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LIGNANS AND SESQUITERPENE LACTONES FROM *ARTEMISIA SIEVERSIANA* AND *INULA RACEMOSA*

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Key Word Index—*Artemisia sieversiana*; *Inula racemosa*; Compositae; lignans; sesquiterpene lactones; guaianolides; eudesmanolide; sterols; antifungal activity.

Abstract—The aerial parts of *Artemisia sieversiana* afforded, in addition to β-sitosterol, stigmasterol and daucosterol, two novel lignans as well as one known and three new guaianolides. The roots of *Inula racemosa* gave β-sitosterol, daucosterol and isoalantolactone. The structures were determined by a combination of spectral methods (IR, EIMS, ^{1}H and ^{13}C NMR, DEPT, COSY, NOESY and HETCOR). All isolates were subjected to antifungal tests. Isoalantolactone, a major sesquiterpene lactone of *I. racemosa*, was found to be active against the human pathogenic fungi, *Aspergillus flavus*, *A. niger*, *Geotrichum candidum*, *Candida tropicalis* and *C. albicans* at concentrations of 50, 50, 25, 25 and 25 μg/ml, respectively. The taxonomic significance of the characterized constituents is discussed briefly.

INTRODUCTION

Artemisia sieversiana Ehrhart ex Willd and *Inula racemosa* Hook. f. are traditional Chinese drugs which have been used as antimicrobial agents for nearly a thousand years [1]. So far, the constituents of these plants collected in China are still not clear although the species growing outside China have been shown to contain sesquiterpene lactones, some of them being biologically active [2–6]. In continuation of our search for structurally novel and/or antimicriobial natural products from traditional Chinese medicines [7–9], we have reinvestigated the two title species collected in the northwestern part of China where the geographic and climatic conditions are different from those in other parts of the world. The results are discussed in this paper.

RESULTS AND DISCUSSION

Repeated fractionation of the extract of the aerial parts of *A. sieversiana* gave two new lignans (**1** and **2**) as well as one known (**3**) and three new (**4–6**) guaianolides, together with β-sitosterol, stigmasterol and daucosterol.

The ^{1}H NMR spectrum of compound **1** indicated that it was a methoxy derivative of sesamin (see Experimental) [10]. This hypothesis was subsequently confirmed by the ^{13}C NMR spectrum of compound **1** which exhibited 21 carbon resonances consisting of one methoxy, twelve (five methine and seven quaternary) aromatic, four (two ketal and two oxygenated) methylene, and four methine (two oxygen-bearing) carbon signals. Scrutiny of the ^{1}H NMR spectra of compound **1**, 2-methoxysesamin and 2,2′-dimethoxysesamin showed that the doublets of H-7 and H-7′ of **1** (at δ 4.71 and 4.70) appeared at upper field compared to the H-7 signal (at δ 5.02) of 2-methoxysesamin and the two-proton doublet (at δ 4.99) arising from H-7 and H-7′ of 2,2′-dimethoxysesamin [10]. This might be due to steric hindrance between the tetrahydrofuran ring and the methoxy group at C-2 and/or C-6 affecting the orientation of the benzene ring and exerting thereby a more paramagnetic effect on H-7. Therefore, lignan **1** was 5-methoxysesamin.

The EIMS, ^{1}H and ^{13}C NMR spectra of compound **2** showed that it was also a lignan with molecular formula of $C_{22}H_{26}O_8$. A pair of double doublets at δ 3.86 and 3.30, ascribable to a hydroxymethyl, revealed the presence of a *seco*-derivative [11]. This proposal was reinforced by the COSY spectrum of **2** which allowed assignment of all proton signals. The doublet of H-7′ at δ 4.84 showed long range couplings with the two-proton singlet of H-2′ and H-6′ at δ 6.57. In the NOESY spectrum of **2**, this singlet due to H-2′ and H-6′ showed a correlation with the six-proton singlet of two methoxy groups at δ 3.87. These spectral

