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2′-*O*-DEMETHYLPSOROMIC ACID FROM USNEA SP.

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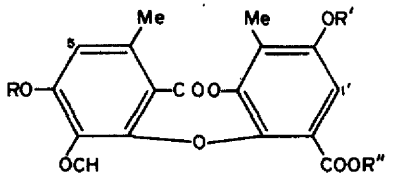
The depsidone psoromic acid (1) has been reported [1–3] in many lichen genera where it is often accompanied by a second depsidone which has been named conpsoromic by Culberson [4]. In this paper we report the isolation of the latter compound and the determination of its structure as 2′-*O*-demethylpsoromic acid (2).



	R	R′	R″
(1)	H	Me	H
(2)	H	H	H
(3)	Me	Me	Me
(4)	H	H	Me

Continuous extraction of the lichen with hexane afforded usnic acid identical (PMR, IR) with an authentic sample. Subsequent extraction of the lichen with Me_2CO afforded a mixture of psoromic and 2′-*O*-demethylpsoromic acids which was readily separated by fractional crystallization from Me_2CO. The PMR spectrum of the depsidone in DMSO-d_6 showed two 3-proton singlets at δ2.20 and 2.50 assigned to the 3′- and 6-Me groups respectively. The presence of two aromatic protons was indicated by the two 1-proton singlets at δ7.10 and 6.90. The latter signal, the broader of the two, was shown by double resonance to be coupled to the Me at δ2.50 and was assigned to the H-5. A 1-proton signal at δ10.53, attributable to an aldehyde proton, completed the spectrum. This spectrum was very similar to that of psoromic acid but lacked the –OMe resonance (δ3.90) and showed the H-1′ resonance shifted slightly up-field with respect to the corresponding resonance (δ7.18) in psoromic acid. Methylation of (2) with MeI/K_2CO_3 in Me_2CO gave Me psoromate Me ether (3) while treatment with CH_2N_2 afforded the Me ester (4). The structure of (3) was verified by comparison (IR, PMR) with an authentic sample prepared from psoromic acid and thus verified the structure of (2).

EXPERIMENTAL

PMR spectra were determined on a 60-MH_2 instrument.

Isolation of 2′-O-*demethylpsoromic acid.* Lichen was collected on rocks in Mifafi (alt. 3600), State of Mérida (MFK No. 106 on deposit in the herbarium of this faculty). The air-dried ground thallus was continuously extracted with hexane for 24 hr. On standing, the soln deposited yellow crystals of usnic acid. Subsequent extraction of lichen with Me_2CO afforded a white solid which was shown (TLC, Si gel HF_{254}; C_6H_6–dioxane–HOAc; 90:25:4) to consist of a mixture of two compounds. Fractional crystallization of the mixture from Me_2CO gave psoromic and 2′-*O*-demethylpsoromic acids mp 285° (Me_2CO–H_2O). IR_{max}^{KBr} cm^{-1} 2500–3600 (*br*), 1690, 1650, 1575, 1435, 1268, 1154, 1117, 800. (Found: C, 59.21; H, 3.36%. Calc. for $C_{17}H_{12}O_8$: C, 59.30; H, 3.48%.)

Permethylation of (2). The acid (100 mg), anhyd K_2CO_3 (200 mg), and dry Me_2CO (10 ml) were refluxed with MeI (1 ml) for 7 hr. After filtration, filtrate was evaporated to dryness to give Me psoromate Me ether mp 232° (MeOH–H_2O). PMR ($CDCl_3$) δ2.27 (*s*, 3 H, 3′-Me), 2.55 (*s*, 3 H, 6-Me), 3.84 (*s*, 3 H, OMe), 3.93 (*s*, 3 H, 2 × OMe), 6.66 (*s*, 1 H, H-5), 6.95 (*s*, 1 H, H-1′), and 10.31 (*s* 1 H, aldehyde). IR_{max}^{KBr} cm^{-1} 1731, 1705, 1692, 1600, 1550, 1380, 1340, 1279, 1251, 1213.

Me ester of (2). The depsidone (30 mg) was dissolved in Me_2CO (10 ml), cooled to 0° and treated with a slight excess of CN_2N_2 in Et_2O. After standing for 30 min the solvent was evaporated to give the Me ester as white crystals mp 226°. PMR (DMSO-d_6); 2.20 (*s*, 3 H, 3′-Me), 2.47 (*s*, 3 H, 6-Me), 3.85 (*s*, 3 H, OMe), 6.78 (*s*, 1 H, H-5), 7.03 (*s*, 1 H, H-1′), and 10.36 (*s*, 1 H, aldehyde). Psoromic Me ester was prepared in a similar manner to give white crystals mp 214° (MeOH–H_2O). PMR (DMSO-d_6)δ; 2.20 (*s*, 3 H, 3′-Me), 2.47 (*s*, 3 H, 6-Me), 6.72 (*s*, 1 H, H-5), 7.02 (*s*, 1 H, H-1) and 10.38 (*s*, 1 H, aldehyde).

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