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DEOXYBARTEMIDIOLIDE, A CLERODANE-TYPE DITERPENE FROM *BACCHARIS ARTEMISIOIDES*

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Key Word Index—*Baccharis artemisioides*; Compositae; deoxybartemidiolide; clerodane; diterpene.

Abstract—A re-examination of *Baccharis artemisioides* leaves revealed the presence of one new natural product with a clerodane skeleton named deoxybartemidiolide, 15,16-epoxy-*trans*-cleroda-3,13(16),14-triene-20,12*S*-19,2(*β*)-diolide. The structure was determined by chemical and physical methods.

INTRODUCTION

The American genus *Baccharis* (Compositae) has been found to be a rich source of diterpenes, triterpenes and aromatic compounds. A large number of clerodane diterpenes have also been isolated from plants of this genus. Our recent examination of the aerial parts of *Baccharis artemisioides* H. et A. [1] has led to the isolation of the diterpene bartemidiolide (**1**). A further examination of this plant has led to the isolation of another diterpene, deoxybartemidiolide (**2**) as a minor component.

RESULTS AND DISCUSSION

High resolution mass spectrometry established the molecular formula of **2** as $C_{20}H_{22}O_5$. The presence of ions at *m/z* 81, 94 and 95.0520 (C_6H_6O) in the mass spectrum together with the ^1H NMR spectrum, which showed signals at δ7.35, 7.30 and 6.29, indicated the presence of a *β*-substituted furan.

The IR spectrum revealed absorptions attributable to two carbonyl groups (1760; 1750 cm^{-1}) as part of two lactone rings which were in agreement with the signals at δ176.1 and 174.1 in the ^{13}C NMR spectra.

The ^1H NMR spectrum showed signals at δ1.06 (*d*, *J* = 6.7 Hz) and 1.71 (*d*, *J* = 1.6 Hz) which were ascribed to a secondary methyl group and to a methyl-vinyl group, respectively. The ^{13}C NMR spectra, with carbon multiplicities determined by DEPT, confirmed the presence of four aromatic carbons (three–CH = and one–C =) and two olefinic carbons (–CH = and –C =) which accounted for all degrees of unsaturation requested by the molecular formula.

The ^1H NMR spectrum also revealed two one-proton signals at δ4.92 (*dd*, *J* = 5.0; 3.2 Hz) and 5.29 (*dd*, *J* = 8.5; 8.5 Hz appearing as triplet), on the other hand the ^{13}C NMR spectra showed two doublets at δ72.40 and 72.01; these facts were indicative of two oxygen-bearing methine groups which accounted for all the oxygen sustituted carbon atoms in the molecule.

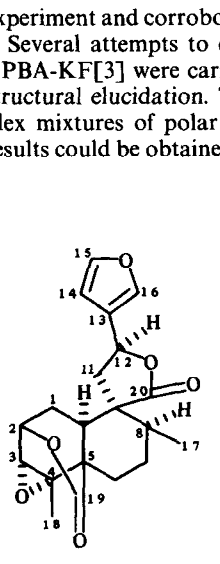
The olefinic proton showed resonance at δ6.07 (*dd*, *J* = 5.0; 1.6 Hz) and the irradiation of this signal removed the 1.6 Hz coupling from the 1.71 doublet as well as the 5.0 Hz coupling in the 4.92 double doublet.

All the above data are in good agreement with structure **2** corresponding to a clerodane-type furane diterpene which contains *δ*-and *γ*-lactones rings. The first lactone is in ring A from C-2 to C-5 and the latter lactone connects C-12 to C-9 as a *spyro*-system.

The detection of vicinal proton–proton couplings determined from the ^1H–1D and 2D–COSY spectra allowed unambiguous identification for the H-11α, H-11*β*, H-8 and H-10 which showed resonances at δ2.14 (*dd*, *J* = 14.0; 8.5 Hz), 2.41 (*dd*, *J* = 14.0; 8.5 Hz), 1.63 (*m*) and 2.10 (*m*), respectively. The protons at C-1 appeared as complex multiplets at δ1.60 and 2.20.

Assignments of ^{13}C NMR chemical shifts were made with the aid of off-resonance spectra and DEPT and are given in Table 1. The exact chemical shifts for C-2 (72.40), C-12 (72.01), C-3 (127.19) and for the furan protons were obtained from the ^{13}C–^1H(HCCORR) 2D correlation experiment and corroborated by the data given in ref. [2].

