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2-Methoxypsoromic Acid, a New Lichen Depsidone from *Pertusaria* and *Sulcaria* Species

John A. Elix,[A] *Judith H. Wardlaw,*[A] *Alan W. Archer*[B] *and Walter Obermayer*[C]

[A] Department of Chemistry, The Faculties, Australian National University, Canberra, A.C.T. 0200.
[B] 14 Romford Road, Epping, N.S.W. 2121.
[C] Institut für Botanik, Karl-Franzens-Universität Graz, Holteigasse 6, A-8010 Graz, Austria.

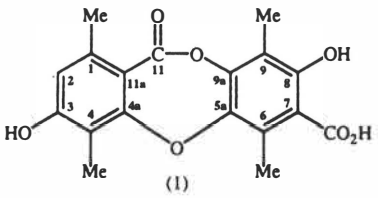
The depsidone 2-methoxypsoromic acid (4-formyl-3-hydroxy-2,8-dimethoxy-1,9-dimethyl-11-oxo-11*H*-dibenzo[*b*,*e*][1,4]dioxepin-6-carboxylic acid) (9) has been identified in several lichen species. The structure of compound (9) followed from a combination of spectroscopic data.

It appears likely that the majority of β-orcinol depsidones arise biosequentially from the common precursor hypoprotocetraric acid (1) by stepwise oxidation reactions.[1–4] Secondary *O*-methylation, nuclear chlorination, decarboxylation or side-chain esterification can be observed at various oxidation levels, ultimately leading to the vast array of naturally occurring derivatives.[3–5] From a biosynthetic viewpoint the lichen depsidone psoromic acid (2) is considered to be one of the most highly derived β-orcinol depsidones isolated from these organisms. In this compound the B-ring has not only undergone decarboxylation at position 7, but the 6-methyl group has been oxidized to a carboxy group. Six structurally related depsidones have been isolated from lichen sources including 2′-*O*-demethylpsoromic acid (3),[6] methyl psoromate (4),[7] methyl 2′-*O*-demethylpsoromate (5),[7] siphulellic acid (6),[8] methyl 2,7-dichloronorpsoromate (7)[9] and methyl 2,7-dichloropsoromate (8).[9]

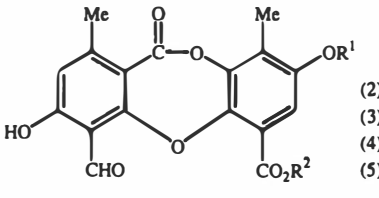
In this paper we describe the isolation and structural elucidation of a further biosynthetically related compound, 2-methoxypsoromic acid (9). This compound was detected in two lichens, *Sulcaria sulcata* (Lev.) Bystrek ex Brodo & D. Hawksw. and a *Pertusaria* species.

Extraction of the *Pertusaria* species with acetone, followed by the recrystallization of the extract led to the isolation of 2-methoxypsoromic acid (9), the structure of which followed from the spectroscopic properties.

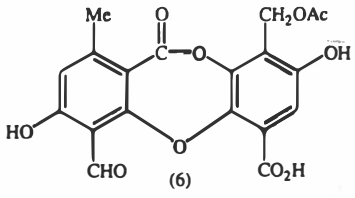
In particular the ^{1}H n.m.r. spectrum showed two *C*-methyl resonances (δ 2·33, 2·47), two *O*-methyl signals (δ 3·83, 3·88), an aromatic proton signal (δ 7·20), an aldehyde proton (δ 10·63) and an intramolecularly hydrogen-bonded hydroxy signal (δ 12·59). High-resolution mass measurement on the molecular ion established that the molecular formula of (9) was $C_{19}H_{16}O_9$. In addition to the molecular ion, the e.i. mass spectrum of (9) showed fragment ions at



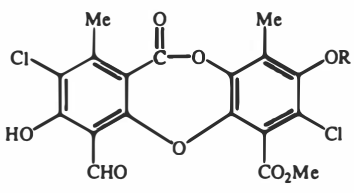
(1)



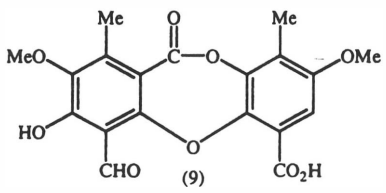
	R^1	R^2
(2)	Me	H
(3)	H	H
(4)	Me	Me
(5)	H	Me



(6)



(7) R = H
(8) R = Me



(9)

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m/z 360, 359, 342, 341, 208 and 207 consistent with that expected for structure (9). Indeed the fragment ions observed at m/z 208 and 207 arising from the A-ring confirmed that this ring was substituted by the methoxy group (the corresponding A-ring fragments occur at m/z 179 and 177 in psoromic acid).[10] Like other aldehyde-containing β-orcinol depsidones,[10] 2-methoxypsoromic acid (9) did not exhibit an M − 1 peak typical of aromatic aldehydes, presumably due due to the presence of alternative, low-energy fragmentation pathways in this multifunctional molecule.

