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SHORT COMMUNICATION

THE CONSTITUENTS OF SOLORINA CROCEA: AVERYTHRIN 6-MONOMETHYL ETHER AND METHYL GYROPHORATE

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Abstract—The anthraquinone averythrin 6-monomethyl ether (III) and the depside methyl gyrophorate (V) were isolated from the lichen Solorina crocea (L.) Ach.

INTRODUCTION

THE CONSTITUENTS of *Solorina crocea* (L.) Ach., a lichen with bright orange undersurface and orange green upper surface, growing on damp soil at high altitudes, were investigated by Koller and Russ,¹ who proposed a structural formula (I) for the red pigment, solorinic acid.^{2,3} Recently, Anderson, Thomson and Wells⁴ confirmed Koller's structure of solorinic acid (I) by modern methods and by synthesis, while they reported the occurrence of norsolorinic acid (II) in the same lichen.



¹G. KOLLER and H. RUSS, Monatsh. Chem. 70, 54 (1937).

- ² W. ZOPF, Ann. Chem. 284, 111 (1895).
- ³ O. HESSE, J. Prakt. Chem. 292, 425 (1915).
- ⁴ H. A. ANDERSON, R. H. THOMSON and J. W. WELLS, J. Chem. Soc. (c), 1727 (1966).

This paper deals with the isolation of a probably new anthraquinone pigment, averythrin 6-monomethyl ether (III), and a new depside, methyl gyrophorate (V), along with solorinic acid (I) from S. crocea collected at Mt. Whistler, B.C., Canada.

RESULTS

From the ethereal extracts of *Solorina crocea*, solorinic acid (I) was separated as an orangered crystalline precipitate. From the filtrate, an orange-red pigment, compound A, and a colourless compound, compound B, were obtained by chromatography on silica gel.

The compound A, m.p. 215°, is soluble in Na₂CO₃ solution and shows a purple coloration with magnesium acetate in alcohol. The i.r. spectrum, ν_{max}^{KBr} (cm⁻¹); 1670, 1610 is similar to that of solorinic acid, while the u.v. spectrum, $\lambda_{max}^{dloxane}$ 223, 255 (sh), 267, 292, 320 and 445 nm, resembles that of averythrin, a metabolite of Aspergillus versicolor.⁵ In the mass spectrum, the pigment A gave a molecular ion peak at 368 (68 %) and fragments of mass units 353 (4.2 %), 339 (28%), 325 (48%), 311 (100%), 300 (56%) and 286 (16%). The high resolution mass spectrum showed the molecular ion peak at $368 \cdot 1260 \pm 17$. (Calc. for $C_{21}H_{20}O_6$:M⁺ 368.12598.) The molecular peak of pigment A, 368, is 16 less than that of solorinic acid (384), and the base peak of pigment A is M C_4H_9 (311) in contrast to that of solorinic acid at $M - C_5 H_{11}$ (313). The NMR spectrum in d₆-acetone showed following signals: $CH_3 - CH_2$ $(\delta 0.90, t J = 7.0 Hz), -CH_2 - CH_2 - (\delta 1.38, m), -CH_2 - CH = CH - (\delta 1.83, m), OCH_3$ $(\delta 3.98, s)$, -CH=CH- $(\delta 6.10 \text{ and } 5.42 \text{ m})$, aromatic H $(\delta 7.13, s)$, aromatic H $(\delta 7.24 \text{ and } 5.42 \text{ m})$ 6.75, J = 2.5 Hz), OH (δ 12.69, 12.23 and 10.68, s). These spectral data indicate the presence of hexenyl side-chain attached to 1,3,8-trihydroxy-6-methoxyanthraquinone nucleus. Due to the shortage of material, no further evidence could be obtained for showing that compound A is the 6-methyl ether of averythrin, but this structure is the most likely one, in view of its co-occurrence with solorinic acid,

