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STUDIES ON CHILEAN LICHENS, XIV.[1] 2′-*O*-METHYLHIASCIC ACID, A NEW TRIDEPSIDE IN *CATILLARIA CORYMBOSA*

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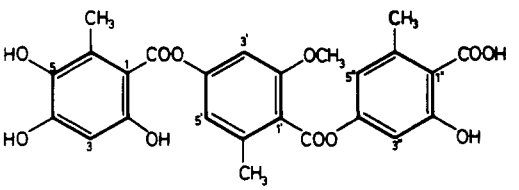
ABSTRACT.—2′-*O*-Methylhiascic acid [**1**], a new tridepside, was isolated from *Catillaria corymbosa*, an Antarctic lichen. Its structure was established by spectroscopic data.

In the course of our chemotaxonomic survey of the lichens of the Chilean flora, the study of *Catillaria corymbosa* (Hue) Lamb was undertaken. The chemistry of *Catillaria*, a lichen genus of the family Lecideaceae, is poorly known. Usnic acid, atranorin, (−)-placodiolic acid, (−)-pseudoplacodiolic acid, fumarprotocetraric acid, and zeorin have been reported from members of the genus (2).

$CHCl_3$ and Me_2CO lichen extracts were subjected to cc to yield atranorin (3), chloroatranorin (3) and 2′-*O*-methylhiascic acid [**1**], a new tridepside. These compounds, derived from hiascic acid, constitute a limited group of lichen substances. Elix and co-workers isolated 5-*O*-methylhiascic acid (4) and 4,5-di-*O*-methylhiascic acid (5) from *Parmelia horrescens* and *Parmelia pseudofetiscens*. Recently, Elix *et al.* (6) reported the structure of 2-*O*-methylhiascic acid from *Parmelinopsis neodamaziana*, in addition to 5-*O*-methylhiascic acid and 2,4,5-tri-*O*-methylhiascic acid.



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The structure of 2′-*O*-methylhiascic acid [**1**] was deduced from its spectral data. The ir spectrum showed two carbonyl absorptions due to depside ester linkages at 1720 and 1665 cm^{-1}. In the ^1H-nmr spectrum signals were exhibited corresponding to an isolated one-proton singlet at δ 1.54, assigned to a phenolic function at C-2 associated with an ester group, and a two-proton singlet at δ 9.94, assigned to phenolic groups at position 4 and 5. Aromatic protons at 3″, 3′, 5″, and 5′ appeared, respectively, as a series of four doublets at δ 6.69, 6.66, 6.60, 6.56, all with $J = 2.05$ Hz, and a one-proton singlet at δ 6.38, corresponding to position 3. A methoxyl function was detected as a singlet at δ 3.63, and three methyl groups appeared as singlets at δ 2.43, 2.37, and 2.27. The ^{13}C nmr (Table 1) confirmed the presence of three methyl groups at positions 6, 6′, and 6″ (21.3, 19.32, and 13.28 ppm); one methoxyl group at 59.79 ppm, and five non-substituted aromatic carbons (7,8). The mass spectrum did not exhibit a molecular ion, in

[1]For Part XIII, see Vinet *et al.* (1).

TABLE 1. ^{13}C-nmr Spectral Data of Compound **1**.

Carbon	Ppm
C-1	109.53
C-2	153.63[a]
C-3	101.76
C-4	153.77[a]
C-5	156.77
C-6	138.98
C-7	166.48[b]
C-8	21.31[c]
C-1′	118.13
C-2′	160.03
C-3′	107.16[d]
C-4′	152.21[e]
C-5′	114.12[f]
C-6′	137.98
C-7′	165.69[b]
C-8′	19.32[c]
2′-OMe	59.79
C-1″	118.13
C-2″	140.10
C-3″	107.35[d]
C-4″	152.03[e]
C-5″	114.15[f]
C-6″	138.98
C-7″	170.90
C-8″	13.28[c]

[a–f]Values may be interchanged.

agreement with similar results on other tridepsides derived from hiascic acid (4–6), and the principal ion fragments at *m/z* 168 (7), 166 (12), 165 (5), 151 (12), 138 (26), 124 (100) corresponded to rings formed by rupture of diphenyl ester linkages (4,5,7,8). The fragments due to ring B (*m/z* 165 and 138) are the only ones which explain the presence of a methoxyl group. Moreover, the peaks at δ 6.66 and 6.56 of the ^{1}H-nmr spectrum refer to aromatic protons on 3′ and 5′, respectively, and are explained by a reciprocal meta-type influence. This assignment is confirmed by comparison with the ^{13}C-nmr spectra of other tridepsides with the same B-ring structure (8). Finally, it is well known that all para-depsides derived biogenetically from β-orcinol are always methylated at positions 6 and 6′ (9,10); this leaves the 2′-position in ring B as the only plausible site for the methoxy group.

EXPERIMENTAL

GENERAL METHODS.—Mp's were determined on a Kofler hot plate and are uncorrected. ^{1}H- and ^{13}C-nmr spectra were recorded in DMSO-d_6 on a Varian XL-100 spectrometer operating at 100 MHz and 25.15 MHz, respectively, with TMS as internal standard. The chemical shift values are reported in ppm and the coupling constants in Hz. Eims were obtained by direct inlet with 70 eV using a Varian MAT CH-7 instrument. Ir spectra were recorded using KBr pellets (Perkin Elmer model 683). Si gel G (Merck) and Si gel 60 F-254 (Merck) were used for cc and tlc (0.25 mm), respectively.

PLANT MATERIAL.—*C. corymbosa* was collected on soil and rocks at Caleta Copper Mine, Robert Island, Antarctica, in February 1987. Voucher specimens are deposited at the herbarium of the School of Chemistry and Pharmacy, Universidad de Valparaiso, Chile.

EXTRACTION AND ISOLATION.—The air-dried lichen thalli (730 g) were triturated and extracted with $CHCl_3$ (1.5 liters × 2) at room temperature for 24 h. Evaporation of the solvent gave the crude extract (12.8 g) that was chromatographed on a column of Si gel. Elution was conducted with mixtures of C_6H_6 and EtOAc of increasing polarity, affording three compounds monitored by tlc on Si gel with toluene-EtOAc-HCOOH (35:5:1) as the eluent. A similar Me_2CO extract (13 g), worked up in the same way, afforded the same compounds, atranorin and chloroatranorin, which were identified by direct comparison (mp, tlc, and ^{1}H nmr), and 2′-*O*-methylhiascic acid [**1**].

2′-*O*-METHYLHIASCIC ACID [**1**].—Crystallized from Me_2CO as colorless prisms: mp 207–209°; ir ν max 3300, 2920, 2880, 1720, 1665, 1600, 1250, 840, 795 cm^{-1}; ^{1}H-nmr δ 10.54 (1H, s, 2-OH), 9.94 (2H, s, 4-OH, 5-OH), 6.69 (1H, d, J = 2.05 Hz, H-3″), 6.66 (1H, d, J = 2.05 Hz, H-3′), 6.60 (1H, d, J = 2.05 Hz, H-5″), 6.56 (1H, d, J = 2.05 Hz, H-5′), 6.38 (1H, s, H-3), 3.63 (3H, s, 2′-OMe), 2.43 (3H, s, 6-Me), 2.37 (3H, s, 6″-Me), 2.27 (3H, s, 6′-Me); eims *m/z* (rel. int.) 168 (7), 166 (12), 165 (5), 151 (12), 138 (26), 135 (10), 124 (100), 123 (68), 111 (17), 107 (12), 95 (27), 94 (11), 78 (58), 63 (72).

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