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EREMOPHILANES FROM SENECIO DESFONTAINEI

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ABSTRACT.—Four eremophilanes have been isolated from the aerial parts of Senecio desfontainei, including a new one, 11-hydroxyeremophil-6(7),9(10)-dien-8-one [4]. The structures were established by high field nmr spectroscopy.

The genus Senecio is rich in eremophilanes, furoeremophilanes, and pyrrolizidines, as well as other classes of natural products (1-4), and several compounds have been reported from Senecio desfontainei Druce (= S. coronopifolius Desf.) (Compositae) (5-7). Reinvestigation of this species afforded a new eremophilane 4, in addition to three previously reported compounds 1-3.

The ¹H-nmr data of 4 differed from those of 1-3; the downfield chemical shift of H-12 and H-13 at δ 1.46 and their presence as a singlet indicated that C-11 must bearing a hydroxyl function. This was verified by an ir absorption at 3550 cm⁻¹ as well as a ¹³C-nmr signal at δ 71.8 (C-11). Spin decoupling allowed the assignment of H-1, H-1', and H-4. The narrow doublet at δ 6.07 (H-9) showed a long range coupling with a multiplet at δ 2.37 (H-1), while irradiation of H-15 changed the signal at δ 1.56 (H-4). The mass spectrum exhibited peaks at m/z 234 for the molecular ion and at m/z 219 and 201 indicating loss of a methyl group followed by elimination of H₂O. ¹³C-nmr data (see Experimental) also supported the proposed structure.

- 1 X=H
- 2 $X = \beta O H, H$
- $3 X = \alpha OH, H$

EXPERIMENTAL

PLANT MATERIAL.—The aerial parts of S. desfontainei were collected from Bourg El-Arab, Alexandria, Egypt, in March 1987. A voucher specimen (A 319) is deposited in the Department of Botany, El-Minia University.

EXTRACTION AND ISOLATION OF TERPENOIDS.—The air-dried aerial parts (1 kg) of S. desfontainei were extracted with Et₂O-MeOH-petroleum ether (40–60°) (1:1:1) at room temperature as reported previously (8). The fraction eluted with Et₂O-petroleum ether (1:3) was further separated by hplc {RP 8, MeOH-H₂O (6:4)] to give 1 (30 mg), 2 (17 mg), 3 (19 mg), and 4 (9 mg). The spectral data of the known compounds 1 (9), 2 (10), and 3 (10) were identical to those reported in literature.

11-HYDROXYEREMOPHIL-6(7), 9(10)-DIEN-8-ONE [4].—[α]²⁴D - 15.0 (c = 2, CHCl₃); ir ν max (CHCl₃) cm⁻¹ 3550, 3000, 1650, 1600; ms m/z (rel. int.) [M]⁺ 234 (65), [234 - 15]⁺ 219 (100), [219 - 18]⁺ 201 (85); ¹H nmr (400 MHz, CDCl₃, TMS as internal standard) δ 6.94 (1H, s, H-6), 6.07 (1H, d, J = 1.5 Hz, H-9), 2.37 (1H, m, H-1), 1.99 (1H, m, H-1'), 1.56 (1H, m, H-4), 1.46 (6H, s, H-12 and H-13), 1.13 (3H, s, H-14), and 1.08 (3H, d, J = 7 Hz, H-15); ¹³C nmr (400 MHz, CDCl₃, C-1 to C-15) δ 32.5, 30.1, 28.0, 41.7, 43.6, 124.6, 169.4, 188.1, 149.5, 141.1, 71.8, 28.8, 28.9, 17.0, 16.3. (Signals for C-1–C-3, C-7–C-10, and C-12 and C-13 may be interchanged.)

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