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SESQUITERPENE LACTONES FROM *VIGUIERA DELTOIDEA*

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Key Word Index—*Viguiera deltoidea*; Helianthеae; Asteraceae; sesquiterpene lactones.

Abstract—Three sesquiterpene lactones, 2',3'-dihydroniveusin-A, 2',3'-dihydroniveusin-B and 3-acetylchamissonin, were isolated from the dichloromethane extract of leaves of *Viguiera deltoidea*. The structures were established on the basis of physical and spectroscopic data and that of 3-acetylchamissonin was also confirmed by X-ray analysis.

INTRODUCTION

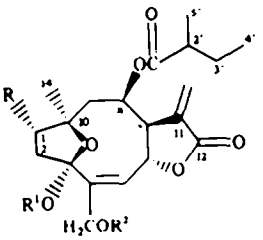
Viguiera and *Helianthus* are considered to be closely related genera and available chemical data support this view. Almost all species so far investigated in both genera contain either sesquiterpene lactones or diterpenes or both [1–5]. *Viguiera deltoidea* Gray also produces sesquiterpene lactones, with two of them being similar to those isolated from *Helianthus niveus* [3]. The dried leaves of *V. deltoidea* have now afforded three sesquiterpene lactones: **1**, **2** and **7** (0.26%, 0.08% and 0.2%).

RESULTS AND DISCUSSION

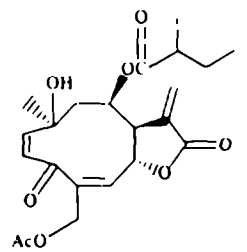
The IR spectrum of **1** showed characteristic absorption for an α,β-unsaturated γ-lactone at 1760 cm^{-1} and an ester absorption at 1735 cm^{-1}. Comparison of the ^1H NMR spectrum of **1** (see Experimental) with that of niveusin-A [3] indicated that they differed only in their ester side chains; that is, instead of an angelate side chain as in niveusin-A, **1** contains a 2-methylbutanoate group (a 3-proton triplet at δ0.83 and a 3-proton doublet at δ1.01). In the ^{13}C NMR spectra of **1**, a saturated ester side chain also followed from the absence of a third pair of sp^2 carbon signals which were observed for the angeloyloxy moiety of niveusin-A(3). Moreover, the ^{13}C NMR spectrum of **1** had a doublet at δ41.2 for C-2' and another triplet at δ26.5 for C-3' in accord with a saturated side chain. Other signals for **1** were identical to those of niveusin-A, except for the signal for C-14 (22.2 ppm) (see Table 1). A comparative analysis of the ^{13}C NMR data for **1**, niveusin-A and -B and for a similar compound with a C-8 angeloyloxy suggested the following revisions in the assignments for niveusin-A previously reported [3]: thus, the δ20.5 quartet in the spectrum of niveusin-A should be assigned to C-5', not C-14, and the 22.3 quartet previously assigned to C-5' should be assigned to C-14 and the 15.7 quartet previously assigned to C-20 represents C-4'.

When **1** was acetylated with acetic anhydride and pyridine, the tri- (**3**), di- (**4**) and mono- (**5**) acetates were obtained. The β-orientation of the ester side chain at the C-8 position was established by the coupling pattern in the spectra of **1** and its derivatives (H-8, *ddd*, J = 5, 5, 10 Hz). Therefore, **1** must be 2',3'-dihydroniveusin-A.

The IR spectrum of **2** appeared similar to that of **1**. While the ^1H NMR spectrum of **2** was also similar to that of **1**, integration indicated that there were three protons in the δ4.0–4.3 region in **2** rather than four protons as in **1**. The well separated ^{13}C NMR signals of **2**, which showed that there was one less hydroxyl-bearing carbon atom in **2** than in **1**, made it possible with the help of single frequency off resonance decoupling experiments to formulate **2** as $C_{20}H_{28}O_7$. The mass spectrum of **2** gave a molecular ion at m/z 380 (1%) in accord with this conclusion. When **1**



	R	R^1	R^2
1	OH	H	H
2	H	H	H
3	OAc	Ac	Ac
4	OAc	H	Ac



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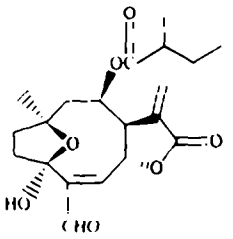

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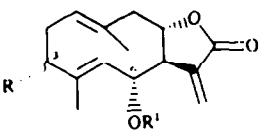

