD_3COCD_3 was used as a solvent (δ 130.3, C-1′, 130.6, C-2′, C-6′). For determining positions of methoxyl and hydroxyl groups, HMQC and HMBC spectra were obtained. The HMBC correlations of δ_H 3.77 (OMe) with δ_C 159.6 (C-4′), δ_H 7.23 (H-2′, H-6′) with δ_C 159.6 (C-4′) and 130.3 (C-1′), δ_H 6.50 (H-1) with δ_C 130.3 (C-1′); δ_H 4.48 (H-3) with δ134.7 (C-1″), 142.2 (C-4) and 132.5 (C-2), δ_H 7.04 (H-2″, H-6″) with δ_C 156.8 (C-4″), suggested that the methoxyl and hydroxyl groups were connected to C-4′ and C-4″, respectively. H-1 and H-2 must be *cis* according to their coupling constant ($J_{7/8} = 11.4$ Hz) (Marini-Bettolo, Nicoletti, Messana, Galeffi, Msonthi & Chapya, 1985; Tsui & Brown, 1996). Hinokiresinol (Hirose, Oishi, Nagaki & Nakatsuka, 1965; Enzell, Hirose & Thomas, 1967; Enzell, Tomas & Wahlberg, 1967) was reported as having *trans*-stereochemistry at the 1,2-double bond, and nyasol (Marini-Bettolo et al., 1985; Tsui & Brown, 1996) was reported as its *cis*-isomer. Thus, the structure of compound **1** was determined as (−)-4′-*O*-methyl-nyasol.

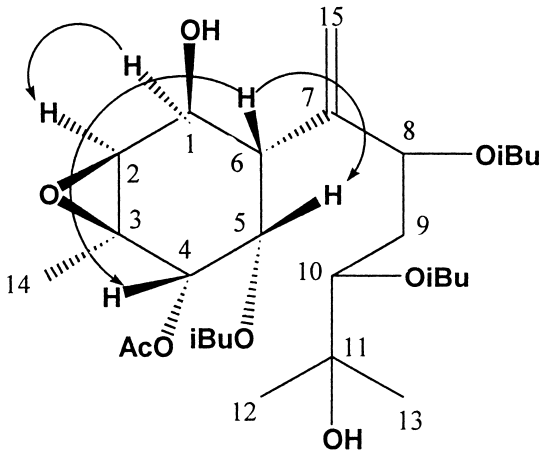
Compound **2** was obtained as a colorless gum. The ^{13}C NMR spectrum of 2 showed the presence of three isobutyryl groups [δ 175.0, 176.4, 176.2 (CO), 33.8, 33.9, 34.1 (CH), 18.6, 18.7, 18.8, 18.9, 19.0, 19.2 (CH_3)] and an acetyl group (δ 170.0, 20.4). Excluding the four ester groups, the ^{13}C NMR and DEPT spectra exhibited 15 carbon signals, including three methyls, two methylenes (δ 34.6 and one olefinic carbon at δ 116.2), seven methines (six oxygenated at δ 66.7, 62.6, 71.5, 70.0, 73.5, 74.9), and three quaternary carbons (two oxygenated at δ 57.2, 72.4, one olefinic carbon at δ 141.9). The EI mass spectrum of **2** gave a molecular ion peak at *m*/*z* 500 $[M]^+$ and an obvious $[M\text{-}H_2O]^+$ ion peak at *m*/*z* 482. Combining the ^{13}C NMR data analysis and ^{1}H NMR data suggested the molecular formula of **2** was $C_{29}H_{46}O_{11}$.

The ^{1}H and ^{13}C NMR spectral data of **2** were similar to those of four known sesquiterpene polyalcohols (Chen et al., 1996). However, the chemical shift values of C-2 (δ 62.6) and C-3 (δ 57.2) in compound **2** showed significant upfield shift, suggesting there was an epoxy between C-2 and C-3; this was confirmed by analysis of an HMBC experiment.

In the HMBC spectrum of **2**, correlations of δ_H 4.57 (H-1) with δ_C 62.6 (C-2), 57.2 (C-3) and 70.0 (C-5), δ_H 4.96 (H-4) with δ_C 170.0 (Ac) and 70.0 (C-5), δ_H 5.22 (H-5), 4.72 (H-8), 5.48 (H-10) with δ_C 175.0, 176.4, 176.2 (CO), confirmed the positions of epoxy and four ester groups. The relative stereochemistry of **2** was determined on the basis of the coupling constants (see Table 2) of H-1, H-2, H-4, H-5, H-6 and correlations of the NOESY spectrum. Thus, compound **2** was



Scheme 1. ^{1}H-^{1}H COSY corrrelations of **1**.

