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A 19-HYDROXYWITHANOLIDE FROM *JABOROSA LEUCOTRICHA*

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Key Word Index—*Jaborosa leucotricha*; Solanaceae; 19-hydroxywithanolide; steroidal lactones; jaborosalactone O.

Abstract—From leaves of *Jaborosa leucotricha* a new withanolide 17α,19-dihydroxy-5β,6β-epoxy-1-oxo-22R-witha-24-enolide has been isolated and characterized by spectroscopic methods (^{1}H and ^{13}C NMR, MS); 19-hydroxywithanolides have not been previously reported.

INTRODUCTION

Continuing with our investigations on the withanolides of *Jaborosa* Miers. species [1] we have isolated from *Jaborosa leucotricha*, besides the already reported jaborosalactone L (**1**) [2], a new withanolide named jaborosalactone O to which structure **2** has been assigned based on analytical and spectroscopic evidence. Although 19-hydroxylated steroidal lactones are known in the cardenolide and bufadienolide families, this is the first report of a naturally occurring 19-hydroxy withanolide.

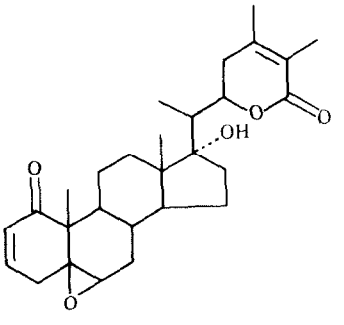
RESULTS AND DISCUSSION

The ^{1}H NMR spectrum of **2** (Table 1) did not show olefinic protons indicating a 2,3-dihydrowithanolide structure. The 5β,6β-epoxide was inferred from the broad signal at δ3.12 corresponding to H-6, suggesting a 1-oxo-5β,6β-epoxywithanolide. Regarding the side chain, this was closely related to that of jaborosalactone L [2]. The presence of two methyl signals at δ1.87 and 1.92 was consistent with an α,β-unsaturated lactone bearing methyl groups at positions C-24 and C-25 (H-27 and H-28), and the complex signal of H-22 was clearly observed at 4.58. The multiplicity observed for the latter signal and the doublet at δ1.00 assigned to H-21 confirmed the absence of a hydroxyl group at C-20. The signal for methyl-18 at δ0.81 was consistent with the presence of a 17α-hydroxyl. Finally, the absence of a singlet for H-19 in the δ0.8–1.4 region, and the appearance of an AB quartet at 3.94–4.22 suggested the presence of a hydroxyl group at C-19.

Final confirmation for this structure was obtained from the ^{13}C NMR spectrum (Table 2) and the relative phase of the signals in the APT spectrum [3] which showed only four methyl groups that were coincident with C-18, 21, 27 and 28 of jaborosalactone L. The methylene signal at δ62.7 was assigned to C-19. The stereochemistry at C-17 could be inferred from the chemical shifts of C-21 (δ9.5) and C-18 (14.7) and by comparison with the spectrum of jaborosalactone L.

Table 1. ^{1}H NMR spectral data for relevant protons of compound **2**

H	δ	Mult.	*J* (Hz)
6	3.12	*br s*	
18	0.81	*s*	
19A	3.94	*dd*	11; 1.5
19B	4.22	*d*	11
21	1.00	*d*	7
22	4.58	*ddd*	10; 6.5; 3
27	1.87	*br s*	
28	1.92	*br s*	



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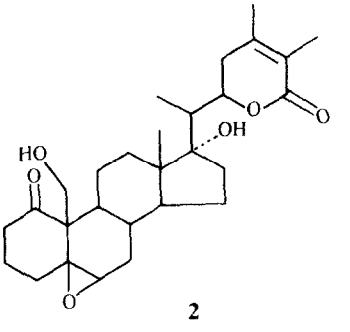

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Table 2. ^{13}C NMR spectral data of compound **2**

C	δ
1	210.7
2	31.4[a]
3	31.1[a]
4	35.6
5	64.1
6	59.3
7	21.5
8	30.6
9	42.4[b]
10	55.9
11	18.0
12	31.9[c]
13	48.1
14	50.8
15	23.5
16	36.4
17	84.9
18	14.7
19	62.7
20	42.6[b]
21	9.5
22	78.5
23	32.7[c]
24	150.0
25	121.3
26	166.7
27	12.3
28	20.4

[a–c]Interchangeable values.

EXPERIMENTAL

Mps: uncorr. ^1H and ^{13}C NMR spectra were measured at 100.1 and 25.2 MHz, respectively, in $CDCl_3$. Chemical shifts are given in ppm downfield from TMS (int. standard). Mass spectra were determined at 70 eV by direct inlet.

Plant material and isolation procedure. Whole *Jaborosa leucotricha* (Speg.) A. T. Hunziker plants were collected at El Carrizal, Dept. Luján, Mendoza province (Argentina). A voucher specimen was deposited at the Museo Botánico, Universidad Nacional de Córdoba under No 24810. Dried and pulverized leaves (1.24 kg) were extracted successively with hexane and Et_2O and the insoluble material was further extracted with EtOH. The residue obtained after evaporation of the ethanolic extract was fractionated on a silica gel column; elution with hexane–EtOAc mixtures of increasing polarity provided 2 fractions containing withanolides. The less polar fraction was identified as jaborosalactone L (**1**) by ^1H and ^{13}C NMR spectra. The second fraction was characterized as 17α,19-dihydroxy-5β,6β-epoxy-1-oxo-22*R*-witha-24-enolide (jaborosalactone O) (**2**) (35 mg); crystals from EtOAc, mp 191–193°; MS *m/z* (rel. int.): 457 $[M-Me]^+$ (1), 443 (19), 311 (18), 271 (13), 227 (19), 213 (27), 211 (24), 197 (24), 159 (25), 137 (37), 125 (100), 109 (59).

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