	R	R^1
7	α-OAc	H
8	α-OAc	Ac
11	β-OAc	H

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Table 1. ^{13}C NMR spectral data of 2',3'-dihydroniveusin-A (1), 2',3'-dihydroniveusin-B (2) and 3-acetylchamissonin pyrazoline (10) [recorded at 22.6 MHz, δ (ppm) with TMS as internal standard]

	1		2	10*
C	$CDCl_3$	Me_2CO-d_6	$CDCl_3$	$CDCl_3$
1	77.3 *d*	77.6	37.3 *t*	126.4 *d*
2	45.6 *t*	46.6	41.0 *t*	30.8 *t*
3	106.2 *s*	106.7	106.2 *s*	76.2 *d*
4	135.8 *s*	137.7	136.5 *s*	135.1 *s*
5	131.1 *d*	128.8	131.1 *d*	130.1 *d*
6	75.3† *d*	76.0	75.4† *d*	65.5 *d*
7	50.0 *d*	50.6	49.9 *d*	60.4 *d*
8	71.3† *d*	72.7	71.9† *d*	80.1 *d*
9	39.1 *t*	39.8	39.3 *t*	47.3 *t*
10	86.5 *s*	86.9	83.2 *s*	134.0 *s*
11	142.2 *s*	144.4	143.7 *s*	100.7 *s*
12	170.2 *s*	170.2	170.3 *s*	172.7 *s*
13	123.4 *t*	122.8	123.4 *t*	25.8 *t*
14	21.9 *q*	22.2	28.2 *q*	15.8 *q*
15	65.3 *t*	64.1	65.8 *t*	16.8 *q*
1'	175.7 *s*	175.5	175.8 *s*	79.8 *t*
2'	41.2 *d*	41.8	41.2 *d*	170.3 *s*
3'	26.5 *t*	27.0	26.5 *t*	21.3 *q*
4'	16.7 *q*	17.0	16.7 *q*	—
5'	11.6 *q*	11.8	11.6 *q*	

*The numbering scheme of the last three signals for compound **10** is as following: C-1', the CH_3 attached to the N in the pyrazoline group; C-2', the carbonyl of the acetate; C-3', the methyl group of the acetate.

†These signals are interchangeable within each column.

was oxidized by Jones reagent, the aldehyde **6** was obtained. In the ^1H NMR spectrum of **6**, the signal of H-7 was observed at δ4.40 (multiplet), typical for a furanoheliangolide-type sesquiterpene lactone. All the available data were in accord with formulation of **2** as 2',3'-dihydroniveusin-B [3].

Compound **7** exhibited a molecular ion at *m/z* 306 for $C_{17}H_{22}O_5$. The IR spectrum also showed α-methylene-γ-lactone absorption at 1745 cm^{-1} and an ester absorption at 1725 cm^{-1}. A ^1H NMR signal at δ2.10 (singlet, 3 protons) confirmed that an acetoxy side chain was present. However, the remaining signals of both the ^1H and ^{13}C NMR spectra of **7** were not easily interpretable. But the sharp mp (160–161°) and the observation of a single spot on TLC indicated that **7** was pure. Together, these data suggested that **7** existed as conformational isomers in solution. Compound **8**, the acetylation product of **7**, also exhibited broadened ^1H NMR signals, and the spectrum was identical to the one previously reported for chamissonin diacetate [6]. The mp (174–175°) [7, 8] and co-chromatography (see Experimental) confirmed that they were identical. When **7** was reacted with diazomethane to yield **9** and **10**, only two sharp allylically coupled signals were observed in each spectrum for the methyl groups. The ^1H NMR data of **9** and **10** were different from those reported by Bohlmann [9] only for H-3 and H-2. Judging from this evidence, together with the different melting points of the diacetates of **7** and **11**, we assigned the structure of **7** as the 3α-isomer of **11**, e.g. 3-acetychamissonin*. The assignable ^{13}C NMR signals of **10** also supported this structure. The X-ray analysis of **7** (which will be published elsewhere by W. H. Watson and co-workers) confirmed this structure assignment (i.e. 3*R*, 6*R*, 7*R*, 8*S*).

*Gershenzon *et al.* [10] recently suggested on the basis of H-3 coupling constants that **11** might be 3-acetylchamissonin; however, we now conclude that the structure of **11** was correctly reported [9].