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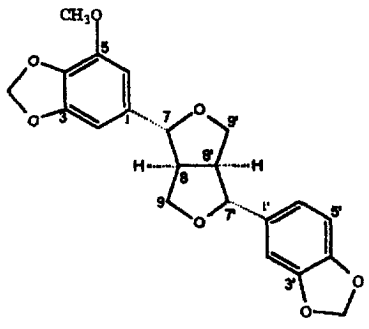

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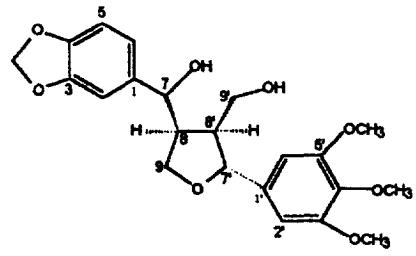

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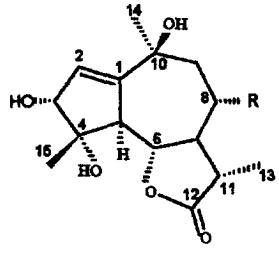

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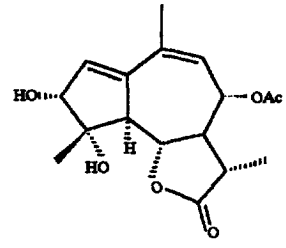

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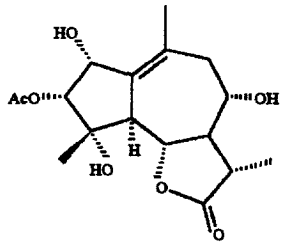

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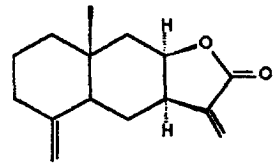

7 (isoalantolactone)

features, along with another methoxy singlet at δ 3.84, substantiated the presence of 3′,4′,5′-trimethoxy groups. Furthermore, a doublet (J = 7.0 Hz) of H-7 at δ 4.41, showing long range couplings with H-2 and H-6, indicated the presence of a 7-hydroxy group. A two-proton singlet at δ 5.94, together with splitting patterns of H-2, H-5 and H-6, required a 3,4-dioxymethylene function. The formulated stereochemistry of compound **2** was assigned by its NOESY spectrum in which a correlation of H-8 with H-8′ was discerned (but none between H-8′ and H-7′). However, the configuration of C-7 was not determined. We have named compound **2** sieversol.

The spectral data of compound **4** were very close to those of **3**, indicating the presence of a guaianolide. The ^{13}C NMR and COSY spectra of **4** reinforced this proposal. All proton and carbon signals were assigned by two-dimensional NMR experiments (COSY, NOESY and HETCOR). The olefinic proton signal of H-2 at δ 5.82, which coupled to the H-3 signal at δ 3.79, showed an allylic coupling with the H-5 doublet at δ 2.79 requiring a 1,2-double bond and a 3-hydroxy group. Furthermore, a pair of three-proton singlets at δ 1.33 and 1.18 indicated 4,10-dihydroxy functions. The assignment of the given stereochemistry was accomplished by the NOE correlations of H-2 with H-14 and H-3, of H-15 with H-3 and H-6, and of H-7 with H-13 in the NOESY spectrum of **4**. Therefore, lactone **4** was 3α,4α,10β-trihydroxy-11βH-guai-1-en-12,6α-olide.

In the EIMS spectrum of compound **5**, an intense protonated molecular ion was observed at m/z 323 with the parent ion appearing at m/z 322. This mass spectral evidence, combined with the ^{13}C NMR data and DEPT experiments, disclosed that the molecular formula of **5** was $C_{17}H_{22}O_6$. The ^{1}H and ^{13}C NMR spectra of **5** were similar to those of **3** and revealed that **5** was also a guaianolide. All proton and carbon signals were assigned by COSY, NOESY and HETCOR spectra and supported the above hypothesis. A pair of broadened olefinic proton singlets at δ 6.08 (H-2) and 5.42 (H-9), together with four olefinic

carbon signal indicated the presence of a 1,9-diene system. This deduction was further rationalized by the downfield-shift of H-14 and the upfield-shift of C-14 when compared to those of **3** (Experimental). Other substituents and the configurations were ascertained as for compounds **3** and **4**. Thus, the structure of **5** was determined as 3α,4α-dihydroxy-8α-acetoxy-11βH-guai-1,9-dien-12,6α-olide.

