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GUAIANE SESQUITERPENES FROM *DECACHAETA SCABRELLA*

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Abstract—From the dichloromethane extract of leaves of *Decachaeta scabrella*, in addition to three known guaianolides and two flavonoids, a new guaianolide, 11α,13-dihydroxerantholide, and two new guaiane acids, pechueloic acid and 11,13-dihydropechueloic acid, were characterized. The structures of the new compounds were determined by spectral and chemical methods.

INTRODUCTION

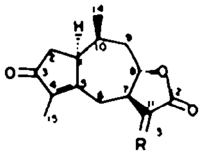
As part of our interest in the genus *Decachaeta* (tribe Eupatorieae) [1, 2], here we report the isolation and structural elucidation of guaiane sesquiterpenes from the leaves of *D. scabrella* (B. L. Robinson) King and Robinson.

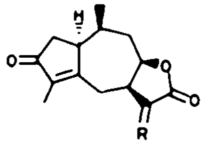
Decachaeta scabrella, *D. thieleana* and *D. ovatifolia* represent the three chemically investigated members of subgenus *Polydenia* of *Decachaeta* [3]. *Decachaeta thieleana* [4, 5], like *D. scabrella*, yielded guaiane sesquiterpenes while *D. ovatifolia* mainly afforded unusual 7-α-hydroxysesquiterpene lactones [1].

RESULTS AND DISCUSSION

The known guaianolides from *D. scabrella* were identified as xerantholide (**1**) [6, 7], 8-epixerantholide (= achalensolide) (**4**) [5, 8] and 11β-13-dihydro-8-epixerantholide (**5**) [8] by spectral data and direct comparison of their physical properties with those reported previously for these compounds.

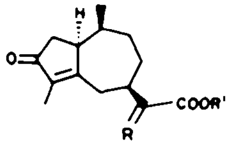
The EIMS of the new lactone **2** exhibited a molecular ion at m/z 248 in accord with the molecular formula $C_{15}H_{20}O_3$. The IR absorptions of **2** indicated the presence of a γ-lactone (1765 cm^{-1}) and an α,β-unsaturated ketone (1690 and 1632 cm^{-1}). The ^1H NMR and ^{13}C NMR spectra (Table 1) of **2**, together with the above spectral data, suggested that **2** was the dihydrolactone derivative of either **1** or **4**. Direct comparison of the spectral data of **2** with those for known derivatives of **1** and **4** established that **2** was not 11β,13-dihydroxerantholide [7] or a dihydro derivative of **4** [8]. Thus, **2** had to be 11α,13-dihydroxerantholide, a compound prepared previously by catalytic hydrogenation of **1** [9] but for which no spectral data had been reported. Xerantholide was hydrogenated over Pd/C to yield a mixture of **2** and **3** (ratio *ca* 15:85). The natural product **2** was found to be identical in all respects with the synthetic 11α,13-dihydroxerantholide.

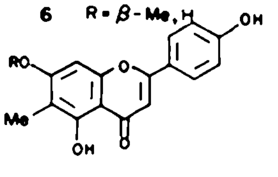




1 R = CH₂
2 R = β-Me, H
3 R = α-Me, H

4 R = CH₂
5 R = α-Me, H
6 R = β-Me, H





7 R = CH₂, R' H
8 R = CH₂, R' Me
9 R = Me, H, R' H

10 R = H
11 R = Me

Table 1. ^{13}C NMR of compounds **1**, **2**, **3**, **7** and **9** (90.8 MHz, $CDCl_3$, TMS as internal standard)

