

## Chemical Studies on Lichens

### 8.\* Schizopeltic Acid, a Novel Lichen Dibenzofuran

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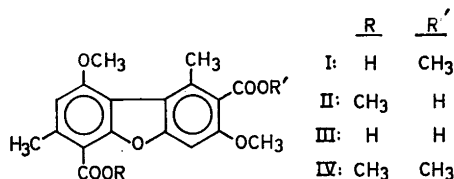
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The two fruticose North American lichens *Schizopelte californica* Th. Fr. and *Reinkella parishii* Hasse (both Roccellaceae) contain a new lichen acid, for which the name schizopeltic acid is proposed.

The acid melts at 228–230°. Analysis leads to the empirical formula  $C_{19}H_{18}O_7$ . The UV spectrum ( $\lambda_{max}$  241, 274, 290, 301, and 314 nm) suggests a dibenzofuranoid structure.<sup>1</sup> The IR spectrum shows two bands in the carbonyl region, corresponding to an ester and a carboxyl group. The NMR spectrum reveals the presence of five methyl groups, of which two are directly bonded to an aromatic ring, and two aromatic protons.

Upon hydrolysis with either sodium hydroxide or concentrated sulphuric acid, schizopeltic acid affords di-*O*-methylpannaric acid (III),<sup>2</sup> identified by comparison with an authentic sample. When schizopeltic acid is treated with diazomethane, dimethyl di-*O*-methylpannarate (IV)<sup>2</sup> is obtained, identified in the same way.

From this it follows that schizopeltic acid must be represented by either structure I or II.



**Experimental.** All melting points are uncorrected. The IR spectra were recorded with a Perkin-Elmer 137 (KBr discs). The UV spectrum was recorded with a Bausch & Lomb Spectronic 505. The microanalysis was carried out by the Analytical Department at the Institute of Chemistry, Uppsala.

Voucher specimens are to be found in the herbarium of Uppsala Botanical Museum (UPS). *Schizopelte californica* from California,

U.S.A., collected in 1966, quotation number R. Sant. 17887; *Reinkella parishii*, California, U.S.A., 1966, R. Sant. 17888.

Dry and grounded *Schizopelte californica* (24 g) was extracted continuously with acetone (500 ml) for 48 h. The acetone was evaporated and the solid residue treated with ether (200 ml). The ethereal solution was discarded and the remaining solid treated with 5 % sodium hydrogen carbonate ( $3 \times 100$  ml). Upon acidification (2 N hydrochloric acid) of the combined extracts, a precipitate was obtained, which was repeatedly recrystallized from aqueous acetone to yield schizopeltic acid (1.15 g, 4.8 %), m.p. 228–230°. (Found: C 63.5; H 5.22.  $C_{19}H_{18}O_7$  requires: C 63.7; H 5.06.) UV (in ethanol):  $\lambda_{max}$  241, 274, 290, 301, and 314 nm,  $\epsilon$  31 000, 15 000, 13 500, 10 000, and 10 500, respectively. IR:  $\nu_{max}$  1725 and 1680  $cm^{-1}$ . NMR (in  $(CD_3)_2SO$ ): signals at 2.61, 2.70, 3.94, 6.83, and 7.34 ppm (internal reference TMS), integrated 3:3:9:1:1.

Treated as above, *Reinkella parishii* (11 g) also afforded schizopeltic acid (0.42 g, 3.8 %).

Schizopeltic acid (25 mg) was dissolved in 2 N sodium hydroxide (10 ml) and kept at 60° over night. The precipitate formed upon acidification with dilute hydrochloric acid was recrystallized from ethanol to give di-*O*-methylpannaric acid (13 mg), m.p. 238–43° (decomp.), identified by comparison with an authentic specimen (IR, mixed m.p.).

Schizopeltic acid (25 mg) was dissolved in ice-cooled concentrated sulphuric acid (3 ml). After 5 min the solution was poured onto ice. The precipitate was recrystallized from ethanol to give di-*O*-methylpannaric acid (15 mg), identified as above.

Schizopeltic acid (40 mg) was dissolved in acetone (100 ml) and treated with an excess of ethereal diazomethane. After evaporation of the solvent, the residue was recrystallized from methanol to give dimethyl di-*O*-methylpannarate, (31 mg), m.p. 166–68°, identified as above.

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1. Shibata, S. *Acta Phytochim. (Japan)* **14** (1944) 9.
2. Åkermark, B., Erdtman, H. and Wachtmeister, C. A. *Acta Chem. Scand.* **13** (1959) 1855.

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