The EIMS, ^{1}H and ^{13}C NMR spectral data of compound **6** showed that it was a guaianolide possessing a molecular formula $C_{17}H_{24}O_7$, identical to that of **3**. All of the ^{1}H and ^{13}C NMR data were assigned by COSY, HETCOR and NOESY spectra. The three-proton singlet of H-14 showed homoallylic couplings with the doublet of H-2 at δ 4.18 and the H-5 doublet indicating the presence of 1,10-double bond and 2-hydroxy group. The H-2 signal coupled further to the doublet of H-3 at δ 4.85, shifted downfield by ca 1 ppm from those of **3**–**5**. This observation, along with an acetate singlet at δ 2.04, demonstrated the acetoxy group on C-3. Moreover, the three-proton singlet of H-15 at δ 1.32 and the splitting pattern of the H-5 signal indicated the presence of a 4-hydroxy group. The 8α-hydroxy function was verified by the H-8 signal at δ 4.71 (*ddd*, J = 10.6, 10.6, 2.2 Hz) which was moved upfield by ca 0.7 ppm from those of **3** and **5**. This was reinforced by the correlation between H-8 and H-6 in the NOESY spectrum of **6**. The stereochemistry at the other chiral centres was established by the observed NOE correlations of H-15 with H-2, H-3 and H-6, and of H-2 with H-14 and H-3. Therefore, lactone **6** was 2α,4α,8α-trihydroxy-3α-acetoxy-11βH-guai-1(10)-en-12,6α-olide.

Fractionation of the extract of the roots of *I. racemosa* afforded β-sitosterol, daucosterol and a large amount of isoalantolactone (**7**) which was identified by comparing its spectral data with those in the literature [12].

All constituents isolated were tested for their antifungal activities against human pathogenic fungi by established methods [8, 13]. Isoalantolactone inhibited the growth of *Aspergillus flavus*, *A. niger*, *Geotrichum candidum*, *Candida tropicalis* and *C. albicans* with MICs being 50, 50, 25, 25 and 25 μg/ml, respectively.

This phytochemical investigation to *A. sieversiana* shows its close relationship to *A. xerophytica* as 8α-oxygenated guaianolides, and lignans were also detected in this species [14, 15]. Furthermore, the roots of *I. racemosa* distributed in the northwest of China was found to be a rich source of isoalantolactone, a ringworm fungicide [5].

EXPERIMENTAL

General

^{1}H (500 MHz), ^{13}C (125 MHz) and 2D NMR: Bruker AMX-500 NMR spectrometer with TMS as int. standard; EIMS: HS-ZAB mass spectrometer. Other apparatus and chemicals used in this study were as described earlier [16].

Plant material

The aerial parts of *A. sieversiana* and roots of *I. racemosa* were collected in July 1992 in Gansu Province, China. The voucher specimens (GC9207 and GC9216, respectively) identified by Prof. G. L. Zhang were deposited in the Herbarium of the Department of Biology, Lanzhou University, Lanzhou 730000, China.

