

CLERODANE DITERPENOIDS AND ACETYLENIC LACTONES FROM *BACCHARIS PANICULATA*

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ABSTRACT.—Two new neoclerodanes diterpenoids paniculadiol [**1**] and paniculadiol diacetate [**2**] were isolated from *Baccharis paniculata*, together with two acetylenic lactones and other known compounds. Their structures were elucidated by chemical and spectroscopic means.

In a continuation of our phytochemical study on the American genus *Baccharis* (Asteraceae) (1), we have examined *Baccharis paniculata* DC. var. *floribunda* from northern Chile. In addition to known compounds, two new neoclerodanes (diterpenoids **1** and **2**) and two acetylenic lactones (**3** and **4**) were isolated.

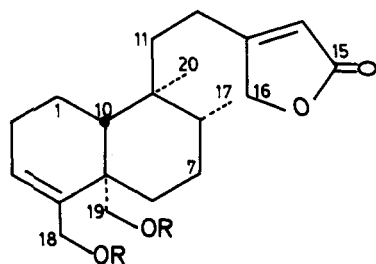
The ^1H -nmr spectrum of **1** showed signals characteristic for a tricyclic clerodane skeleton: a tertiary and a secondary methyl group, two olefinic protons, one of them (δ 5.70) indicative of a β -substituted- γ -butenolide (1730 cm^{-1}), together with a pair of AB systems at δ 3.68–4.05 and δ 3.48–3.85 corresponding to two hydroxymethylene groups at C-18 and C-19, respectively (2–4). The structure **1** was fully corroborated by the ^{13}C -nmr spectrum, which also defined the relative configuration of the C-17 and C-20 methyl group as well as the *trans*-AB junction by analogy with the data on a number of closely related clerodane diterpenes (3, 5, 6).

The ^1H -nmr spectrum of the second clerodane diterpenoid **2** clearly showed

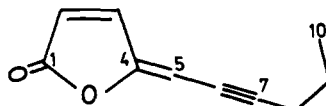
that it corresponded to the diacetylated derivative of **1**, which was confirmed by examining the acetylation products of **1**.

The absolute configuration of **1**, for which we suggest the trivial name paniculadiol, was not established, but it very probably corresponds to that shown in keeping with its negative molecular rotation values as also shown by related neoclerodanes (7) of well established absolute configuration isolated so far from *Baccharis* (5, 8, 9).

The structures of the acetylenic lactones **3** and **4** were established with spectroscopic data and comparison with published values of similar derivatives (10, 11); the (*Z*) and (*E*) isomers are readily distinguished by the absorption due to H-5, which is always at 0.35–0.45 ppm higher field in the (*Z*)-isomer [**3**] than in the (*E*)-isomer [**4**] (11, and references cited therein). The ^{13}C -nmr spectra of these lactones had not been reported previously. This lactone (of unspecified configuration) has been reported in many *Aster*, *Conyza*, and *Boltonia* species (8), but this is the first report of its occurrence in *Baccharis*.



1 R=H
2 R=Ac



3 (*Z*)-isomer
4 (*E*)-isomer

Other compounds isolated from *B. paniculata* in this study included lachnophyllum ester (a likely precursor of lactone **3**), oleanolic acid, and the flavonoid axillarine, all of them identified by direct comparison with authentic samples.

EXPERIMENTAL

PLANT MATERIAL.—*B. paniculata* var. *floribunda* was collected in La Serena (IV Region) in October 1985, and was identified by Rodomiro Osorio (Universidad de La Serena). Voucher specimens are kept at the herbarium of Prof. Osorio.

EXTRACTION AND ISOLATION.—The aerial parts of *B. paniculata* (4.2 kg) were percolated at room temperature with MeOH. The crude extract (380 g) was first partitioned between CHCl_3 and MeOH-H₂O (1:9), then the CHCl_3 solubles were partitioned between petroleum ether and MeOH-H₂O (9:1) to give aqueous MeOH solubles (20 g). This extract was first fractionated by flash cc on Si gel eluted with mixtures of increasing polarity of petroleum ether and EtOAc. Repeated cc on Si gel of suitable fractions afforded pure compounds.