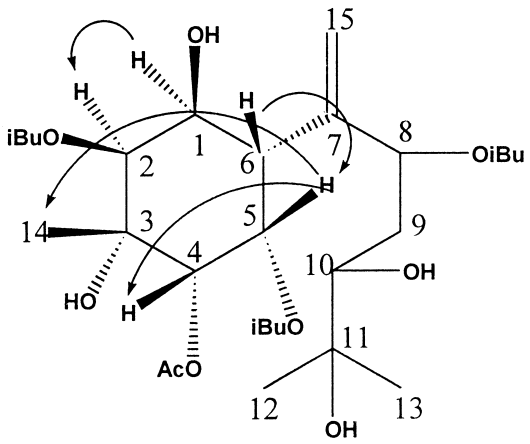


Scheme 2. NOESY correlations of compound **2**.

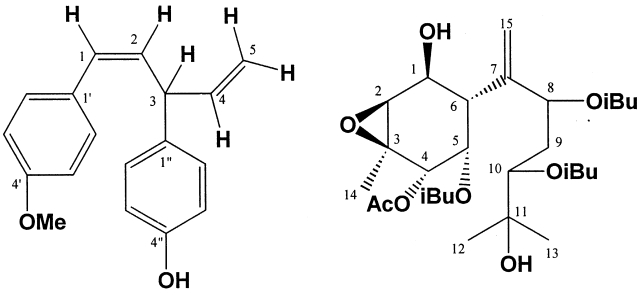
determined to be 2β,3β-epoxy-4α-acetyl-5α,8,10-triisobutyryl-1,11-dihydroxybisabolene (Scheme 2).

Compound **3**, was obtained as a colorless gum; its EI mass spectrum gave an $[M\text{-}H_2O]^+$ ion peak at *m/z* 500, suggesting the molecular formula to be $C_{29}H_{48}O_{12}$, which was confirmed by ^1H NMR (see Table 2), ^{13}C NMR and DEPT spectral data (see Table 3). The ^{13}C NMR spectrum of **3** showed the presence of three isobutyryl groups [δ 175.2, 176.4, 176.9 (CO), 34.2, 34.2, 34.3 (CH), 18.6, 18.9, 19.0, 19.1, 19.2, 19.4 (CH_3)] and an acetyl group (δ 169.8, 20.6). Excluding these four ester groups, the ^{13}C NMR and DEPT spectra exhibited 15 carbons, including three methyls (δ 22.8, 23.2, 25.9), two methylenes (δ 35.5 and one olefinic carbon at δ 118.2), seven methines (six oxygenated at δ 65.6, 76.1, 71.7, 70.4, 77.5, 75.0), and three quaternary carbons (two oxygenated at δ 74.0, 72.6, one olefinic carbon at δ 141.1). The ^1H NMR spectrum also showed the presence of six oxymethine protons at δ 4.60 (1H, *dd*, *J* = 11.6, 2.5 Hz, H-1), 5.36 (1H, *d*, *J* = 2.9 Hz, H-2), 4.98 (1H, *d*, *J* = 3.6 Hz, H-4), 5.56 (1H, *t*, *J* = 3.2 Hz, H-5), 5.34 (1H, *t*, *J* = 6.2 Hz, H-8), 3.34 (1H, *br d*, *J* = 9.6 Hz, H-10); a methine proton at δ 2.97 (1H, *dd*, *J* = 11.6, 2.5 Hz, H-6) and two terminal double bond protons at δ 5.24 (1H, *s*, H-15) and 5.45 (1H, *s*, H-15). The ^1H and ^{13}C NMR spectral data of **3** were also very similar to those reported for four sesquiterpene polyalcohols (Chen et al., 1996); **3** was thus assumed to be a monocyclic sesquitepenoid.

The ^1H and ^{13}C NMR data were assigned on the basis of ^1H–^1H COSY, HMBC and HMQC spectral analysis. In the HMBC spectrum of **3**, correlations of δ_H 5.36 (H-2) with δ_C 175.2 (isobutyryl-CO), δ_H 4.98 (H-4) with δ_C 169.8 (acetyl-CO), δ_H 5.56 (H-5) with δ_C 176.4 (isobutyryl-CO), and δ_H 5.34 (H-8) with δ_C 176.9 (isobutyryl-CO), suggested that the acetyl was connected with C-4 and three isobutyryls were connected with C-2, C-5 and C-8. The relative stereochemistry was determined by NOESY experiment and from analysis of the coupling constants of H-1, H-2, H-4, H-5 and H-6 (see Table 2). Thus compound **3** was identified as 4α-acetyl-2β,5α,8-triisobutyryl-1β,3α,10,11-tetrahydroxybisabolene (Scheme 3).

