Phytochemistry, Vol. 25, No. 7, pp. 1765–1766, 1986.
Printed in Great Britain.

0031-9422/86 $3.00 + 0.00
Pergamon Journals Ltd.

JABOROSALACTONE L, A WITHANOLIDE FROM *JABOROSA LEUCOTRICHA*

David Lavie, Hugo E. Gottlieb*, Mauricio J. Pestchanker† and Oscar S. Giordano†

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel; *Department of Chemistry, Bar-Ilan University, Ramat Gan, Israel; †The Department of Organic Chemistry, Universidad Nacional de San Luis, 786 General-Paz, 5700 San Luis, Argentina

(*Received* 29 *August* 1985)

Key Word Index—*Jaborosa leucotricha*; Solanaceae; withanolides; steroidal lactones; jaborosalactone L.

Abstract—From the plant *Jaborosa leucotricha* a new withanolide 17α-hydroxy-5β,6β-epoxy-1-oxo-22*R*-witha-2,24-dienolide has been isolated and fully characterized.

INTRODUCTION

Within the framework of a collaborative effort, the constituents of the leaves of *Jaborosa leucotricha* (Solanaceae) were investigated and a new withanolide named jaborosalactone L was assigned structure **1**, based on analytical and spectroscopic evidence.

RESULTS AND DISCUSSION

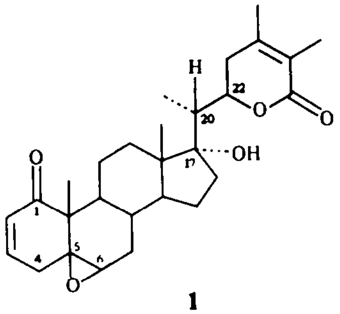
Compound **1**, $C_{28}H_{38}O_5$ (M^+ 454), showed in the UV spectrum an absorption at λ_{max} 224 nm (ε 32 000) EtOH. This value and its high intensity are characteristic for the overlapping of two chromophores, the α,β-unsaturated carbonyl and the unsaturated lactone system, both characteristic of the withanolide group of compounds. The IR spectrum indicated the presence of the two unsaturated systems (1700 and 1670 cm^{-1}) [1].

The ^1H NMR spectrum of **1** was most informative and included several features which are common in withanolides [1] (see Table 1). Thus, ring A is characterized as possessing a 2-en-1-one system, with a methylene at C-4 and a non-protonated C-5. The 5,6-epoxide is inferred from the presence of a broad triplet at δ3.13 corresponding to H-6. As for the side chain, the α,β-unsaturated lactone is identified by its two allylic methyl groups and the clearly observed oxymethine proton H-22. The 21-Me signal appears as a doublet, and H-20 in fact is clearly seen as a *qd* at δ2.31; this multiplicity suggests a 17-hydroxyl function. Irradiation of the H-20 line causes both the collapse of the 21 doublet and simplification of the H-22 signal to a *dd*. Final confirmation of structure **1** is provided by the ^{13}C NMR spectrum.

The carbon chemical shifts for **1** (see Table 2) can be compared to known data for a substantial number of other withanolides [2]. Thus, the presence and stereochemistry of the 5,6-epoxide is established with certainty (see **9** in ref. [2]). The only other functional groups in the molecule are the side chain lactone and a tertiary alcohol. The suggested 17α-hydroxyl structure is corroborated by comparison to compound **16** in ref. [2], which only differs in the substitution pattern of rings A/B, and which has virtually the same ^{13}C shifts as **1** for ring D and the side chain. All these data corroborate the proposed structure **1** assigned to jaborosalactone L.