Extraction and isolation

The chopped air-dried plant material of *A. sieversiana* (2.5 kg) was extracted twice for 48 h at room temp. with MeOH–Et_2O–petrol (2:2:1). Evapn. of the solvent from the combined extracts *in vacuo* at 50° gave a tarry residue which was refluxed with MeOH until it was completely dissolved. The soln. was kept at −5° for 24 h and then filtered to remove the waxy ppt which had formed. Distillation of MeOH *in vacuo* from the filtrate afforded a black gum (65.5 g) which was subsequently subjected to CC on silica gel (1500 g) using petrol containing gradually increased amounts of Me_2CO followed by an Me_2CO–MeOH gradient (100:1 → 1:1). Eight CC frs (F-1: 0.7 l; F-2: 0.9 l; F-3: 0.85 l; F-4: 1.2 l; F-5: 1.4L; F-6: 1.0 l; F-7: 0.8 l; F-8: 0.5 l) were collected based on TLC monitoring (F-1: 6.0 g; F-2: 5.0 g; F-3: 5.2 g; F-4: 4.0 g; F-5: 5.5 g; F-6: 5.3 g; F-7: 4.9 g; F-8: 11 g). F-1 and F-8 contained nothing of interest. F-2 was sepd by silica gel (150 g) cc with a petrol–Me_2CO gradient (100:1 → 1:2) yielding mainly β-sitosterol (685 mg) and stigmasterol (34 mg). CC of F-3 with the petrol–EtOAc gradient (5:1 → 1:3) afforded F-3/1, F-3/2 and F-3/3. Repeated CC of these three frs with petrol–EtOAc (3:1) and gel filtration over Sephadex LH-20 with $CHCl_3$–MeOH (1:1) gave compounds **1** (31 mg) and **2** (44 mg). CC of F-4 with a petrol–EtOAc gradient (5:1 → 1:3) afforded **2** (12 mg) and two frs (F-4/1 and F-4/2). Repeated gel filtration of F-4/1 over Sephadex LH-20 with $CHCl_3$–MeOH (1:5) afforded **5** (13 mg) and a pigment mixture. F-5, was combined with F-4/2 and further sepd by CC utilizing a petrol–EtOAc gradient (4:1 → 1:7) to afford two frs (F-5/1 and F-5/2). Gel filtration of F-5/1 over Sephadex LH-20 with $CHCl_3$–MeOH (1:5) gave compounds **5** (6 mg) and **2** (14 mg). Gel filtration of F-5/2 over Sephadex LH-20 with $CHCl_3$–MeOH (1:1) yielded mainly compound **4** (12 mg). F-6 was fractionated by CC with $CHCl_3$–MeOH gradient (50:1 → 1:2) to yield F-6/1, F-6/2 and F-6/3. Repeated gel filtration of F-6/1 over Sephadex LH-20 with MeOH afforded **6** (17 mg). Gel filtration of F-6/2 over Sephadex LH-20 with MeOH afforded **4** (6 mg). F-7 was combined with F-6/3 and then subjected to CC using a $CHCl_3$–MeOH gradient to give two frs F-7/1 and F-7/2. Repeated filtration on Sephadex LH-20 of F-7/1 afforded **6** (12 mg). F-7/2

was subjected to repeated gel filtration with $CHCl_3$–MeOH (1:1) to yield daucosterol (viz, β-sitosterol-β-D-glucopyranoside, 45 mg).

The air-dried roots (1.2 kg) of *I. racemosa* were extracted and purified in a very similar manner. Thus, the extract (53.5 g) was sepd by repeated CC on silica gel and gel filtration over Sephadex LH-20 (150 g) to afford finally lactone **7** (24.5 g), β-sitosterol (27 mg) and daucosterol (75 mg).

Bioassays

In vitro antifungal activity against five human pathogenic fungi (*Aspergillus flavus*, *A. niger*, *Geotrichum candidum*, *Candida tropicalis* and *C. albicans*) was measured by established methods [8, 13].