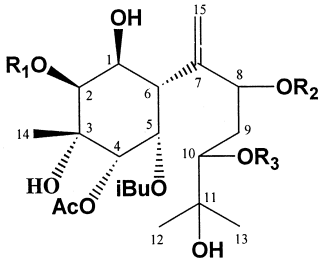


Scheme 3. NOESY correlations of compound 3.



1

2



3 $R_1 = R_2 = iBu$ $R_3 = H$
4 $R_1 = Ang$ $R_2 = iBu$ $R_3 = H$
5 $R_1 = Ang$ $R_2 = H$ $R_3 = iBu$

3. Experimental

3.1. General apparatus

IR spectra were recorded on a Nicolet-170 SX spectrometer, NMR spectra were recorded on a Bruker AM 400 spectrometer and mass spectra on a ZAB-HS instrument. Optical rotation was measured with a JASCO-20C auto recording polarimeter. HPLC was performed on a Gilson-Model 116 equipped with Whatman partisil 10 ODS C_{18} (9 × 250 mm) column. Silica gel (200–300 mesh) was used for column chromatography.

3.2. Plant material

The whole plants of *Cremanthodium ellisii* Kitam were collected in Huzhu county, Qinghai province of China in August 1994, and identified by Prof. Zhang Guo-liang of Lanzhou University. A voucher specimen (PV-005) has been preserved at the Herbarium of our Institute of Organic Chemistry.

Table 1
^1H ^{13}C NMR and DEPT spectral data of **1** (δ, ppm, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)[a]

	CD_3COCD_3			$CDCl_3$		
	δ_C	DEPT	δ_H	δ_C	DEPT	δ_H,
1	128.9	CH	6.50 (*d*, 11.4)	128.6	CH	6.53 (*d*, 11.4)
2	132.5	CH	5.70 (*t*, 11.4)	131.6	CH	5.67 (*t*, 11.4)
3	47.8	CH	4.48 (*m*)	46.8	CH	4.51 (*m*)
4	142.2	CH	6.00 (*ddd*, 17.6, 11.4, 6.0)	140.7	CH	6.01 (*ddd*, 17.6, 11.4, 6.0)
5	114.6	CH_2	5.15–5.19 (*m*)	115.0	CH	5.65–5.70 (*m*)
1′	130.3	C		129.8	C	
2′, 6′	130.6	CH	7.23 (*d*, 8.5)	129.8	CH	7.22 (*d*, 8.5)
3′, 5′	114.4	CH	6.89 (*d*, 8.5)	113.6	CH	6.86 (*d*, 8.5)
4′	159.6	C		158.5	C	
1′′	134.7	C		135.6	C	
2′′, 6′′	129.3	CH	7.04 (*d*, 8.5)	128.8	CH	7.10 (*d*, 8.5)
3′′, 5′′	116.1	CH	6.76 (*d*, 8.5)	115.3	CH	6.77 (*d*, 8.5)
4′′	156.8	C		154.0	C	
MeO	55.4	CH_3	3.77 (*s*)	55.2	CH_3	3.81 (*s*)

[a] TMS as internal standard.

3.3. Extraction and isolation of compounds

The air-dried, powered whole plants (7.5 kg) of *C. ellisii* Kitam were extracted three times (each for a week) with MeOH at room temperature. After concentration of the combined extracts under reduced pressure, the extract (340 g) was chromatographed over a silica gel column and eluted with petroleum ether–Me_2CO (from 20:1 to 2:1), then with MeOH; five fractions were obtained. Fraction 1 (petroleum ether–Me_2CO, 10:1) was chromatographed over silica gel and eluted with petroleum ether–EtOAc (6:1), yielding compound **6** (200 mg). Fraction 2 (petroleum ether–Me_2CO, 8:1) was chromatographed over silica gel and eluted with petroleum ether–Me_2CO (6:1), yielding compound **7** (20 mg). Fraction 3 (petroleum ether–Me_2CO, 6:1) was rechromatographed over silica gel and eluted with petroleum ether–Me_2CO (4:1), yielding compound **1** (30 mg). Fraction 4 (petroleum ether–Me_2CO, 3:1) was chromatographed over silica gel and eluted with petroleum ether–EtOAc (4:1), yielding two mixtures (A and B). The mixtures were separated by HPLC (reversephase column, H_2O–MeOH, 1:3); compounds **2** (20 mg) and **3** (25 mg), **4** (20 mg) and **5** (60