C	1	2	3	7	9
1	44.2 *d*	45.2 *d*	45.0 *d*	46.2 *d*	45.5 *d*
2	40.3 *t*	40.7 *t*	40.3 *t*	41.4 *t*	40.7 *t*
3	207.0 *s*	206.9 *s*	207.1 *s*	209.6 *s*	208.8 *s*
4	139.8 *s*	139.5 *s*	139.2 *s*	137.9 *s*	137.2 *s*
5	169.7 *s*	170.2 *s*	171.0 *s*	171.2 *s*	175.9 *s*
6	30.0 *t*	27.9 *t*	31.1 *t*	36.6 *t*	29.4 *t*
7	45.1 *d*	42.6 *d*	47.9 *d*	37.8 *d*	38.4 *d*
8	81.3 *d*	81.0 *d*	81.2 *d*	31.7 *t*	27.6 *t*
9	41.5 *t*	41.1 *t*	41.2 *t*	38.5 *t*	38.4 *t*
10	33.0 *d*	32.8 *d*	32.9 *d*	35.3 *d*	36.0 *d*
11	139.2 *s*	39.6 *d*	41.9 *d*	145.9 *s*	45.0 *d*
12	169.8 *s*	178.8 *s*	178.1 *s*	176.2 *s*	179.0 *s*
13	120.0 *t*	10.8 *q*	12.7 *q*	125.1 *t*	11.5 *q*
14	12.7 *q*	12.7 *q*	12.7 *q*	12.2 *q*	12.1 *q*
15	8.1 *q*	8.1 *q*	8.1 *q*	7.9 *q*	7.3 *q*

The IR spectrum of **7** indicated the presence of an α,β-unsaturated carboxyl group (3300, 2560 and 1700 cm^{-1}), as well as the presence of a cyclopentenone ring (1685 and 1620 cm^{-1}), similar to those found in compounds **1**–**6**. The EIMS of **7** exhibited a molecular ion at m/z 248 ($C_{15}H_{20}O_3$) while the ^{13}C NMR and other spectral data indicated a similar structure to those of **1**–**6** except for **7** having an α,β-unsaturated carboxylic acid instead of the lactone ring. The ^{1}H NMR data of **7** were very similar to those of methyl pechueloate (**8**) [7]; and indeed methylation of **7** gave **8**.

The ^{1}H NMR of **9**, except for the presence of a second secondary methyl doublet (δ1.21) replacing signals for H-13a and H-13b as in **7**, was similar to the one recorded for **7**. The EIMS of **9** showed a molecular ion at m/z 250 ($C_{15}H_{22}O_3$). These spectral data indicated that **9** was 11,13-dihydropechueloic acid. This assignment was confirmed by the catalytic hydrogenation (Pd/C) of both pechueloic acid (**7**) and 8-epixerantholide (**4**) to **9**. The hydrogenolytic cleavage of the lactone ring of **4** being similar to those of *O*-acetylisophotosantonic lactone [10].

EXPERIMENTAL

General. ^{1}H NMR and ^{13}C NMR spectra in $CDCl_3$ with TMS as an internal standard at 200 MHz and 22.6 MHz, respectively.

Plant material. The aerial parts of *D. scabrella* were collected on Oct 23, 1983 from 9.4 miles south of Autlan de Navarro on Mex 80, the road to Barra de Navidad, Jalisco, Mexico by T. J. Ayers and R. Scott. Voucher specimen on deposit in the University of Texas (T. J. Ayers *et al.* No. 325).

Extraction and isolation of the compounds. Whole leaves (880 g) were extracted with CH_2Cl_2 for 15 min. The filtered slurry was concentrated (*ca* 43 g) and mixed with 1 l. Me_2CO, and allowed to stand in the refrigerator overnight. The precipitated hydrocarbons were removed by filtration over a celite pad and the filtrate was concentrated to give the final extract (38 g). This material was chromatographed as previously described [1] to yield **1** (9.4 g), **2** (11 mg), **4** (80 mg), **5** (28 mg), **7** (120 mg), **9** (10 mg), **10** (14 mg) and **11** (33 mg).

11α,13-*Dihydroxerantholide* (**2**). Gum; IR ν_{max}^{KBr} cm^{-1}: 2925, 1765, 1690, 1632, 1460, 1380, 1330, 1208, 985; ^{1}H NMR: δ4.36 (1H, *ddd*, J = 3.8, 9.8 and 11.8 Hz, H-8), 3.18 (1H, *m*, H-1), 2.84 (1H, *d* (*br*), J = 19.2 Hz, H-6α), 2.81 (1H, *dq*, J = 7.3 and 7.7 Hz, H-11), 2.65 (1H, *ddd*, J = 1.1, 6.6 and 19.3 Hz, H-2β), 2.64 (1H, *m*, H-7), 2.49 (1H, *dd* (*br*), J = 10 and 19.2 Hz, H-6β), 2.43 (1H, *dt*, J = 3.9 and 13 Hz, H-9β), 2.28 (1H, *m*, H-10), 2.11 (1H, *d* (*br*), J = 19.3 Hz, H-2α), 1.84 (1H, *dt*, J = 4, 11.8 and 13 Hz, H-9α), 1.70 (3H, *d*, J = 1.7 Hz, H-15), 1.28 (3H, *d*, J = 7.7 Hz, H-13), and 0.73 (3H, *d*, J = 7.3 Hz, H-14); EIMS (probe) m/z (rel. int.): 248 $[M]^+$ (100), 233 $[M - Me]^+$ (4.9), 220 $[M - CO]^+$ (7.5), 191 (19.8), 161 (42.9), 133 (35.6) and 91 (69.4).

