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TWO TRITERPENOIDS FROM *BOEHMERIA EXCELSA*

M. LUISA OYARZÚN, JUAN A. GARBARINO, VICENTE GAMBARO, JEAN GUILHEM* and CLAUDINE PASCARD*

Departamento de Química, Facultad de Ciencia, Universidad Federico Santa María, Casilla 110-V, Valparaíso, Chile; *Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France

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Key Word Index *Boehmeria excelsa*; Urticaceae; triterpenoids; boehmerone; boehmerol.

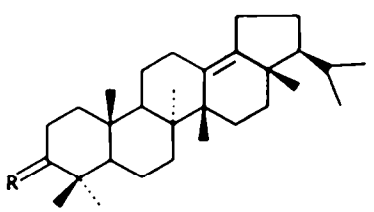
Abstract—Two new triterpenoids, boehmerone and boehmerol, and the known compounds ursolic acid and betulinic acid were isolated from the bark of *Boehmeria excelsa*. The structures of the new compounds were established by spectroscopic methods and X-ray analysis.

INTRODUCTION

Boehmeria excelsa (Bert. *ex* Steud) Wedd [1], commonly known as 'manzano', is an endemic shrub growing on Robinson Crusoe Island, Juan Fernández archipelago, Chile [1]. Up to now, nothing has been reported about the chemistry of this plant. In this study we have examined the petrol extract from the bark of *B. excelsa*. As a result, two new pentacyclic triterpenoids have been isolated, for which we propose the names boehmerone (**1**) and boehmerol (**2**). The relative configuration of **2** was determined by X-ray analysis.

RESULTS AND DISCUSSION

In the mass spectrum of compound **1**, the molecular ion peak at *m/z* 424 suggested the molecular formula $C_{30}H_{48}O$. A fragment at *m/z* 381 $[M-43]^+$ corresponded to the loss of an isopropyl group. Two intense peaks, one at *m/z* 205 (present in most of the pentacyclic triterpenoids) [2] and another at *m/z* 189, suggested that compound **1** belonged to the hopane or lupane group [3]. The IR spectrum showed strong absorption at 1715 cm^{-1} (C=O). The ^1H NMR spectrum showed two doublets centred at δ0.94 and 0.89 (3H each, J = 6.6 Hz, Me-29, Me-30), which confirmed the presence of the isopropyl group. The absence of peaks above δ2.7 indicated that the only double bond present, as suggested by the molecular formula, were tetra-substituted. This was in agreement with the ^{13}C NMR spectrum, which had two singlets at δ141.8 (C-18) and 131.3 (C-13). Furthermore, this spectrum confirmed the presence of the carbonyl group by means of the singlet at δ220.0 (C-3) [4]. The APT ^{13}C NMR showed 8 methyls, 10 methylenes, 4 methines and 8 quaternary carbons. On the basis of these spectral data, **1** was presumed to be a triterpene of the hopane or lupane type possessing a carbonyl group at C-3 and one tetra-substituted double bond in either ring D or ring A. An exhaustive bibliographic review of the ^{13}C NMR and ^1H NMR data of the hopane and lupane compounds [4–10] indicated that **1** was an unusual triterpene. It was named boehmerone (**1**).