Table 2
^1H NMR spectral data of compounds **2**–**5** ($CDCl_3$, δ, ppm, 400 MHz, TMS)

	2	**3**	**4**	**5**
H-1	4.57 (*dd*, 11.6, 4.0)	4.60 (*dd*, 11.6, 2.9)	4.56 (*dd*, 11.6, 2.7)	4.65 (*dd*, 11.6, 2.6)
2	2.97 (*d*, 4.0)	5.36 (*d*, 2.9)	5.47 (*d*, 2.7)	5.49 (*d*, 2.6)
4	4.96 (*d*, 3.5)	4.98 (*d*, 3.5)	5.08 (*d*, 2.8)	4.98 (*d*, 3.6)
5	5.22 (*dd*, 3.5, 2.7)	5.56 (*t*, 3.5)	5.53 (*m*)	5.54 (*m*)
6	3.00 (*dd*, 11.6, 2.7)	2.97 (*dd*, 11.6, 3.5)	3.03 (*br d*, 11.6)	3.01 (*br d*, 11.6)
8	4.72 (*d*, 9.2)	5.34 (*t*, 6.2)	4.93 (*dd*, 9.2, 2.8)	3.34 (*br d*, 9.2)
9	1.67 (*m*)	1.63–1.65 (*m*)	1.65 (*m*)	1.57–1.65 (*m*)
9′	1.83–1.89 (*m*)	1.85–1.89 (*m*)	1.95 (*m*)	1.81–1.88 (*m*)
10	5.48 (*t*, 3.6)	3.34 (*br d*, 9.6)	4.04 (*br d*, 9.6)	5.37 (*t*, 6.8)
12	1.09–1.22 (*m*)	1.05–1.21 (*m*)	1.13–1.26 (*m*)	1.10–1.20 (*m*)
13	1.09–1.22 (*m*)	1.05–1.21 (*m*)	1.13–1.26 (*m*)	1.10–1.20 (*m*)
14	1.09–1.22 (*m*)	1.05–1.21 (*m*)	1.13–1.26 (*m*)	1.10–1.20 (*m*)
15	5.10 (*s*)	5.24 (*s*)	5.09 (*s*)	5.23 (*s*)
15′	5.31 (*s*)	5.45 (*s*)	5.26 (*s*)	5.46 (*s*)
Isobutyryl				
CH	2.53–2.66 (*m*)	2.54–2.69 (*m*)	2.55–2.64 (*m*)	2.53–2.63 (*m*)
CH_3	1.09–1.22	1.05–1.21	1.13–1.26	1.10–1.20
OAc	2.05 (*s*)	2.05(*s*)	2.05(*s*)	2.04 (*s*)
Angeloyl				
CH_3			1.13–1.26	1.10–1.20
CH			6.14 (*dq*, 7.2, 1.5)	6.13 (*dq*, 7.2, 1.5)

Table 3
^{13}C NMR and DEPT spectral data of compounds **2**–**5** (δ, ppm, TMS, $CDCl_3$, 100 MHz)

	2	**3**	**4**	**5**
1	66.7(CH)	65.6(CH)	65.2(CH)	65.5(CH)
2	62.6(CH)	76.1(CH)	76.2(CH)	76.1(CH)
3	57.2(C)	74.0(C)	74.3(C)	74.1(C)
4	71.5(CH)	71.7(CH)	71.7(CH)	71.7(CH)
5	70.0(CH)	70.4(CH)	71.5(CH)	70.4(CH)
6	43.6(CH)	40.8(CH)	41.6(CH)	40.9(CH)
7	141.9(C)	141.1(C)	145.6(C)	141.1(C)
8	73.5(CH)	77.5(CH)	76.7(CH)	74.9(CH)
9	34.6(CH_2)	35.5(CH_2)	35.5(CH_2)	35.4(CH_2)
10	74.9(CH)	75.0(CH)	71.4(CH)	77.3(CH)
11	72.4(C)	72.6(C)	72.0(C)	72.6(C)
12	25.9(CH_3)	23.2(CH_3)	25.8(CH_3)	22.8(CH_3)
13	26.1(CH_3)	25.9(CH_3)	25.8(CH_3)	25.8(CH_3)
14	23.9(CH_3)	22.8(CH_3)	22.9(CH_3)	23.1(CH_3)
15	116.2(CH_2)	118.2(CH_2)	114.2(CH_3)	118.1(CH_3)
OAc	170.0, 20.4	169.8, 20.6		
Isobutyryl	175.0, 176.4, 176.2; 33.8, 33.9, 34.1; 18.6, 18.7, 18.8, 18.9, 19.0, 19.2	175.2, 176.4, 176.9; 34.2, 34.2, 34.3; 18.6, 18.9, 19.0, 19.1, 19.2, 19.4	177.7, 176.0; 34.2, 34.2; 18.6, 18.8, 19.0, 19.2	176.7, 175.2; 34.1, 34.1; 18.5, 18.9, 19.0, 19.1
Angeloyl			167.1, 139.3, 127.2, 20.5, 15.9	167.0, 139.1, 127.2, 20.5, 15.8