Table 1. ^{1}H n.m.r. data (δ) for psoromic acid (2) and 2-methoxypsoromic acid (9)

Proton	(2)[11,A]	(2)[B]	(9)[B]
1-Me	2·44	2·54	2·47
9-Me	2·18	2·33	2·33
2-OMe	—	—	3·83
8-OMe	3·82	3·88	3·88
H 2	6·84	6·69	—
H 7	7·08	7·18	7·20
4-CHO	10·42	10·61	10·63
3-OH		12·34	12·59

[A] Spectrum run in $(CD_3)_2SO$.
[B] Spectrum run in $CDCl_3$.

Table 2. ^{13}C n.m.r. data (δ) for psoromic acid (2) and 2-methoxypsoromic acid (9)

Carbon	(2)[12,A]	(2)[B]	(9)[B,C]
1-Me	21·1	22·1	14·7
9-Me	9·2	9·9	9·7
2-OMe	—	—	60·1
8-OMe	56·0	56·6	56·4
4-CHO	193·7	196·4	196·7
6-CO_2H	165·3	166·2	166·1
C 1	152·4	154·4	155·5
C 2	116·8	118·1	161·3[b]
C 3	163·9	166·0	161·5[b]
C 4	110·6	111·6	112·0[c]
C 4a	164·4	161·7	166·0
C 5a	142·3	144·8	144·8[a]
C 6	129·7	123·1	123·0
C 7	107·7	108·8	108·6
C 8	154·5	156·0	155·7
C 9	122·6	124·8	124·4
C 9a	143·0	144·8	144·9[a]
C 11	160·4	158·3	159·7
C 11a	111·5	113·5	112·9[c]

[A] Spectrum run in $(CD_3)_2SO$.
[B] Spectrum run in $(CD_3)_2CO$.
[C] The assignment of chemical shifts bearing superscripts may be interchanged with shifts bearing the same superscript lower-case letter.

Ultimately, the marked similarities between the ^{1}H and ^{13}C n.m.r. spectra of psoromic acid acid (2) and 2-methoxypsoromic acid (9) (Tables 1 and 2), as well as the expected differences, were completely consistent with the formulation (9).

From a biosynthetic viewpoint, 2-methoxypsoromic acid (9) is a particularly highly derived β-orcinol depsidone, and the first representative of this class of compound where an aromatic nucleus has undergone *C*-hydroxylation.

Experimental

The general experimental details have been described previously.[13]

Extraction of Pertusaria *sp.*

The lichen *Pertusaria* sp. was collected on a tree trunk in *Nothofagus*–Cunoniaceae-dominated regrowth at an altitude of 2360 m on Mt. Kaindi, 5 km west of Wau, Morobe Province, Papua New Guinea, H. Streimann 17646, 13 March 1982 (CANB).

The lichen material (68 mg) was dried and extracted repeatedly with warm acetone. The combined acetone extract was then concentrated and on cooling *2-methoxypsoromic acid* (9) (4·8 mg, 7%) crystallized in colourless needles, m.p. >350° (dec.) (Found: mol. wt, 388·0792. $C_{19}H_{16}O_9$ requires mol. wt, 388·0794). The homogeneity of this compound was confirmed by high-performance liquid chromatography (h.p.l.c.) and ^{1}H n.m.r. spectroscopy. ν_{max} (KBr) 3520, 3250, 3150, 3000, 1730, 1640, 1580 cm^{-1}. Mass spectrum m/z 388 (M, 30%), 360 (24), 359 (100), 342 (20), 341 (43), 315 (15), 314 (30), 275 (18), 208 (20), 207 (16), 183 (12), 182 (15), 167 (30), 164 (16), 150 (13), 149 (95), 139 (13), 137 (12), 136 (17), 135 (13), 129 (10), 127 (12), 123 (16), 122 (12), 121 (20), 115 (15), 113 (15), 111 (17), 109 (15), 107 (15), 106 (22), 105 (24). Standard thin-layer chromatography (t.l.c.) R_F values:[14,15] R_F (A) 0·35; R_F (B′) 0·44; R_F (C) 0·39. Standard h.p.l.c.:[7,16] R_I 22; R_t 24·09 min.

Detection of 2-Methoxypsoromic Acid (9) by Comparative Chromatography

The lichen *Sulcaria sulcata* (Lev.) Bystrek ex Brodo & D. Hawksw. was collected on dead *Salix*, 8 km south of Tongjug village, 360 km east of Lhasa near bend of river Tsangpo, north side of Gyala Peri, Nyainqentanglha Shan, Xizang province, Tibet, China, at an altitude of 3350 m, W. Obermayer 6840 (GZU). Comparative h.p.l.c. and t.l.c. indicated the presence of atranorin (minor), 2-methoxypsoromic acid (9) (major) and an unknown (trace). The h.p.l.c. was coupled to a photodiode array detector for ultraviolet spectroscopic comparisons. By this means the spectra of the components eluting from the chromatogram were recorded and computer-matched against a library of ultraviolet spectra recorded for the authentic lichen metabolites under identical conditions. For the above substances the correlation of the ultraviolet spectra was greater than 99·9%.

Acknowledgments

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