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STUDIES ON CHILEAN LICHENS, XIII.[1] POLYSUBSTITUTED DEPSIDES FROM *LECANIA BRIALMONTII*

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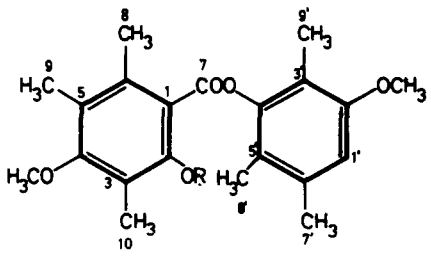
ABSTRACT.—From *Lecania brialmontii* two new polysubstituted depsides, brialmontins 1 [**1**] and 2 [**2**], were isolated. Their structures were established by spectroscopic techniques, particularly ^{13}C nmr.

The lichen genus *Lecania* (Lecanoraceae) is widely distributed in temperate zones (2), but the chemistry of the genus is poorly known. It has been reported that a neutral substance, lecanin, of unknown structure, has been isolated from *Lecania aispopila* (3).

As a continuation of the systematic survey on lichen substances from the Chilean flora, we examined *Lecania brialmontii* (Vain) Zahlbr., a frequent species in maritime Antarctica (4). This paper describes the isolation and characterization of two new polysubstituted depsides, brialmontin 1 [**1**] and brialmontin 2 [**2**].

The polysubstituted depsides make up a limited group of lichen substances previously isolated from *Nephroma arcticum* (5), *Erioderma* sp. (6), *Pseudocyphellaria endochrysea* (7), and *Pseudocyphellaria pickeringii* (8).



1 R=Me
2 R=H

Petroleum ether, $CHCl_3$, and Me_2CO extracts of the lichen *L. brialmontii* yielded a mixture of two main components that were separated to afford the compounds **1** and **2**.

Brialmontin 1 [**1**] was identified on the basis of the following spectroscopic evidence. The ir band at 1730 cm^{-1} and a ^{13}C-nmr peak at 167.1 ppm are consistent with the depside ester linkage. The ^1H nmr showed the typical singlet signals for methoxy and methyl groups and an isolated aromatic one-proton singlet at δ 6.63. These assignments were confirmed by the ^{13}C-nmr spectrum (Table 1). The mass spectrum of **1** exhibited a molecular ion at *m/z* 372 ($C_{22}H_{28}O_5$) and two major fragment ions at *m/z* 207 (100%) and *m/z* 165, formed by rupture of the ester linkage, in common with most other depsides (5,7, 9–11), and the absence of the $[M-H_2O]^+$ ion, in agreement with the above-mentioned nmr analysis.

The ir spectrum of brialmontin 2 [**2**] showed the presence of a broad hydroxy band at 3400 cm^{-1} and a carbonyl group at 1650 cm^{-1} due to the depside ester linkage, in agreement with a ^{13}C-nmr peak at 170.4 ppm. The ^1H-nmr spectrum displayed the presence of typical signals for methoxy and methyl groups, a singlet at δ 6.66, and a one-proton singlet at δ 11.42 due to the hydroxy group. Examination of the ^{13}C-nmr spectrum of **2** supported these assign-

[1]For Part XII, see Quihot *et al.* (1).

TABLE 1. ^{13}C-nmr Spectral Data of Compounds **1** and **2**.

Carbon	Compound	
	1	**2**
C-1	120.9	122.0
C-2	158.9	161.9
C-3	116.7	116.6
C-4	154.6	156.9
C-5	124.7	120.1
C-6	135.2	138.0
C-7	167.1	170.4
C-8	17.2[a]	19.3[a]
C-9	12.5[b]	12.6[b]
C-10	9.7[c]	9.6[c]
C-2-OMe	61.9[d]	—
C-4-OMe	60.1[d]	60.0
C-2′-OMe	55.7	55.7
C-1′	110.2	110.2
C-2′	155.8	156.8
C-3′	122.2	120.0
C-4′	148.6	150.2
C-5′	126.4	125.0
C-6′	133.5	135.2
C-7′	20.5[a]	20.4[a]
C-8′	12.6[b]	12.6[b]
C-9′	9.7[c]	9.1[c]

[a–d]Assignments with the same superscript in the same column may be interchanged.

ments (Table 1). In addition the mass spectrum of **2** showed a molecular ion peak at *m/z* 358 ($C_{21}H_{26}O_5$) and two principal fragments at *m/z* 193 (100%) and *m/z* 165 corresponding to the rupture of the depside ester linkage (5,7,11).