mg) were obtained, Fraction 5 (MeOH) was chromatographed over a polyamide column and eluted with H_2O–MeOH (3:1), yielding compounds **8** (100 mg) and **9** (150 mg).

3.4. (−)-4′-O-methyl-nyasol (*1*)

(−)-4′-*O*-methyl-nyasol (**1**), obtained as a colorless gum; $[\alpha]_D^{25} - 42.2^\circ$ (*c* 0.64, $CHCl_3$), IR (KBr): 3600, 3400, 2959, 2867, 1717, 1664, 1465, 1379, 1056, 953 cm^{-1}; UV ($CHCl_3$) (log ε): 244.0 (4.78), 284.7 (4.23) nm; EIMS: *m*/*z* (%) 266 $[M]^+$ (45), 251 (13), 223 (8), 196 (40), 181 (27), 158 (24), 149 (100), 121 (22), 107 (22), 91 (18), 77 (26), 57 (44); HR-EIMS: *m*/*z* 266.1284 (Calcd. for $C_{18}H_{18}O_2$, 266.1307); ^1H, ^{13}C NMR and DEPT spectral data: see Table 1.

3.5. 2β,3β-epoxy-4-acetyl-5α,8,10-triisobutyryl-1,11-didydroxybisabolene (*2*)

2β,3β-epoxy-4-acetyl-5α,8,10-triisobutyryl-1,11-didydroxybisabolene (**2**), obtained as a colorless gum; $[\alpha]_D^{20} - 68.4^\circ$ (*c* 0.25, $CHCl_3$); IR (KBr): 3479, 3075, 2976, 2935, 2878, 1716, 1644, 1386, 1358, 1228, 1202 cm^{-1}, EIMS *m*/*z* (%) 482 $[M\text{-}H_2O]^+$ (1.9), 464 (1.5), 441 (1.8), 424 (1.2), 397 (1.5), 353 (1.5), 335 (1.3), 293 (1.2), 288 (1.0), 265 (2.3), 264 (2.3), 263 (1.3), 258 (1.4), 249 (1.9), 247 (3.8), 246 (5.5), 239 (1.7), 231 (2.8), 223 (2.0), 221 (3.0), 195 (2.0), 188 (6.5), 178 (6.8), 161 (7.0), 149 (5.3), 141 (4.4), 135 (5.4), 123 (20), 97 (6.1), 86 (28), 84 (36), 71 (80), 59 (17), 43 (100); ^1H NMR spectral data: see Table 2; ^{13}C NMR spectral data: see Table 3.

3.6. 4α-acetyl-2β,5α,8-triisobutyryl-1β,3α,10,11-tetrahydroxybisabolene (*3*)

4α-acetyl-2β,5α,8-triisobutyryl-1β,3α,10,11-tetrahydroxybisabolene (**3**), obtained as a colorless gum; $[\alpha]_D^{20} - 47.4^\circ$ (*c* 0.28, $CHCl_3$), IR (KBr): 3482, 3088, 2974, 2927, 1727, 1649, 1467, 1375, 1229, 1152, 1058 cm^{-1}, EIMS: *m*/*z* (%) 500 $[M\text{-}H_2O]^+$ (1.2), 441 (4.7), 424 (2.9), 423 (2.1), 397 (2.0), 353 (4.8), 335 (2.1), 275 (1.4), 265 (4.0), 247 (4.5), 239 (3.0), 223 (4.9), 221 (3.7), 205 (16), 179 (11), 177 (13), 161 (10), 151 (6.3), 141 (13), 133 (5.8), 123 (13), 107 (5.8), 97 (18), 83 (53), 71 (100), 59 (22), 43 (67). ^1H NMR spectral: data see Table 2. ^{13}C NMR spectral data: see Table 3.

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