*5-Methoxysesamin (**1**).* Gum; IR ν_{max}^{KBr} cm^{-1}: 1655, 1630, 1525, 1510; EIMS *m/z* (rel. int.): 384 $[M]^+$ (100), 353 $[M-OMe]^+$ (5), 191 (21); ^1H NMR ($CDCl_3$) δ: 6.84 (1H, *br d*, *J* = 2.0 Hz, H-2′), 6.80 (1H, *br dd*, *J* = 8.0, 2.0 Hz, H-6′), 6.78 (1H, *d*, *J* = 8.0 Hz, H-5′), 6.54 and 6.52 (1H each, *br d*, *J* = 2.0 Hz, H-2 and H-6), 5.97 and 5.95 (2H each, *s*, O-CH_2-O × 2), 4.71 and 4.70 (1H each, *br d*, *J* = 7.3 Hz, H-7 and H-7′), 4.24 (2H, *m*, H-9a and H-9′a), 3.91 (3H, *s*, OMe), 3.88 (2H, *m*, H-9b and H-9′b), 3.05 (2H, *m*, H-8 and H-8′); ^{13}C NMR ($CDCl_3$, multiplicities by DEPT experiments) δ: 135.0 (*s*, C-1), 105.4 (*d*, C-2), 134.7 (*s*, C-3), 143.7 (*s*, C-4), 149.1 (*s*, C-5), 100.1 (*d*, C-6), 85.9 (*d*, C-7), 54.4 (*d*, C-8), 71.8 (*t*, C-9), 135.8 (*s*, C-1′), 106.5 (*d*, C-2′), 147.2 (*s*, C-3′), 148.0 (*s*, C-4′), 108.2 (*d*, C-5′), 119.4 (*d*, C-6′), 85.8 (*d*, C-7′), 54.3 (*d*, C-8′), 71.8 (*t*, C-9′), 56.7 (*q*, OCH_3), 101.6 (*t*, OCH_2O), 101.1 (*t*, OCH_2O).

*Sieversol (**2**).* Gum; IR ν_{max}^{KBr} cm^{-1}: 3600–3380, 1605; EIMS *m/z* (rel. int.): 401.0 $[M-OH]^+$ (29), 400.0 $[M-H_2O]^+$ (100), 207.0 (27), 197.0 (45), 169.0 (46), 148.9 (60), 135.0 (48); ^1H NMR ($CDCl_3$) δ: 6.87 (1H, *br d*, *J* = 2 Hz, H-2), 6.82 (1H, *br dd*, *J* = 8.0, 2.0 Hz, H-6), 6.77 (1H, *d*, *J* = 8 Hz, H-5), 6.57 (2H, *br s*, H-2′ and H-6′), 5.94 (2H, *s*, O-CH_2-O), 4.84 (1H, *br d*, *J* = 5.6 Hz, H-7′), 4.41 (1H, *br d*, *J* = 7.0 Hz, H-7), 4.11 (1H, *dd*, *J* = 8.2, 2.3 Hz, H-9a), 3.86 (1H, *dd*, *J* = 11.0, 3.5 Hz, H-9′a), 3.87 (6H, *s*, OMe × 2), 3.84 (3H, *s*, OMe), 3.81 (1H, *dd*, *J* = 8.2, 7.0 Hz, H-9b), 3.30 (1H, *dd*, *J* = 11.0, 7.0 Hz, H-9′b), 3.34 (1H, *m*, H-8′), 2.87 (1H, *m*, H-8); ^{13}C NMR ($CDCl_3$, multiplicities by DEPT experiments) δ: 135.0 (*s*, C-1), 106.5 (*d*, C-2), 147.2 (*s*, C-3), 148.0 (*s*, C-4), 108.2 (*d*, C-5), 119.6 (*d*, C-6), 82.1 (*d*, C-7), 50.1 (*d*, C-8), 71.0 (*t*, C-9), 134.1 (*s*, C-1′), 102.4 (*d*, C-2′), 153.2 (*s*, C-3′), 136.8 (*s*, C-4′), 153.2 (*s*, C-5′), 102.4 (*d*, C-6′), 87.6 (*d*, C-7′), 54.5 (*d*, C-8′), 69.7 (*t*, C-9′), 60.9 (*q*, OCH_3), 56.1 (*q*, OCH_3), 56.1 (*q*, OCH_3), 101.1 (*t*, OCH_2O).