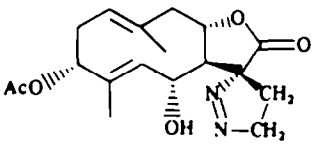
EXPERIMENTAL

Viguiera deltoidea Gray was collected 30 miles south of El Rosario, Baja California Norte in Mexico along Highway 1 by John Norris. A voucher specimen (JN No. 429) is deposited in the Herbarium of the University of Texas at Austin and was determined by Alan Whittemore (Department of Botany, University of Texas at Austin).

Dried leaves of *V. deltoidea* (360 g) were extracted with 7 l. of CH_2Cl_2 (× 2). The extracts were combined and evaporated to dryness, then dissolved in Me_2CO and kept in a refrigerator overnight. After filtering to remove the ppt the soln was evaporated to yield 18.5 g of residue. The residue was first separated by CC (silica gel using hexane–EtOAc gradient solvent system) and further by Sephadex LH-20 columns (cyclohexane–CH_2Cl_2–MeOH, 7:4:1) to give **1**, **2** and **7**.

2',3'-Dihydroniveusin-A (**1**). Colourless gum (960 mg). IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 1760 (γ-lactone), 1735 (CO_2R), 1660 (C=C). EIMS (probe) 70 eV *m/z* (rel. int.): 396 $[M]^+$ (1), 378 $[M-H_2O]^+$ (5), 360 $[378-H_2O]^+$ (2), 276 $[M-H_2O-C_5H_{10}O_2]^+$ (27), 258 $[276-H_2O]^+$ (26), 85 $[C_5H_9O]^+$ (40), 57 $[C_4H_9]^+$ (100). ^1H NMR (200 MHz, $CDCl_3$): δ0.83 (3H, *t*, H-4'), 1.01 (3H, *d*, H-5'), 1.54 (3H, *s*, H-14), 4.0–4.3 (4H, H-1, H-7 and H-15 overlapped each other, the AB quartet of H-15 could be observed by adding a drop of D_2O), 5.35 (1H, *br t*, H-6), 5.60 (1H, *ddd*, *J* = 5.3, 5.3, 10.2 Hz, H-8), 5.65 (1H, *d*, *J* = 2 Hz, H-13a), 5.85 (1H, *d*, *J* = 3.7 Hz, H-5), 6.27 (1H, *d*, *J* = 2.3 Hz, H-13b); in C_6D_6 $CDCl_3$: δ0.81 (3H, *t*, H-4'), 1.00 (3H, *d*, H-5'), 1.41 (3H, *s*, H-14), 3.60 (1H, *br s*, H-1), 3.92 (1H, *d*, *J* = 12.7 Hz, H-15a), 4.02 (1H, H-15b, partly overlapped by H-7), 4.10 (1H, *m*, H-7), 5.20 (1H, *br t*, H-6), 5.32 (1H, *d*, *J* = 1.8 Hz, H-13a), 5.61 (1H, *ddd*, *J* = 5, 5, 10 Hz, H-8), 5.09 (1H, *d*, *J* = 3.5 Hz, H-5), 6.20 (1H, *d*, *J* = 2.3 Hz, H-13b). ^{13}C NMR: see Table 1.

Acetylation of **1**. Compound **1** (170 mg) was acetylated with



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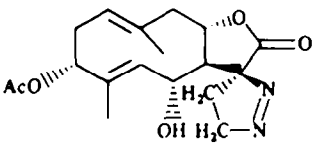

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Ac_2O–pyridine at room temp. for 3 hr. After the usual work-up and purification on prep. TLC (hexane–EtOAc, 1.5:1), 54 mg of pure **3** and 98 mg of a mixture of **4** and **5** were obtained. The mixture was passed through a Sephadex LH-20 column (cyclohexane–CH_2Cl_2–MeOH, 7:4:1), 40 mg **4** and 10 mg **5** were afforded. Triacetate (**3**), IR ν_{max}^{KBr} cm^{-1}: 3120, 1760, 1730, 1660. EIMS (probe) 70 eV, *m/z* (rel. int.): 462 $[M - AcOH]^+$ (2), 402 $[M - 2 \times AcOH]^+$ (62), 258 $[M - C_{11}H_{20}O_7]^+$ (100), 215 [258 – MeCO]$^+$ (90), 85 $[C_5H_9]^+$ (67), 57 $[C_4H_9]^+$ (69), 43 [MeCO]$^+$ (69). No molecular ion was observed. ^1H NMR (200 MHz, $CDCl_3$): δ0.83 (3H, *t*, H-4'), 1.02 (3H, *d*, H-5'), 1.42 (3H, *s*, H-14), 2.63 (2H, *d*, J = 3.5 Hz, H-2), 4.28 (1H, *d*, J = 13.2 Hz, H-15a), 4.34 (1H, *m*, H-7), 4.66 (1H, *d*, J = 13.2 Hz, H-15b), 5.15 (1H, *t*, J = 3.5 Hz, H-1), 5.38 (1H, *m*, H-6), 5.60 (1H, H-8, overlapped by H-13a), 5.62 (1H, *d*, J = 2.2 Hz, H-13a), 5.94 (1H, *d*, J = 3 Hz, H-5), 6.28 (1H, *d*, J = 2.7 Hz, H-13b), 2.04 (3H, *s*, OAc), 2.08 (3H, *s*, OAc), 2.14 (3H, *s*, OAc).