	Compound B	Tenuiorin
NMR data (100 M Hz in d ₆ -DMSO)	2.26 (s) 3H 2.37 (s) 3H 2.38 (s) 3H 3.82 (s) 3H OCH ₃ 6.22 (b.s) 2H 6.66 (unresolved d) 4H Arom. H	2.27 (s) $3H$ 2.38 (s) $3H$ Arom. CH_3 2.42 (s) $3H$ 3.76 (s) $3H$ 3.82 (s) $3H$ 6.34 (b.s) $2H$ 6.62 (unresolved d) $4H$ Arom. H
Mass spectra	332 (1.8%) 182 (41%) 151 (52%) 150 (100%) 122 (47%) 94 (14%)	332 (3-7%) 182 (59%) 165 (100%) 164 (36%) 151 (89%) 150 136 (13%) 122 (93%) 94 (36%)

TABLE 1. NMR AND MASS SPECTRA OF COMPOUND B AND TENUIORIN

⁵ J. C. ROBERTS and P. ROFFEY, J. Chem. Soc. 3666 (1965).

The colourless compound, compound B, m.p. 288°, gave a blood-red colour with bleaching powder and no colour with *p*-phenylenediamine (PD reagent) or ferric chloride. The i.r. spectrum of compound B (ν_{max}^{KBr} (cm⁻¹); 1735 (sh), 1670 and 1616), is very similar to that of gyrophoric acid (VI) or tenuiorin (VII)* (ν_{max}^{KBr} (cm⁻¹) 1735 (sh), 1680 and 1610). The mass and NMR spectra of compound B closely resemble those of tenuiorin, except they show the absence of one OCH₃ group from compound B (Table 1). The above results suggest that compound B is methyl gyrophorate (V). Methylation of compound B with diazomethane gave a product identical with methyl tetramethylgyrophorate in i.r. and mass spectra. The identity was finally established by the comparison of TLC and i.r. spectra of substance B acetate and methyl tetraacetyl gyrophorate.

EXPERIMENTAL

The Isolation of Compound A

Lichen thalli (35 g) were extracted with ether in a Soxhlet. The extract was concentrated to separate solorinic acid, obtained as an orange-red precipitate from benzene (150 mg, m.p. 203°). Mass spectrum m/e (%): 384 (M⁺, 32·5), 366 (12·5), 341 (41·7), 328 (23·9), 313 (100) and 300 (5·7).

After removing the precipitate, the mother liquor was chromatographed on a silica gel column. The orange band of compound A was eluted with benzene-acetone (99:1), and this fraction was chromatographed further on silica gel using the same solvent system. Compound A (8 mg, m.p. 215°) was obtained as orange-red crystals from MeOH. Substance B was contained in the fraction eluted with benzene-acetone (9:1). On recrystallization from benzene-acetone compound B (90 mg, m.p. 288°) was obtained as colourless needles.

Demethylation of compound \hat{A} with HBr in AcOH gave a product, purified by preparative TLC, which showed λ_{max}^{EiOH} 221, 255 (sh), 266, 294, 323 and 453 nm, identical with that of averythrin.

Methylation of compound B with CH₂N₂ in Et₂O gave methyl tetramethylgyrophorate (from MeOH) (5.2 mg, m.p. 223–225°), i.r. $\nu_{\text{max}}^{\text{KBF}}$ (cm⁻¹): 1755, 1735, 1605. Mass spectrum m/e (%): 343 (14.7), 196 (100), 165 (23.5), 164 (12.7), 136 (12.0), 121 (13.2), 93 (6.6), 65 (6.5). The i.r. and mass spectra were identical with those of an authentic specimen of permethylated gyrophoric acid.

Acetylation of compound B with Ac₂O in pyridine gave compound B acetate (from acetone) (8.0 mg, m.p. 202-203°), i.r. v_{max}^{KBr} (cm⁻¹): 1770, 1750, 1615. The i.r. spectrum of the acetate was identical with that of methyl tetraacetyl gyrophorate prepared from tetraacetylgyrophoric acid.⁶

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* Gyrophoric acid was isolated from Gyrophora esculenta Miyoshi and tenuiorin was isolated from Peltigera aphthosa (L.) Willd.

⁶ G. Koller, Monatsh. Chem. 61, 147 (1932).