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THE STRUCTURE OF LEPRARIC ACID, A LICHEN CHROMONE

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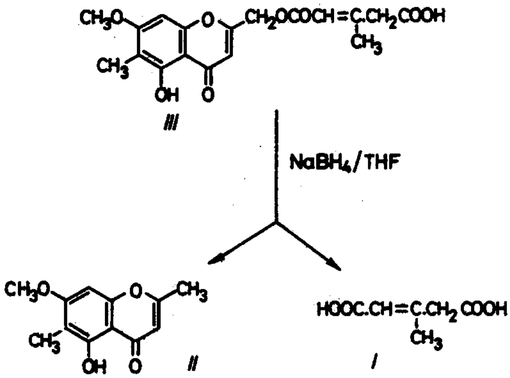
The constituents of the lichen Lepraria latebrarum Ach. have been studied by Zopf (1,2) and Hesse (3,4). Besides roccellic acid, atranorin and other compounds, the above named authors isolated a substance of unknown structure and called it lepraric acid. The compound formed colourless crystals of m.p. 155-156°C (decomp.) and its molecular formula was reported as $C_{19}H_{18}O_9$ (cf. for instance ref. 4); the occurence of lepraric acid in other lichens has not been reported.

Besides roccellic acid, from the above mentioned lichen, collected in Middle Slovakia, an unstable substance, m.p. 155-156,5°C (decomp.) was isolated by means of ether extraction and crystallization from a mixture chloroform-benzene, the formula of which according to elemental analysis and NMR spectrum was $C_{18}H_{18}O_8$. In the mass spectrum, the molecular ion was absent; only ion M-COOH of mass 317 has been observed. The compound contained two active hydrogen atoms and one methoxy group (Zeisel method). The infrared spectrum exhibited bands due to an aromatic system (1496 and 1595 cm^{-1}), a chromone system (1659 and 1625 cm^{-1}), α,β-unsaturated ester and carboxyl group (1714 cm^{-1}) and a carboxyl group (strong diffuse band at 2700-3300 cm^{-1}). The ultraviolet spectrum corroborated the presence of an aromatic system as well (λ_{max} 216, 233, 251, 292 nm; log ε 4.39; 4.46; 4.37; 3.88). According to NMR spectrum (measured in d_6DMSO and $CDCl_3$; Varian HA-100 instrument), the compound contained a methyl group on an aromatic nucleus (3H; 7,63 τ), methoxy group on aromatic nucleus (3H, 6.11 τ), $CH_3.C{=}CH.CO$- grouping (3H;

·7.82 τ), one proton at 4.28 τ, further -CO.CH$_2$.C=C- group (2H; singlet at, 6.93 τ),-COOCH$_2$-group) 2H; singlet at 4.91 τ) and two methine protons at 3.51 τ and 3.89 τ. The first singlet at 3.51 τ might be alloted to a proton on an aromatic nucleus and the other at 3.89 τ to a proton of -CO.CH=C- type.

Because of the presence of an ester group, we reduced lepraric acid by sodium borohydride in aqueous terahydrofuran and isolated neutral crystalline substance of m.p. 161-162°C (light petroleum). The other product was a crystalline acid, m.p. 138-141°C of molecular formula $C_6H_8O_4$ which gave positive tetranitromethane test. On hydrogenation, the acid yielded β-methylglutaric acid, m.p. 85°C (benzene), the identity of which has been proved by NMR spectrum and mixed melting point with authentic sample and further by comparison of methylesters by means of GC and infra-red spectra. The unsaturated acidic material was therefore a mixture of cis- and trans β-methylglutaconic acid (I), this was also in accordance with the melting point of the isolated acid.



The neutral compound (m.p. 161-162°C) was identified by means of infrared, ultraviolet and NMR spectra as eugenitin and the identity corroborated by mixed melting point with an authentic sample (II) /5/. Unlike lepraric acid, its methyl ester prepared on treatment with diazomethane exhibited in the infrared spectrum an additional carbonyl maximum at 1740 cm^{-1} due to non conjugated ester. The maximum at 1714 cm^{-1} in the spectrum of lepraric acid must therefore belong to the carbonyl of the conjugated ester as well as to the carboxyl group.

On the basis of all above discussed facts, lepraric acid has the structure III. Besides siphulin (6), lepraric acid represents a less common compound of chromone type found in lichens.

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