2-Hydroxyconviresnic acid, a new depsidone from the lichen Sulcaria sulcata

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Abstract: A new depsidone, 2-hydroxyconviresnic acid, has been detected in a chemical race of the lichen Sulcaria sulcata, and the structure confirmed by partial organic synthesis.

The lichen Sulcaria sulcata (Lev. apud Jacqem.) Bystreck ex Brodo & D. Hawksw. (Parmeliaceae) is well known for its chemical diversity, and has recently been shown to exhibit at least six major chemical races (Obermayer & Elix 2002). In a continuation of our chemotaxonomic investigations of this species (Elix et al. 1999, Elix et al. 2000), we have recently encountered the new lichen metabolite 2-hydroxyconviresnic acid (3), together with its congeners virensic acid (1) and 2-hydroxyvirensic acid (2) in chemical race 3 (Figure 1).

Materials and Methods

Authentic material of 2-hydroxyconviresnic acid (3) was synthesized in the following manner. Sodium trisectoxyborohydride (42 mg, 0.20 mmol) was added to a solution of 2-hydroxyvirensic acid (2) (15 mg, 0.04 mmol) in anhydrous dioxane (14 ml), and the mixture stirred and heated at 80°C for 20 hours. The dioxane was then evaporated under reduced pressure, the residue dissolved in ethyl acetate and the solution washed in turn with dilute sulfuric acid, water (×2) and dried (MgSO4). Evaporation of the solvent afforded 2-hydroxyconviresnic acid (8.0 mg, 53%) as a colourless solid. 1H n.m.r. (CD3COCD3) δ 2.18, 2.30, 2.70, 3s, ArMe; 5.13, s, CH2. Mass spectrum m/z 273 (24%), 231, 213, 200, 265, 172 (39), 142 (41), 137 (25), 132 (31), 129 (25), 121 (27), 119 (25), 115 (23), 111 (24), 109 (31), 107 (30), 105 (57), 104 (43) and 91 (100) Standard TLC Rf values: Rf (A) 0.06; Rf (B) 0.22; Rf (C) 0.40; Rf (G) 0.28. Standard HPLC: Rf 18.2 min.; Rf 0.20.

Chromatography

Natural compounds were characterized by thin-layer chromatography (TLC) according to the methods standardized for lichen products (Culberson 1972, Elix & Ernst-Russell 1993), and by high-performance liquid chromatography (HPLC) with retention index values (Ri) calculated from benzoic acid and salicin acid controls (Elix et al. 2002, Feige et al. 1993). The HPLC was coupled to a photodiode array detector for ultraviolet spectroscopic comparisons. By this means, the ultraviolet spectra observed for the various compounds eluting in the HPLC chromatogram were recorded and computer-matched against a library of ultraviolet spectra recorded for authentic metabolites under identical conditions. In the present case, the correlation of ultraviolet spectra of the synthetic depsidone (3) with that of the lichen metabolite was greater than 99.9%.

Lichen Material

Sulcaria sulcata (Lev. apud Jacqem.) Bystreck ex Brodo & D. Hawksw.
China. Tibet, prov. Xizang, Nyainqentanglia Shan, 360 km E of Lhasa, near bend of the river Tsangpo, N side of Gyala Peri: 5 km S of Dongxiang village, 29°54′N, 94°52′E, 3200–3500 m, on Prunus in Rhododendron-Abies forest, W. Obermayer 06462, 20.08.1994 (GZU).

Discussion and Results

We have now confirmed the co-occurrence of atranorin and the depsidones (1)–(3) in a chemical race of Sulcaria sulcata. Although the depsidones virensic acid (1) and 2-hydroxyvirensic acid (2) are known lichen metabolites (Elix et al. 2000, Huneck & Yoshimura 1996), 2-hydroxyconviresnic acid (3) has not hitherto been recorded as occurring in nature. Comparisons were conducted between the synthetic depsidone (3) and the total acetone extracts from the several specimens of Sulcaria sulcata by TLC in four independent solvent systems and HPLC coupled to a photodiode array detector for ultraviolet spectroscopic comparisons. By this means, extracts of Sulcaria sulcata (chemical race 3) were shown to contain atranorin (minor), virensic acid (1) (minor), 2-hydroxyvirensic acid (2) (major) and 2-hydroxyconviresnic acid (3) (minor) (Figure 2).

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References


Figure 1. Structure of depsidones present in Sulcaria sulcata, chemical race 3.

Figure 2. HPLC of methanol extract of Sulcaria sulcata (chemical race 3) [W. Obermayer 06648 (GZU)]; Rf 18.2 min = 2-hydroxyvirensic acid (3); Rf 23.2 min = 2-hydroxyvirensic acid (2); Rf 25.8 min = virensic acid (1); Rf 29.4 min = atranorin.