Paniculadiol [1].—Compound **1** (880 mg), colorless oil: $[\alpha]_{589}^{25} -1.72^\circ$, $[\alpha]_{578} -1.78^\circ$, $[\alpha]_{546} -20.7^\circ$, $[\alpha]_{436} -41.4^\circ$, $[\alpha]_{36} -102.3^\circ$ ($c = 0.29$, CHCl_3); ir ν max (CHCl_3) 3350, 3500–3100, 1730, 1230 cm^{-1} ; ms (70 eV) m/z (rel. int.) $[\text{M} - \text{CH}_2\text{OH}]^+ 303.1962$ (1) (calcd for $\text{C}_{19}\text{H}_{27}\text{O}_3$, 303.1942), $[303 - \text{H}_2\text{O}]^+ 285$ (7), $[285 - \text{side chain} + \text{H}]^+ 173$ (37), $[\text{C}_8\text{H}_9]^+ 105.0719$ (100) (calcd for C_8H_9 , 105.0709); ^1H nmr (200 MHz, CDCl_3) δ 0.73 (s, 3H, H-20), 0.76 (d, 3H, $J = 7.9$, H-17), 3.48 (d, 1H, $J = 11.6$, H-19), 3.60 (d, 1H, $J = 11.5$, H-18), 3.85 (d, 1H, $J = 10.6$, H-19'), 4.06 (d, 1H, $J = 11.5$, H-18'), 4.67 (d, 2H, $J = 1.6$, H-16), 5.62 (t, 1H, $J = 3.2$, H-3), 5.7 (bs, 1H, H-14); ^{13}C -nmr (50 MHz, CDCl_3) δ 174.4 (s, C-15), 171.3 (s, C-13), 144.9 (s, C-4), 128.7 (d, C-3), 114.9 (d, C-14), 73.2 (d, C-16), 64.6 (t, C-19), 63.9 (t, C-18), 46.3 (d, C-10), 42.9 (s, C-5), 38.8 (s, C-9), 36.5 (d, C-8), 35.4 (t, C-11), 31.0 (t, C-6), 26.9 (t, C-7), 26.7 (t, C-2), 22.3 (t, C-12), 18.7 (q, C-20), 17.3 (t, C-1), 15.8 (q, C-17).

Paniculadiol-18,19-diacetate [2].—Colorless oil (70 mg): ir ν max (film) 2950–2860, 1730, 1230; ^1H nmr (60 MHz, CDCl_3) δ 0.73 (s, 3H, H-20), 0.76 (d, 3H, $J = 7$, H-17), 2.02 (s, 6H, MeCO), 3.95 (d, 1H, $J = 10$, H-19), 4.45 (d, 1H, $J = 10$, H-19'), 4.58 (bs, 2H, H-18), 4.67 (bs, 2H, H-16), 5.62 (m, 1H, H-3), 5.72 (bs, 1H, H-14).

Acetylation of paniculadiol [1] in the usual manner (Ac_2O , pyridine, room temperature, 4 h) gave a product identical (tlc, ir, ^1H -nmr) to paniculadiol diacetate [2].

Acetylenic lactone 3.—Colorless oil (80 mg): ir ν max (CCl_4) 3040, 2960, 2930, 2870, 2205, 1792, 1635, 1550, 1330, 1100, 938 cm^{-1} ; ms (70 eV) m/z (rel. int.) $[\text{M}]^+ 162$ (85), $[\text{M} - \text{Me}]^+ 147$ (18), $[\text{M} - \text{C}_2\text{H}_5]^+ 133$ (31), $[\text{M} - \text{C}_3\text{H}_7]^+ 119$ (23), $[\text{M} - \text{C}_2\text{H}_5 - \text{CO}]^+ 105$ (39), $[\text{M} - \text{C}_5\text{H}_{11}]^+ 91$ (35), $[\text{C}_4\text{H}_2\text{O}_2]^+ 82$ (100); ^1H nmr (90 MHz, CDCl_3) δ 1.0 (t, 3H, $J = 7$, H-10), 1.60 (sex, 2H, $J = 7$, H-9), 2.40 (dt, 2H, $J = 2$ and 7, H-8), 5.33 (t, 1H, $J = 2$, H-5), 6.22 (d, 1H, $J = 5$, H-2), 7.43 (d, 1H, $J = 5$, H-3); ^{13}C nmr (25.16 MHz, CDCl_3) δ 169.0 (s, C-1), 156.2 (s, C-4), 143.0 (d, C-3), 120.1 (d, C-2), 104.5 (s, C-6), 95.1 (d, C-5), 75.0 (s, C-7), 22.1 (t, C-8), 21.9 (t, C-9), 13.5 (q, C-10).

Acetylenic lactone 4.—Colorless oil (30 mg): ir ν max (CCl_4) 3040, 2960, 2930, 2870, 2205, 1788, 1638, 1210, 1100, 918 cm^{-1} ; ms (70 eV) m/z (rel. int.) $[\text{M}]^+ 162$ (72), $[\text{M} - \text{Me}]^+ 147$ (20), $[\text{M} - \text{C}_2\text{H}_5]^+ 133$ (28), $[\text{M} - \text{C}_3\text{H}_7]^+ 119$ (28), $[\text{M} - \text{C}_2\text{H}_5 - \text{CO}]^+ 105$ (48), $[\text{M} - \text{C}_5\text{H}_{11}]^+ 91$ (60), $[\text{C}_4\text{H}_2\text{O}_2]^+ 82$ (100); ^1H nmr (90 MHz, CDCl_3) δ 1.0 (t, 3H, $J = 7$, H-10), 1.60 (sex, 2H, $J = 7$, H-9), 2.40 (dt, $J = 2$ and 7, H-8), 5.72 (dd, 1H, $J = 2$ and 1.5, H-5), 6.24 (dd, 1H, $J = 1.5$ and 5, H-2), 7.7 (d, 1H, $J = 5$, H-3); ^{13}C nmr (25.16 MHz, CDCl_3) δ 170.1 (s, C-1), 159.2 (s, C-4), 140 (d, C-3), 121 (d, C-2), 100.6 (s, C-6), 96.0 (d, C-5), 75.8 (s, C-7), 22.1 (t, C-8), 21.9 (t, C-9), 13.5 (q, C-10).

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