1 R = O
2 R = α-H, β-OH

The mass spectral molecular ion peak of boehmerol (**2**) occurred at *m/z* 426 and suggested the molecular formula $C_{30}H_{50}O$. Also three intense peaks occurred at *m/z* 383 $[M-43]^+$, 205 and 189. The IR spectrum showed strong absorption at 3400 cm^{-1} (OH). The ^1H NMR spectrum showed a doublet of a doublet centred at δ3.24 (J = 6 and 12 Hz) characteristic of a proton geminal to a β-hydroxyl group at C-3 and two doublets centred at δ0.96 and 0.91 (3H each, J = 6.0 Hz, Me-29, Me-30) which confirmed the presence of an isopropyl group. Because the spectral data of **1** and **2** were similar, we presumed that both compounds were closely related. In fact, the only difference between them was at C-3: **1** had a carbonyl group in this position and **2** had a β-hydroxyl group there, as demonstrated by oxidizing **2** with Jones reagent [11], affording a product which was identical with **1** (TLC, IR, ^1H NMR, ^{13}C NMR, MS and $[\alpha]_D^{25}$). Since **2** was obtained in much larger amounts than **1** and because both related compounds are unusual triterpenes, we decided to elucidate the structure of boehmerol (**2**) by X-ray analysis, which showed that this was a new pentacyclic triterpene (see Fig. 1). Details of the X-ray analysis are given in the Experimental. By comparison of the ^{13}C NMR spectra of **1** and **2**, and by studying the ^1H NMR, 2D H-correlation and ^1H NMR three-dimensional (COSY) spectra of **1**, we were able to assign the signals as indicated in Table 1.

EXPERIMENTAL

Mps: uncorr. ^1H NMR: 300 or 400 MHz in $CDCl_3$ with TMS as internal standard. ^{13}C NMR: 100 MHz in $CDCl_3$ with TMS as internal standard. Assignments of ^{13}C NMR chemical shifts were

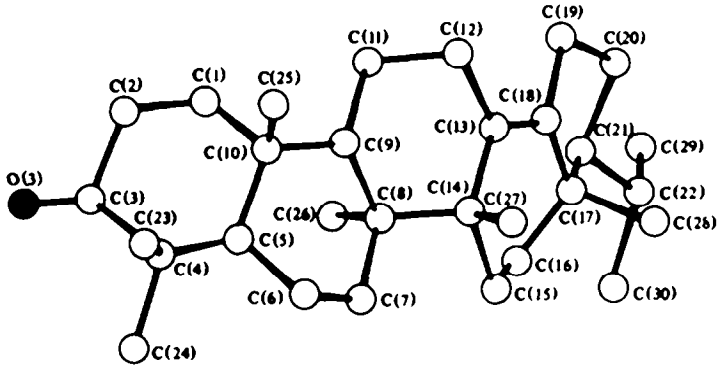


Fig. 1. X-Ray crystal structure of boehmerol (2). The oxygen atom is shaded.

made with the aid of APT at 100 MHz. IR: KBr pellets. MS: direct inlet, 70 eV. GC/MS: FID, He 30 ml/min, temp. programmed 150–290° at 4°/min; 1.8 m × 2 mm packed with 3% OV-17.

The bark of *B. excelsa* was collected on Robinson Crusoe Island in September 1982. A voucher specimen has been deposited at Universidad Federico Santa Maria. The bark (500 g) was extracted with petrol in a Soxhlet apparatus for 35 hr. This extract (5 g) was chromatographed on a silica gel column (200 g) and eluted with mixtures of petrol and EtOAc of increasing polarity.

Table 1. ^{13}C NMR spectral data of compounds 1 and 2

C	1*	2
1	31.7 *t*	33.4 *t*
2	33.8 *t*	29.3 *t*
3	220.0 *s*	79.3 *d*
4	46.9 *s*	39.2 *s*
5	44.1 *d*	46.5 *d*
6	22.3 *t*†	22.7 *t*†
7	30.4 *t*	30.5 *t*
8	41.6 *s*	41.5 *s*
9	47.7 *d*	48.2 *d*
10	36.4 *s*	37.2 *s*
11	20.4 *t*†	19.0 *t*†
12	26.2 *s*	26.4 *s*
13	131.3 *s*	130.8 *s*
14	42.3 *t*	42.6 *t*
15	26.4 *t*	26.5 *t*
16	34.4 *t*	35.0 *t*
17	42.8 *s*	42.7 *s*
18	141.8 *s*	142.0 *s*
19	27.5 *t*	27.5 *t*
20	37.7 *t*	37.6 *t*
21	59.1 *d*	59.2 *d*
22	29.7 *d*	29.8 *d*
23	29.3 *q*	29.1 *q*
24	19.7 *q*	16.1 *q*
25	17.9 *q*	18.0 *q*
26	23.5 *q*	23.0 *q*
27	26.7 *q*‡	26.7 *q*‡
28	25.3 *q*‡	25.7 *q*‡
29	23.0 *q*	23.0 *q*
30	23.0 *q*	23.0 *q*

*Assignments were made with the aid of 2D CH-correlation.