Diacetate (**4**). IR ν_{max}^{KBr} cm^{-1}: 3460 (OH), 3120, 1760, 1730, 1660, 1380, 1240. EIMS (probe) 70 eV, *m/z* (rel. int.): 420 $[M - AcOH]^+$ (3), 378 $[M - C_5H_{10}O_2]^+$ (6), 318 $[M - 102 - AcOH]^+$ (18), 300 $[M - 162 - H_2O]^+$ (3), 85 $[C_5H_9O]^+$ (98), 57 $[C_4H_9]^+$ (100), 43 [MeCO]$^+$ (88). No molecular ion was observed. ^1H NMR (200 MHz, $CDCl_3$): δ0.83 (3H, *t*, H-4'), 1.02 (3H, *d*, H-5'), 1.45 (3H, *s*, H-14), 4.17 (1H, *m*, H-7), 4.51 (1H, *d*, J = 12 Hz, H-15a), 4.77 (1H, *d*, J = 12 Hz, H-15b), 5.28 (1H, *br d*, J = 5.0 Hz, H-1), 5.38 (1H, *br t*, J = 3.9 Hz, H-6), 5.59 (1H, *ddd*, J = 5, 5, 10 Hz, H-8), 5.64 (1H, *d*, J = 2.2 Hz, H-13a), 5.92 (1H, *d*, J = 3.8 Hz, H-5), 5.29 (1H, *d*, J = 2.5 Hz, H-13b), 2.09 (3H, *s*, OAc), 2.16 (3H, *s* OAc).

Monoacetate (**5**). IR ν_{max}^{KBr} cm^{-1}: 3460 (OH), 3100 (C=C), 1770 (γ-lactone), 1730 (COOR), 1660 (conjugated ketone). EIMS (probe) 70 eV *m/z* (rel. int.): 420 $[M]^+$ (2), 318 $[M - C_5H_{10}O_2]^+$ (13), 300 $[M - 102 - H_2O]^+$ (1), 258 $[M - 102 - AcOH]^+$ (26), 85 $[C_5H_9O]^+$ (96), 57 $[C_4H_9]$ (98), 43 [MeCO]$^+$ (100). ^1H NMR (200 MHz, $CDCl_3$): δ0.84 (3H, *t*, H-4'), 1.03 (3H, *d*, H-5'), 1.56 (3H, *s*, H-14), 3.57 (1H, *m*, H-7), 4.63 (1H, *d*, J = 12 Hz, H-15a), 4.95 (1H, *d*, J = 13 Hz, H-15b), 5.38 (1H, H-8, overlapped by H-6), 5.42 (1H, *dd*, J = 1.6, 9.0 Hz, H-6), 5.84 (1H, *d*, J = 1.6 Hz, H-13a), 6.06 (1H, *d*, J = 9.0 Hz, H-5), 6.28 (1H, *d*, J = 17 Hz, H-1), 6.37 (1H, *d*, J = 1.7 Hz, H-13b), 6.98 (1H, *d*, J = 17 Hz, H-2), 2.07 (3H, *s*, OAc).

2',3'-Dihydroniveusin-B (**2**). Colourless gum (225 mg). IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 1760 (γ-lactone), 1740 (CO_2R), 3129, 1660 (C=C). EIMS (probe) 70 eV *m/z* (rel. int.): 380 $[M]^+$ (1), 362 $[M - H_2O]^+$ (21), 344 $[362 - H_2O]^+$ (43), 278 $[M - C_5H_{10}O_2]^+$ (5), 260 $[M - H_2O - C_5H_{10}O_2]^+$ (34), 242 $[M - 2H_2O - C_5H_{10}O_2]^+$ (57), 85 $[C_5H_9O]^+$ (32), 57 $[C_4H_9]^+$ (100). ^1H NMR (200 MHz, $CDCl_3$): δ0.83 (3H, *t*, H-4'), 1.02 (3H, *d*, H-5'), 1.53 (3H, *s*, H-14), 4.05–4.25 (3H, H-7 and H-15, overlapped each other), 5.50 (1H, *br t*, H-6), 5.52 (1H, *ddd*, H-8, partly overlapped by H-6), 5.64 (1H, *d*, J = 2.2 Hz, H-13a), 5.80 (1H, *d*, J = 4.0 Hz, H-5), 6.25 (1H, *d*, J = 2.5 Hz, H-13b). ^{13}C NMR: see Table 1.