*3α,4α,10β-Trihydroxy-8α-acetoxy-11βH-guai-1-en-12,6α-olide (**3**).* ^1H NMR (DMSO-d_6) δ: 5.84 (1H, *br s*, H-2), 5.23 (1H, *ddd*, *J* = 10.5, 7.9, 3.5 Hz, H-8), 4.37 (1H, *dd*, *J* = 10.5, 10.2 Hz, H-6), 3.73 (1H, *br s*, H-3), 2.91 (1H, *br d*, *J* = 10.5 Hz, H-5), 2.59 (1H, *dq*, *J* = 12.0, 7.2 Hz, H-11), 2.19 (1H, *ddd*, *J* = 12.0, 10.5, 10.2 Hz, H-7), 2.02 (3H, *s*, OAc), 1.92 (H, *dd*, *J* = 14.4, 3.5 Hz, H-9β), 1.75 (H, *dd*, *J* = 14.4, 7.9 Hz, H-9α), 1.36 (3H, *s*, H-14), 1.17 (3H, *s*, H-15), 1.11 (3H, *d*, *J* = 7.2 Hz, H-13); ^{13}C NMR (DMSO-d_6, multiplicities by DEPT experiments) δ: 151.1 (*s*, C-1), 126.3 (*d*, C-2), 78.4 (*d*, C-3), 79.1 (*s*, C-4), 57.3 (*d*, C-5), 76.5 (*d*, C-6), 54.8 (*d*, C-7), 71.7 (*d*, C-8), 45.2 (*t*, C-9), 68.6 (*s*, C-10), 40.5 (*d*, C-11), 178.4 (*s*, C-12), 14.8 (*q*, C-13), 29.5 (*q*, C-14), 21.4 (*q*, C-15), 169.6 (*s*, OAc), 21.1 (*q*, OAc).

*3α,4α,10β-Trihydroxy-11βH-guai-1-en-12,6α-olide (**4**).* Gum; IR ν_{max}^{KBr} cm^{-1}: 3400–3200, 1760, 1735; EIMS *m/z* (rel. int.): 264 $[M-H_2O]^+$ (18), 246 $[264-H_2O]^+$ (33), 191 (15), 175 (20), 84 (86), 66 (100); ^1H NMR (DMSO-d_6) δ: 5.82 (1H, *br s*, H-2), 4.19 (1H, *dd*, *J* = 10.5, 10.4 Hz, H-6), 3.79 (1H, *br s*, H-3), 2.79 (1H, *br d*, *J* = 10.5 Hz, H-5), 2.34 (1H, *dq*, *J* = 12.2, 7.3 Hz, H-11), 1.68 (1H, *m*, H-7), 1.76 (2H, *m*, H-8 and H-9), 1.58 (2H, *m*, H-8′ and H-9′), 1.33 (3H, *s*, H-14), 1.18 (3H, *s*, H-15), 1.06 (3H, *d*, *J* = 7.3 Hz, H-13); ^{13}C NMR (DMSO-d_6, multiplicities by DEPT experiments) δ: 151.5 (*s*, C-1), 126.7 (*d*, C-2), 78.8 (*d*, C-3), 79.2 (*s*, C-4), 58.0 (*d*, C-5), 80.7 (*d*, C-6), 52.4 (*d*, C-7), 22.9 (*t*, C-8), 38.7 (*t*, C-9), 69.6 (*s*, C-10), 41.0 (*d*, C-11), 178.9 (*s*, C-12), 12.5 (*q*, C-13), 30.0 (*q*, C-14), 21.6 (*q*, C-15).