†,‡Assignments may be interchanged.

Boehmerone (1). Elution with petrol–EtOAc (49:1) yielded a major compound which was rechromatographed on silica gel (10 g) to give boehmerone (1) (50 mg), mp 176–178° $[\alpha]_D^{25}$ + 12.3° ($CHCl_3$; *c* 0.20). IR ν_{max}^{KBr} cm^{-1}: 2950, 1715, 1470, 1375, 1385, 1110; ^{1}H NMR (400 MHz, $CDCl_3$): δ0.79 (6H, *s*, H-25 and H-26), 0.89 (3H, *d*, *J* = 6.6 Hz, H-29), 0.94 (3H, *d*, *J* = 6.6 Hz, H-30), 1.03 (3H, *s*, H-24), 1.03 (3H, *s*, H-27 or H-28), 1.03 (1H, *m*, H-21), 1.05 (3H, *s*, H-23), 1.08 (3H, *s*, H-27 or H-28); ^{13}C NMR: see Table 1; MS *m/z* (rel. int.): 424 [M]$^+$ (75), 381 (10), 205 (100), 189 (47), 175 (40), 161 (62), 149 (52), 133 (36), 121 (46), 119 (41), 109 (48), 95 (56), 81 (49), 69 (63), 55 (85), 41 (48).

Boehmerol (2). Elution with petrol–EtOAc (24:1) yielded boehmerol (2) (500 mg), mp 215 217°; $[\alpha]_D^{25}$ + 47° ($CHCl_3$; *c* 0.20). IR ν_{max}^{KBr} cm^{-1}: 3400, 2960, 1470, 1380, 1090; ^{1}H NMR (300 MHz, $CDCl_3$): δ0.81 (6H, *s*, H-25 and H-26), 0.91 (3H, *d*, *J* = 6.0 Hz, H-29), 0.96 (3H, *d*, *J* = 6.0 Hz, H-30), 0.96 (3H, *s*, H-24), 1.00 (3H, *s*, H-27 or 28), 1.02 (3H, *s*, H-23), 1.09 (3H, *s*, H-27 or 28), 3.24 (1H, *dd*, *J* = 6.0 and 12.0 Hz, H-3); ^{13}C NMR: see Table 1.

CC also afforded a mixture of sterols: stigmasterol, campesterol and sitosterol, which were identified by GC/MS. Also, by increasing the polarity of the mixture of solvents, we isolated betulinic and ursolic acids, which were found to be identical to authentic samples.

Crystallographic data for boehmerol (2). A flake-like crystal (0.4 × 0.4 × 0.01 mm^3) was mounted on an automatic four-circle diffractometer (Philips PW 1100), using copper K_α radiation. No symmetry being observed, the data were collected assuming a *P*1 space group: a = 29.534(15), b = 7.852(4), c = 6.830(4) Å, α = 121.14(12), β = 93.90(10) and δ = 93.32(10)°. The unit cell contains two molecules. Out of 3771 measured reflections, only 1466 were considered as observed [$I > 3\,\sigma(I)$].

The structure was solved by direct methods [12] and refined by large blocks of least-squares [13]. Due to the small amount of data with respect to the large number of parameters (more than 62 non-hydrogen atoms), the thermal parameters were kept isotropic. One water molecule was found to link two molecules of neighbouring cells through hydrogen bonds. The final *R* factor was 14.8%. The two independent molecules exhibited identical configuration; only one of them is represented in Fig. 1.

The X-ray results show the presence of the double bond (C13)=C(18); mean value 1.31(0.04) Å; an isopropyl group is fixed in the β-position at C-21 and there are two methyl groups at C-4. The two independent molecules in the unit cell are linked together by a strong (2.8 Å) H-bond through the OH groups.

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