Oxidation of **2**. Jones reagent was added to 75 mg of **2** (in 6 ml Me_2CO) under magnetic stirring at a temp. of 5 10°. The reaction was monitored by TLC, and after 30 min stopped by adding *iso*-PrOH. After the usual work-up and purification over prep. TLC (hexane–EtOAc, 1:2), 16 mg of the aldehyde (**6**) was afforded. IR ν_{max}^{KBr} cm^{-1}: 3460 (OH), 3120, 1630 (C=C), 2750 (CHO), 1770 (γ-lactone), 1730 (CO_2R), 1680 (conjugated aldehyde). EIMS (probe) 70 eV, *m/z* (rel. int.): 378 $[M]^+$ (2), 293 $[M - C_5H_9O]^+$ (21), 276 $[M - C_5H_{10}O_2]^+$ (30), 258 $[M - 102 - H_2O]^+$ (17), 99 $[C_5H_7O_2]^+$ (79), 85 $[C_5H_9O]^+$ (92), 57 $[C_4H_9]^+$ (100). ^1H NMR (90 MHz, $CDCl_3$): δ0.80 (3H, *t*, H-4'), 1.00 (3H, *d*, H-5'), 1.56 (3H, *s*, H-14), 4.40 (1H, *m*, H-7), 5.4–5.7 (2H, H-6 and H-8 overlapped each other), 5.68 (1H, *d*, J = 2 Hz, H-13a), 6.31 (1H, *d*, J = 2 Hz, H-13b), 6.71 (1H, *d*, J = 4 Hz, H-5), 9.42 (1H, *s*, CHO, H-15).

3-Acetylchamissonin (**7**). Colourless prism (735 mg). Mp 160–161°. IR ν_{max}^{KBr} cm^{-1}: 3500 (OH), 1745 (γ-lactone), 1725 (CO_2R), 1660 (C=C). EIMS (probe) 70 eV, *m/z* (rel. int.): 306 $[M]^+$ (18), 246 $[M - AcOH]^+$ (17), 43 [MeCO]$^+$ (100). ^1H NMR (200 MHz, $CDCl_3$): δ1.73 (3H, *s*, H-14), 1.63 and 1.87 (3H, *s*, H-15), 3.9–4.5 (*m*, H-8), 4.9–5.4 (H-1, H-3, H-5, H-6, obscured), 6.12 (*br s*, H-13a), 6.42 (*br s*, H-13b), 2.10 (3H, *s*, OAc).

Acetylation of **7**. Compound **7** (99 mg) was acetylated with Ac_2O and pyridine for 7 hr. After the usual work-up and purification over Sephadex LH-20 column, 78 mg of chamissonin diacetate (**8**) was afforded. Colourless plates from EtOAc, mp 175° (lit. 174–175° [7]). Both R_f value and colour were the same when the diacetate was co-chromatographed with authentic chamissonin diacetate using different solvent systems and spraying agents. IR ν_{max}^{KBr} cm^{-1}: 3120, 1760, 1740, 1660. EIMS (probe) 70 eV, *m/z* (rel. int.): 348 $[M]^+$ (29), 289 $[M - MeCO_2]^+$ (47), 246 $[M - 59 - MeCO]^+$ (86), 228 $[M - 2 \times AcOH]^+$ (100), 43 [MeCO]$^+$ (76). ^1H NMR (200 MHz, $CDCl_3$): δ1.72 (3H, *s*, H-14), 1.78 (3H, *d*, J = 1.3 Hz, H-15), 4.0–4.5 (1H, *m*, H-8), 4.9–5.5 (4H, H-1, H-3, H-5, H-6), 5.92 (1H, *br s*, H-13a), 6.39 (1H, *br s*, H-13b), 2.07 (3H, *s*, OAc), 2.11 (3H, *s*, OAc).