*3α,4α-Dihydroxy-8α-acetyloxy-11βH-guai-1,9-dien-12,6α-olide (**5**).* Gum; IR ν_{max}^{KBr} cm^{-1}: 3400–3200, 1760, 1735; EIMS *m/z* (rel. int.): 323 $[M+H]^+$ (9), 322 $[M]^+$ (4), 304 $[M-H_2O]^+$ (4), 262 $[M-HOAc]^+$ (61), 219 (84), 189 (54), 173 (39), 147 (100), 84 (30), 66 (29); ^1H NMR (DMSO-d_6) δ: 6.08 (1H, *br s*, H-2), 5.42 (1H, *br s*, H-9), 5.40 (1H, *br d*, *J* = 11.0 Hz, H-8), 4.32 (1H, *dd*, *J* = 10.5, 10.2 Hz, H-6), 3.80 (1H, *br s*, H-3), 2.91 (1H, *br d*, *J* = 10.5 Hz, H-5), 2.64 (1H, *dq*, *J* = 11.0, 7.0 Hz, H-11), 2.28 (1H, *ddd*, *J* = 10.2, 11.0, 11.0 Hz, H-7), 2.07 (3H, *s*, OAc), 1.90 (3H, *s*, H-14), 1.17 (3H, *d*, *J* = 7.0 Hz, H-13), 1.15 (3H, *s*, H-15); ^{13}C NMR (DMSO-d_6, multiplicities by DEPT experiments) δ: 140.7 (*s*, C-1), 129.3 (*d*, C-2), 77.9 (*d*, C-3), 78.2 (*s*, C-4), 57.8 (*d*, C-5), 76.9 (*d*, C-6), 52.4 (*d*, C-7), 73.4 (*d*, C-8), 133.3 (*d*, C-9), 130.2 (*s*, C-10), 39.9 (*d*, C-11), 178.3 (*s*, C-12), 15.3 (*q*, C-13), 24.6 (*q*, C-14), 21.9 (*q*, C-15), 168.9 (*s*, OAc), 21.0 (*q*, OAc).

*2α,4α,8α-Trihydroxy-3α-acetoxy-11βH-guai-1(10)-en-12,6α-olide (**6**).* Gum; IR ν_{max}^{KBr} cm^{-1}: 3400–3200, 1760, 1735; EIMS *m/z* (rel. int.): 322 $[M-H_2O]^+$ (1), 294 $[322-H_2O]^+$ (2), 262 $[322-HOAc]^+$ (12), 219 (16), 191 (53), 161 (44), 84 (78), 66 (100); ^1H NMR (DMSO-d_6) δ: 4.85 (1H, *d*, *J* = 3.7 Hz, H-3), 4.71 (1H, *ddd*, *J* = 10.6, 10.6, 2.2 Hz, H-8), 4.18 (1H, *br d*, *J* = 3.7 Hz, H-2), 4.03 (1H, *dd*, *J* = 10.5, 10.5 Hz, H-6), 2.65 (1H, *br d*, *J* = 10.5 Hz, H-5), 2.63 (1H, *dq*, *J* = 11.0, 7.0 Hz, H-11), 2.40 (1H, *dd*, *J* = 14.5, 10.6 Hz, H-9α), 2.23 (1H, *ddd*, *J* = 10.6, 10.5, 11.0 Hz, H-7), 2.15 (1H, *dd*, *J* = 14.5, 2.2 Hz, H-9β), 2.04 (3H, *s*, OAc), 1.77 (3H, *s*, H-14), 1.32 (3H, *s*, H-15), 1.18 (3H, *d*, *J* = 7.0 Hz, H-13); ^{13}C NMR (DMSO-d_6, multiplicities by DEPT experiments) δ: 137.8 (*s*, C-1), 75.9 (*d*, C-2), 82.4 (*d*, C-3), 79.9 (*s*, C-4), 56.7 (*d*, C-5), 78.7

(*d*, C-6), 53.6 (*d*, C-7), 71.3 (*d*, C-8), 41.7 (*t*, C-9), 131.3 (*s*, C-10), 39.8 (*d*, C-11), 178.1 (*s*, C-12), 15.2 (*q*, C-13), 23.2 (*q*, C-14), 21.8 (*q*, C-15), 169.6 (*s*, OAc), 21.0 (*q*, OAc).

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