Several attempts to epoxidise **2** with *m*-CPBA or *m*-CPBA-KF[3] were carried out in order to complete the structural elucidation. These reactions resulted in complex mixtures of polar materials from which no useful results could be obtained. This was in agreement with the



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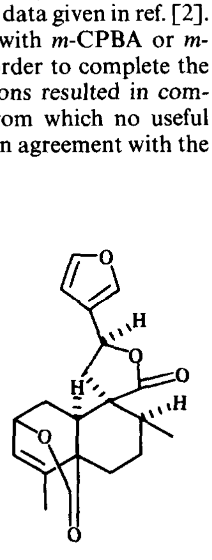

2

Table 1. ^{13}C NMR chemical shifts (in δ values from TMS) of compound **2**

C	δ	C	δ
1	32.47 *t*	11	42.87 *t*
2	72.40 *d*	12	72.01 *d*
3	127.19 *d*	13	125.00 *s*
4	147.64 *s*	14	108.15 *d*
5	48.67 *s*	15	139.70 *d*
6	26.91 *t*[a]	16	144.20 *d*
7	26.23 *t*[a]	17	17.67 *q*
8	42.12 *d*[b]	18	15.78 *q*
9	52.90 *s*	19	174.10 *s*[c]
10	41.61 *d*[b]	20	176.10 *s*[c]

[a–c]Assignment may be interchanged.

unsuccessful epoxidation attempt of other similar 3,4-unsaturated clerodanes reported in ref. [4] and which was attributed to the severely hindered double bond.

Finally, a definitive proof of the identity of **2** was obtained by comparison of the natural product with synthetic material obtained by treatment of **1** with triphenylphosphine–iodine complex [5]. Material recovered in this way proved to be identical in all respects (mp, $[\alpha]_D^{25}$, 200 MHz ^{1}H NMR, IR and MS) with the new natural product.

EXPERIMENTAL

Mp are uncorr; analytical TLC was on silica gel F_{254}; ^{1}H and ^{13}C NMR were at 200 MHz and 50 MHz, respectively, in the Fourier transform mode, in $CDCl_3$ with TMS as int. standard; MS was at 70 eV, direct inlet. Details of the extraction are described in the previous paper [1].

Deoxybartemidiolide (**2**) was isolated from the $CHCl_3$ residue by chromatographed on silica gel 60 H using hexane and hexane–EtOAc mixtures of increasing polarity. The hexane–EtOAc (3:2) yielded 150 mg of **2**.

Physical and spectral data. Mp 151–152°. IR ν_{max}^{KBr} cm^{-1}: 3000, 2950, 1760, 1750, 1450, 1060, 840. MS (HR) *m/z* (rel. int.): 298.1582 $[M-CO_2]^+$ (28), 204. 1105 $[C_{13}H_{15}O_2]^+$ (cleavage of bonds C-9 to C-11 and to C-20) (40), 171 (22), 161 (27), 145 (92), 105 (100), 94 (41), 81 (40), 67.054 $[C_4H_3O]^+$ (furan) (13); $[\alpha]_D^{25}$ + 77.0° ($CHCl_3$; *c* 0.57).

^{1}H *NMR.* δ 1.06 (3H, *d*, $J = 6.7$ Hz, H-17), 1.60 (1H, *m*, H-1), 1.63 (1H, *m*, H-8), 1.71 (3H, *d*, $J = 1.6$ Hz, H-18), 2.10 (1H, *m*, H-10), 2.14 (1H, *dd*, $J = 14.0$, 8.5 Hz, H-11α), 2.20 (1H, *m*, H-1), 2.41 (1H, *dd*, $J = 14.0$, 8.5 Hz, H-11β), 4.92 (1H, *dd*, $J = 5.0$, 5.2 Hz, H-2), 5.29 (1H, *dd*, $J = 8.5$, 8.5, H-12), 6.07 (1H, *dd*, $J = 5.0$, 1.6 Hz, H-3), 6.29 (1H, *dd*, $J = 2.0$, 1.0 Hz, H-14), 7.30 (1H, *br. s*, H-16), 7.35 (1H, *d*, $J = 2.0$ Hz, H-15).

Preparation of **2** *from* **1**. Triphenylphosphine (43 mg) and iodine (42 mg) were dissolved in CH_2Cl_2 (3 ml) followed by addition of a soln of **1** (51 mg) in the same solvent. The reaction was carried out at −60° with stirring, after 10 min the mixture was diluted with H_2O and work-up as in ref. [5]. Further purification by CC yielded 15 mg of **2** identified by comparison of their spectroscopic and physical data with the natural product here reported.

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