EXPERIMENTAL

Mps were measured on a Fisher–Johns apparatus and are uncorrected. Analytical TLC was carried out using chromatoplates (50 × 75 mm, silica gel F_{254}). The NMR spectra were obtained on a Bruker AM-300 spectrometer operating at 300.1



1

Table 1. ^1H NMR spectral signals of relevant protons of compound **1**

H	δ	Mult, *J*(Hz)	H	δ	Mult, *J* (Hz)
3	6.85	*ddd* 10; 6; 2.5	28	1.92	*br s* (3H)
2	6.02	*ddd* 10; 3; 0.5	27	1.87	*br s* (3H)
22	4.59	*ddd* 11; 5.5; 3	19	1.26	*s* (3H)
6	3.13	*br d* 2.5	21	1.01	*d* (3H)
4β	2.99	*ddd* 19; 3; 2.5	18	0.80	*s* (3H)
20	2.31	*qd* 7; 3			

Table 2. ^{13}C NMR data of compound 1

C	δ	C	δ	C	δ	C	δ
1	203.65	8	30.16	15	23.57*	22	78.76
2	129.25	9	44.37	16	36.38	23	32.74
3	144.58	10	47.90	17	85.05	24	150.36
4	33.00	11	23.45*	18	14.82	25	121.44
5	61.99	12	32.18	19	15.05	26	167.13
6	63.31	13	48.40	20	42.71	27	12.33
7	31.21	14	50.07	21	9.39	28	20.46

*Interchangeable.

(^{1}H) and 75.4 MHz (^{13}C), in the Fourier transform mode. All chemical shifts are for $CDCl_3$ solns, using internal TMS as a reference. The carbon shift assignments were aided by single-frequency off-resonance decoupled spectra (irradiation at four different frequencies), which afforded signal multiplicities and correlation to ^{1}H resonances [2]. Mass spectra were determined with a Finnigan GC/MS model 4021.

Isolation procedure. Air dried powdered red leaves of *Jaborosa leucotricha* (Speg.) A. T. Hunz. (5 kg) collected December 1983 from plants bearing flowers and fruit in the area of El Carrizal Mendoza Argentina (classified by L. A. Del Vitto)* were extracted with hot MeOH (12 × 3 l). The solvent was evaporated at red. pres. and the extract diluted with H_2O (9:1) and extracted several times with *n*-hexane. H_2O was then added in the ratio of 4:1 (MeOH–H_2O) and extracted with CCl_4. This was followed by a further dilution to 7:3 and again extracted with $CHCl_3$. This extract (70 g) was chromatographed on silica gel H (Merck). Elution with C_6H_6–EtOAc (19:1) yielded jaborosalactone L (80 mg) crystals from $CHCl_3$–EtOAc, mp 215–217°; $[\alpha]_D + 77°$ (c 0.1; $CHCl_3$); IR$\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3450, 2920, 1700, 1670, 1370, 1200, 1125 and 850; CIMS (64 eV) NH_3 reagent gas, m/z (rel. int.): 455 $[M+1]^+$ (19), 437 $[M-H_2O+1]^+$ (100), 419 (16). Electron impact 28 eV: 454 $[M]^+$ (1), 439 $[M-Me]^+$ (4), 436 $[M-H_2O]^+$ (1), 313 (19), 283 $[M-H_2O-\text{cleavage C-17–C-20}, C_9H_{13}O_3]^+$ (6), 265 (19), 240 (39), 227 (28), 209 (11), 197 (16), 171 (19), 157 (15), 147 (12), 137 (46), 131 (19), 125 $[\text{cleavage of C-20–C-22}, C_7H_9O_2]^+$ (100), 109 (41). (Found: C, 74.36; H, 8.40. $C_{28}H_{38}O_5$ requires: C, 74.07; H, 8.44%. M_r 454.5.)

Acknowledgement—Thanks are due to Dr. M. Cojocaru, Bar-Ilan University for mass spectrometric measurements.

REFERENCES

1. Glotter, E., Kirson, I., Lavie, D. and Abraham, A. (1978) *Bioorganic Chemistry* (van Tamelen, E. E., ed.) Vol. 2, p. 57. Academic Press, New York.
2. Gottlieb, H. E. and Kirson, I. (1981) *Org. Magn. Reson.* **16**, 20.

---

* IADIZA (CRICYT), Mendoza 5500, Argentina. Voucher specimen deposited (MERL No. 36008 and 36010).