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A NEW DIHYDRO-*TRANS*-CLERODANE DIACID FROM *HAPLOPAPPUS CILIATUS*

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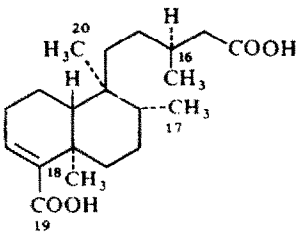
Key Word Index—*Haplopappus ciliatus*; Compositae; new *trans*-clerodane; diterpene; absolute configuration; haplociliatic acid.

A new dihydro-*trans*-clerodane diacid, haplociliatic acid (**1**), was isolated from *Haplopappus ciliatus* (Nutt.) DC. and the structure was determined [1] by X-ray diffraction techniques. The anomalous dispersion of the oxygen atoms was used to determine the absolute configuration. Haplociliatic acid is an isomer of the *cis*-clerodane cistodoic acid [2, 3].



1

The diacid was converted to the dimethylester by reaction with CH_2N_2, and the ^{13}C NMR spectrum at 15.03 MHz was obtained using $CDCl_3$ as solvent. Line assignments were made using single frequency off-resonance decoupling, relaxation techniques and lanthanide induced chemical shifts. The assignments (ppm from TMS) and relative LIS are as follows: C-1, 17.4 (0.10); C-2, 29.4 (0.15); C-3, 136.8 (0.34); C-4, 142.5 (0.46); C-5, 37.6 (0.25); C-6, 35.9 (0.20); C-7, 27.2 (0.10); C-8, 36.1 (0.07); C-9; 38.5 (0.09); C-10, 46.4 (0.15); C-11, 27.2 (0.10); C-12, 35.5 (0.09); C-13, 31.0 (0.24); C-14, 41.6 (0.41); C-15, 173.6 (1.00); C-16, 20.0 (0.15)*; C-17, 15.9 (0.05)†; C-18, 20.7 (0.18)*; C-19, 168.3 (1.00); C-20, 18.5 (0.06)†; and two $-OCH_3$ resonances at 51.1 (0.38) and 51.4 (0.33). Assignments marked * and † are interchangeable.

EXPERIMENTAL

Dried, powdered leaves (4.22 kg) of *Haplopappus ciliatus* (Nutt.) DC. (*Prionopsis ciliata* (Nutt.)), collected around Fort Worth, Texas in September 1977, were extracted with petrol. A few mg of white solid pptd from the extract and were collected. The petrol extract was evapd. to yield 140 g of a gummy residue. This was disolved in a minimum amount of petrol leaving a small quantity of white solid. The combined white solids (50 mg) were recrystallized from EtOH yielding colourless crystals, mp 198–201° (uncorr), $[\alpha]_D^{25}$ −86° (*c* 2.5, EtOH). MS (probe), *m/e* (rel. int.): 336 (M^+; 1), 318 ($M^+ - 18$; 33), 285 (3), 271 (26), 203 (28), 174 (6), 151 (11), 137 (25), 125 ($C_7H_9O_2^+$; 100). $C_{20}H_{31}O_4$. λ_{max}^{EtOH} nm: 212 (ε 17800)(double bond); ν_{max}^{KBr} cm^{-1}; 3350 (acid OH), 2850, 1640 (strong C=O), 1400, 1360, 1260, 1200, 900. PMR, (90 MHz, $CDCl_3$): δ 0.71 (3H, *s*), *ca* 0.82–1.12 (6H, overlapping *d*), 1.24 (3H. *s*), *ca* 1.34–1.65 and 2.1–2.3 (complex *m*), 6.57 (H-3, *t*, $J = 4$ Hz).

The X-ray data were collected on a Syntex $P2_1$ diffractometer system. The crystals belong to space group $P2_12_12_1$ with unit cell dimensions $a = 12.946$ (3), $b = 14.408$ (3), $c = 10.254$ (2) Å and $V = 1917.7$ (7) Å^3.

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