Catalytic hydrogenation of **1**. A soln **1** (200 mg) in EtOAc (15 ml) was hydrogenated over 5% Pd/C (80 mg) at ambient temp. After 4 hr, the catalyst was removed by filtration, the solvent evaporated *in vacuo* and the residual mixture purified by prep. TLC [silica gel (1.5 mm), EtOAc-cyclohexane (4:6), double development] to yield **3** (160 mg) and **2** (29 mg).

Pechueloic acid (**7**). Gum; IR ν_{max}^{KBr} cm^{-1}: 3300 (*br*), 2910, 2560 (*sh*), 1700 (*br*), 1690, 1620, 1440, 1375, 1262, 955, 825, 728 and 698; ^{1}H NMR; δ6.38 (1H, *s*, H-13a), 5.75 (1H, *s*, H-13b), 3.21 (1H, *m*, H-1), 2.91 (1H, *t* (*br*), J = 12 Hz, H-7), 2.88 (1H, *d* (*br*), J = 19 Hz, H-6α), 2.63 (1H, *ddd*, J = 1, 6.5 and 19.3 Hz, H-2β), 2.48 (1H, *dd* (*br*), J = 12 and 19 Hz, H-6β), 2.16 (1H, *m*, H-10), 2.08 (1H, *d* (*br*), J = 19.3 Hz H-2α), 1.73 (2H, *m*, H-9α and H-9β), 1.67 (3H, *d*, J = 1.2 Hz, H-15) and 0.67 (3H, *d*, J = 7.1 Hz, H-14); EIMS (probe) m/z (rel. int.): 248 $[M]^+$ (7.6), 230 $[M - H_2O]^+$ (4.2), 220 $[M - CO]^+$ (2.5), 202 $[M - COOH]^+$ (4.2), 177 $[M - C_3H_3O_2]^+$ (6.9), 149 (6.9) and 84 (100).

Methylation of **7**. A soln of **7** (15 mg) in Et_2O (5 ml) was reacted with excess CH_2N_2 for 5 hr. After the usual work-up, 15 mg of **8** were obtained.

11,13-*Dihydropechueloic acid* (**9**). Gum; IR ν_{max}^{KBr} cm^{-1}: 3200 (*br*), 2920, 2600 (*sh*), 1726, 1695, 1620, 1455, 1382, 1180 and 738; ^{1}H NMR; δ3.13 (1H, *m*, H-1), 2.63 (1H, *d* (*br*), J = 19 Hz, H-6α), 2.62 (1H, *ddd*, J = 1, 6.4 and 19.3 Hz, H-2β), 2.56 (1H, *m*, H-7), 2.47 (1H, *dd* (*br*), J = 12 and 19 Hz, H-6β), 2.14 (1H, *m*, H-10), 2.07 (1H, *d* (*br*), J = 19.3 Hz, H-2α), 1.76 (2H, *m*, H-9α and H-9β), 1.67 (3H, *s* (*br*), H-15), 1.21 (3H, *d*, J = 7 Hz, H-13) and 0.62 (3H, *d*, J = 7.1 Hz, H-14); EIMS (probe) m/z (rel. int.): 250 $[M]^+$ (17), 232 $[M - H_2O]^+$ (4.2), 204 $[M - COOH]^+$ (6.7), 177 $[M - C_3H_5O_2]^+$ (49.5), 147 (30), 133 (36.6), 121 (42.9), 105 (43.9), 91 (79.5) and 55 (100).

Catalytic hydrogenation of **7**. A soln of **7** (20 mg) in EtOAc was hydrogenated over 5% Pd/C to yield **9** (19 mg).

Hydrogenation of **4** (60 mg) yielded a mixture from which prep. TLC afforded **6** (9 mg) and **9** (7 mg).

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