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MALONPROTOCETRARIC ACID FROM *PARMOTREMA CONFORMATUM*

MYLES F. KEOGH

Instituto de Investigación Química, Facultad de Farmacia, Universidad de los Andes, Apartado 142, Mérida, Venezuela

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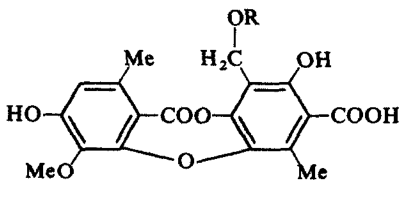
Key Word Index—*Parmotrema conformatum*; lichens; malonprotocetraric acid.

Among the secondary metabolites characteristic of the lichens, only two depsidones, salazinic and protocetraric acids, contain a benzyl alcohol group. While only the acetate of salazinic acid, galbinic acid, is known, three esters of protocetraric acid (**1**) have been isolated. The acetate (**1**), physodalic acid (**2**), and the fumarate (**3**) have been reported from a number of genera [1]. Recently, the succinate (**4**) has been isolated from *Parmelia repens* [2] and has also been reported in a number of species of the genus *Relicina* (Parmeliaceae) [3]. In this paper we report the isolation and structural elucidation of malonprotocetraric acid (**5**), a new member of this series obtained from *Parmotrema conformatum* (Vain.) Hale (Parmeliacea).

TLC analysis of a micro extract of the lichen showed the presence of usnic and protocetraric acids, and a new compound which was subsequently identified as malonprotocetraric acid. Extraction of the ground air-dried thallus with C_6H_6 removed the usnic acid and subsequent extraction with Me_2CO afforded a mixture of (**1**) and (**5**). Fractional crystallization of the mixture from Me_2CO gave pure samples of the two compounds. The protocetraric acid was identified by comparison (IR, NMR) with an authentic sample.

Both the IR and NMR spectra of (**5**) were very similar to those of the esters of (**1**). The NMR spectrum of (**5**) showed an aldehyde proton (δ 10,6), an aromatic proton (6,81) coupled to a methyl (2,50), and two, two-proton singlets (5,25 and 3,37). A second methyl (2,51) completed the spectrum. The signal at 5,25 was assigned to the benzyl methylene and its paramagnetic displacement by 0,6 ppm with respect to the corresponding signal in protocetraric acid indicated that the benzyl OH was acylated. The nature of the acid function was suggested by the two-proton signal at 3,37 which is characteristic of malonic acid and its esters.

The proposed structure was confirmed by synthesis. Protocetraric acid was refluxed with malonic acid in dioxane to afford a product which was identical (TLC, IR, NMR) with the natural product.



(**1**) R = H (**2**) R = Ac
(**3**) R = Fumaryl (**4**) R = Succinyl
(**5**) R = Malonyl

EXPERIMENTAL

Plant material. Samples of *Parmotrema conformatum* (Vain.) Hale (Voucher: MFK 217 in the Herbarium of this Faculty) were collected in la Carbonera, State of Mérida-Venezuela.

Protocetraric acid. Recrystallized from Me_2CO–H_2O (8:2) as white crystals mp 240°d. IR^{KBr}_{max}(cm^{-1}): 1752, 1655, 1649, 1607, 1570, 1270, 1200. NMR (60 MHz) (δ, DMSO-d_6): 2,50 (6H, 2 × Me), 4,63 (2H, Ar–CH_2), 6.81 (1H, ArH), 10,60 (1H, aldehyde).

Malonprotocetraric acid. Recrystallised from Me_2CO as white crystals mp 280°d. IR^{KBr}_{max}(cm^{-1}): 1752, 1735, 1690, 1650, 1275, 1260, 1208. $C_{21}H_{16}O_{12}$ (460.3) (Found: C, 54.62; H, 3.39; $C_{21}H_{16}O_{12}$ requires: c, 54.78; H, 3.47%).

Synthesis of malonprotocetraric acid. A soln of protocetraric acid (100 mg) and malonic acid (100 mg) in dioxane (20 ml) was gently refluxed for 4 hr. The reaction mixture was cooled to room temp., diluted with H_2O, the resulting gelatinous ppt. filtered and washed with H_2O. Recrystallization from Me_2CO removed some unreacted protocetracic acid and afforded the malonprotocetraric acid identical (TLC, IR, NMR) with the natural product.

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