The ^{1}H-nmr spectrum of **2** thus differed from that of **1** only by a slight shift of the 3-proton singlet corresponding to the methyl group at position 5′ and the presence of a bonded phenolic proton singlet at δ 11.42.

In the ^{1}H-nmr spectra of other analogous depsides, such as the pseudocyphellarins A and B and nephroarctin, a corresponding downfield shift was observed for this methyl signal. In addition the carbonyl band due to the depside ester linkage was shifted to longer wave number in the corresponding ir spectra. This is not the case when the 2 position is substituted by a methoxy group (5,7). Moreover, these results indicated that C-1′ was unsubstituted due to decarboxylation of a precursor β-orcinol type polysubstituted depside (12).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's (uncorrected) were determined on a Kofler hot plate. ^{1}H-nmr spectra were recorded at 60 MHz (Varian T-60) in $CDCl_3$ with TMS as internal standard. ^{13}C-nmr spectra were obtained with a Varian XL-100 spectrometer operating at 25.15 MHz in $CDCl_3$ with TMS as internal reference. Eims were recorded by direct inlet with 70 eV ionization in a Varian MAT CH-7 instrument. Ir spectra were recorded as KBr pellets (Perkin-Elmer model 683). Tlc, cc, and ptlc were performed on Si gel from E. Merck, using petroleum ether-EtOAc (30:1) as eluent.

PLANT MATERIAL.—*L. brialmontii* was collected from rocks at the Caleta Copper Mine, Robert Island, Antarctica, in January 1987. Voucher specimens are deposited at the herbarium of the School of Chemistry and Pharmacy, Universidad de Valparaíso, Chile.

EXTRACTION AND ISOLATION.—The air-dried lichen thalli (750 g) were triturated and extracted at room temperature (24 h) successively with petroleum ether (bp 40–60°), $CHCl_3$, and Me_2CO. Extracts were concentrated in vacuum, obtaining 0.5 g, 1.2 g, and 1.6 g of crude material, respectively. This material showed two main products by tlc on Si gel using toluene-EtOAc-HCOOH (35:5:1). The resulting crude materials were chromatographed on a Si gel column and eluted with petroleum ether-EtOAc (30:1), yielding **2** (0.2 g, R_f 0.70) and **1** (1.1 g, R_f 0.62).

BRIALMONTIN 1 [**1**].—Compound **1** was isolated as white prisms, mp 102–104° ($CHCl_3$); ir ν max 2900, 1730, 1620, 1450, 1280, 850 cm^{-1}; ^{1}H nmr δ 6.63 (1H, s, H-1′), 3.81 (6H, s, 2-OMe, 4-OMe), 3.70 (3H, s, 2′-OMe), 2.36 (3H, s, 3′-Me), 2.30 (3H, s, 3-Me), 2.27 (3H, s, 5′-Me), 2.19 (9H, s, 5-Me, 6-Me, 6′-Me); eims (probe) (70 eV) *m/z* (rel. int.) $[M]^+$ 372 (4), 207 (100), 193 (1), 166 (2), 165 (2), 164 (6), 149 (3).

BRIALMONTIN 2 [**2**].—Compound **2** was isolated as white prisms: mp 106–109° ($CHCl_3$); ir ν max 3400, 2495, 1650, 1630, 1275, 810 cm^{-1}; ^{1}H nmr δ 11.42 (1H, s, 2-OH), 6.66 (1H, s, H-1′), 3.84 (3H, s, 4-OMe), 3.75 (3H, s, 2′-OMe), 2.67 (3H, s, 5′-Me), 2.32 (3H, s, 3-Me), 2.25 (3H, s, 3′-Me), 2.22 (3H, s, 5-Me), 2.05 (6H, s, 6-Me, 6′-Me); eims (probe) (70 eV) *m/z* (rel. int.) $[M]^+$ 358 (4), 193 (100), 166 (10), 165 (3), 164 (3), 149 (10).

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