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Chemical Studies on Lichens

27.* The Structure of the Depside Alectorialic Acid

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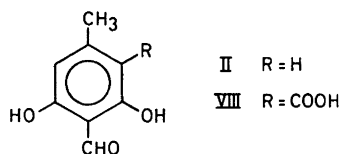
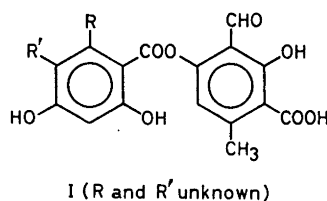
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In 1907 Zopf reported¹ the isolation of a novel compound from *Alectoria nigricans* (Ach.) Nyl., which he named alectorialic acid. The structure remained completely unknown until Solberg in 1967 suggested² the partial formula I for the acid. This was based on colour reactions and on the isolation of atranol (II) from hydrolyzed alectorialic acid. Furthermore, he suggested the empirical formula $C_{22}H_{20}O_{11}$ (Calc. C 57.4; H 4.4). However, elemental analyses (Found: C 57.7; H 4.4) also agree with the formula $C_{18}H_{16}O_9$ (Calc. C 57.4; H 4.3).

Solberg also found alectorialic acid in *Parmelia alpicola* Th. Fr.

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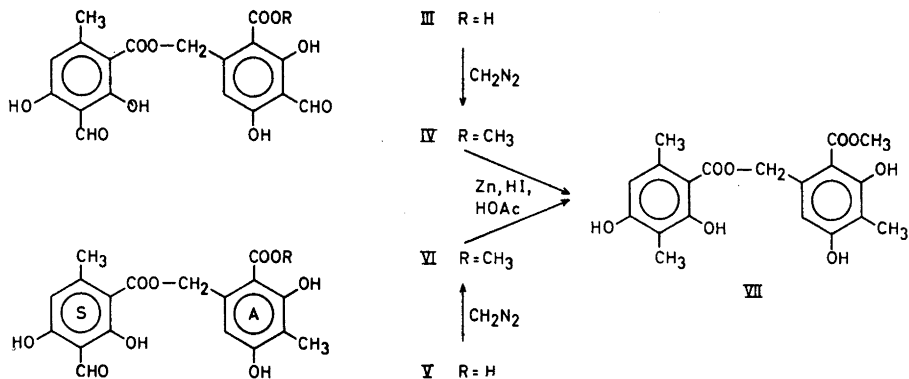
That alectorialic acid is a depside is evident from its UV spectrum,²⁻³ the lack of an M^{+} peak in its mass spectrum, the ready formation of II upon hydrolysis,² and the red colour reaction with calcium hypochlorite.

The NMR spectrum of alectorialic acid (in hexadeuteriodimethylsulphoxide) indicated the presence of two aromatically bound methyl groups (τ 7.63 and 7.99 ppm), one formyl group (τ -0.30 ppm), and two aromatic protons (τ 3.30 and 3.59 ppm). Furthermore, a two-proton singlet at τ 4.40 ppm was highly suggestive of a benzylic ester.

The only depside with a benzylic ester group known from lichens is barbatolic acid (III),⁴ which has been isolated from *Alectoria implexa* (Hoffm.) Nyl.⁴⁻⁵ and *Himantormia lugubris* (Hue) Lamb.⁶ Chemical and biogenetic considerations led us to believe that alectorialic acid might have the closely related structure V.

Upon reduction of methyl barbatolate (IV) Suominen obtained⁴ the depside VII. A similar reduction of methyl alectorialate (VI) afforded the same depside, identified by comparison with an authentic sample. This, taken together with the NMR data, established the structure of V except for the location of the formyl group.

However, since II is formed upon acid hydrolysis of V, the S ring must be haematommic acid (VIII) (II being produced by decarboxylation of VIII).



The A ring cannot afford II (or VIII) since the hydroxymethyl moiety formed upon hydrolysis will not be reduced under the reaction conditions.

Thus the structure of alectorialic acid is proved to be V. It is the second "barbatolic acid type depside" to be found in lichens.

Experimental. The NMR-spectrum was recorded with a Varian A-60, the IR-spectra with a Perkin-Elmer 157 spectrophotometer. All melting points are uncorrected.

Alectorialic acid (V) was obtained from *Alectoria nigricans* (collected at Vadsø, Norway) according to Solberg.² M.p. 176–179°. NMR-spectrum, see above.

Methyl alectorialate (VI). Alectorialic acid (0.25 g) was dissolved in hot dioxane (50 ml). The solution was rapidly cooled to room temperature and ether (125 ml) was added. The solution was further cooled to -5° and diazomethane (from 0.143 g *N*-nitroso-*N*-methylurea) in ether (10 ml) was added. After 10 s the excess of diazomethane was destroyed by addition of glacial acetic acid. The solution was concentrated to 10 ml and hot water (120 ml) was added. The precipitate was collected and recrystallized from methanol to afford VI (0.2 g), m.p. 202–204° (Found: C 58.2; H 4.71. Calc. for $\text{C}_{19}\text{H}_{18}\text{O}_9$: C 58.5; H 4.65).

Reduction of methyl alectorialate (VI). The ester VI (0.125 g) was dissolved in hot acetic acid (6 ml) and hydriodic acid (12 ml; $\rho = 1.7$) was added. The stirred solution was heated on a water bath (70–80°). Zinc powder (3 g) was added in small portions over 30 min. Hydriodic acid (3 ml) was then added and after 10 min

acetic acid (2 ml). Further zinc (1 g) was added in small portions and after 20 min the solution was filtered and diluted with water (50 ml). Sodium sulfite was added and the solution was extracted with ether (4×15 ml). The ether extracts were washed with water and sodium bicarbonate, evaporated to dryness, and the residue dissolved in methanol (4.5 ml) and dioxane (0.5 ml). Hot water (12.5 ml) was added and the precipitate was collected. Repeated reprecipitation gave the depside VII (0.074 g), m.p. 185–186° (lit.⁴ 186°), identified by comparison (IR, mixed m.p.) with an authentic sample, prepared according to Suominen⁴ from barbatolic acid (from *Alectoria implexa*) via the ester IV.

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