Compound **7** (50 mg in 5 ml Et_2O–$CHCl_3$, 1:1) was reacted with CH_2N_2 (in Et_2O) for 3 hr. The usual work-up gave crude products. Separation was made over prep. TLC (hexane–EtOAc, 1:1.5). Compounds **9** (11 mg) and **10** (40 mg) afforded.

Compound **9**. IR ν_{max}^{KBr} cm^{-1}: 3460 (OH), 1770 (γ-lactone), 1730 (CO_2R), 1670 (C=C), 1560 (CN=N). EIMS (probe) 70 eV, *m/z* (rel. int.): 320 $[M - N_2]^+$ (1), 260 $[320 - AcOH]^+$ (5), 242 $[260 - H_2O]^+$ (8), 135 (100), 100 $[C_5H_8O_2]^+$ (66), 43 [MeCO]$^+$ (55). No molecular ion was observed. ^1H NMR (200 MHz, $CDCl_3$): δ1.51 (3H, *s*, H-14), 1.67 (3H, *d*, J = 1.3 Hz, H-15), 2.43 (2H, *br dd*, J = 3.5, 10.5 Hz, H-2), 2.64 (1H, *dd*, J = 10.8, 12.7 Hz, H-9α), 2.99 (1H, *br d*, J = 12.8 Hz, H-9β), 3.44 (1H, *t*, J = 9.6 Hz, H-7), 4.37 (1H, *t*, J = 10 Hz, H-6), 4.38 (1H, *t*, J = 10 Hz, H-8), 4.81 (2H, sharp *m*, H-16), 5.04 (1H, *br d*, J = 10 Hz, H-5), 5.18 (1H, *t*, J = 3 Hz, H-3), 5.20 (1H, H-1 overlapped by H-3), 2.07 (3H, *s*, OAc).

Compound **10**. IR ν_{max}^{KBr} cm^{-1}: 3460 (OH), 1770 (γ-lactone), 1730 (COOR), 1670 (C=C), 1560 (CN=N). EIMS (probe), 70 eV, *m/z* (rel. int.): 320 $[M - N_2]^+$ (2), 260 $[320 - AcOH]^+$ (58), 242 $[260 - H_2O]^+$ (19), 135 (100), 100 $[C_5H_8O_2]^+$ (99), 43 [MeCO]$^+$ (80). No molecular ion was observed. ^1H NMR (200 MHz, $CDCl_3$): δ1.57 (3H, *s*, H-14), 1.63 (3H, *d*, J = 1.3 Hz, H-15), 2.42 (2H, *m*, H-2), 2.52 (1H, H-9α, overlapped by H-7 and H-2), 2.60 (1H, *t*, J = 10 Hz, H-7), 3.03 (1H, *br d*, J = 13.3 Hz, H-9β), 4.55 (1H, *t*, J = 10 Hz, H-6), 4.77 (2H, sharp *m*, H-16), 4.92 (1H, *br d*, J = 10 Hz, H-5), 5.01 (1H, *br t*, J = 10 Hz, H-8), 5.15 (1H, H-1, overlapped by H-3), 5.16 (1H, *t*, J = 3 Hz, H-3β), 2.07 (3H, *s*, OAc).

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REFERENCES

1. Gershenzon, J., Liu, Y. L., Mabry, T. J., Korp, J. D. and Bernal, I. (1980) *Phytochemistry* **23**, 1281.

2. Liu, Y. L., Gershenzon, J. and Mabry, T. J. (1984) *Phytochemistry* **23**, 1967.
3. Ohno, N. and Mabry, T. J. (1980) *Phytochemistry* **19**, 609.
4. Gershenzon, J., Ohno, N. and Mabry, T. J. (1981) *Rev. Latinoam. Quim.* **12**, 53.
5. Melek, F. R., Gershenzon, J., Lee, E. and Mabry, T. J. (1984) *Phytochemistry* **23**, 2277.
6. Yoshioka, H., Mabry, T. J. and Timmermann, B. N. (1973) *Sesquiterpene Lactones*, p. 182. University of Tokyo Press.
7. Geissman, T. A., Turley, R. J. and Murayama, S. (1966) *J. Org. Chem.* **31**, 2269.
8. L'Homme, M. F., Geissman, T. A., Yoshioka, H., Porter, T. H., Renold, W. and Mabry, T. J. (1969) *Tetrahedron Letters* **37**, 3161.
9. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1980) *Phytochemistry* **19**, 115.
10. Gershenzon, J., Mabry, T. J., Korp, J. D. and Bernal, I. (1984) *Phytochemistry* **23**, 2561.