LIPIDS AND PHENOLS OF THE LICHEN Parmelia vagans

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The air-dry lichen Parmelia vagans (Nyl) (2.3 kg) was steeped in petroleum ether (bp 40-70°C). Concentration of the extract yielded a yellow crystalline substance with the composition $C_{18}H_{16}O_7$, mp 204-205 °C, $[\alpha]_D^{20}$ +490° (chlf), R_f 0.40 [TLC, Silufol; n-hexane–ethyl acetate (2:1)]. From its IR, UV and PMR spectra, the substance was identified as usnic acid [1]. Yield 0.46%.

When the extract was concentrated further, a lipid fraction (5.2%) was obtained in the form of a viscous golden liquid, n_D^{20} 1.4992, d_4^{20} 0.947, acid No. 2.8 mg KOH/g, saponification No. 191.2 mg KOH/g, iodine No. 127.3% I_2; unsaponifiable substances 5.4%. The lipids were saponified with a 0.5 N solution of KOH in methanol, which gave unsaponifiable (I) and saponifiable (II) fractions.

Fraction (I) was chromatographed on a column of silica gel and was eluted with petroleum ether. This gave 0.214 g of usnic acid (on the dry raw material).

Fraction (II) was methylated [2] and the methyl esters were analyzed by gas-liquid chromatography on a Vyrukhrom instrument with a flame-ionization detector. GLC conditions: steel column 0.4 × 150 cm filled with Chromaton N-AW (0.20-0.25 mm) upon which 10% of diethyleneglycol succinate had been deposited, the temperature of the column being 198°C and that of the evaporator 250°C.

The fatty acids were identified from their retention times with markers [3]. Fatty-acid composition (%): $C_{8:1}$–1.2; $C_{9:0}$–0.7; $C_{10:0}$–0.5; $C_{11:0}$–0.3; $C_{12:0}$–0.2; C_{X1}–1.3; $C_{13:0}$–0.4; $C_{14:0}$–1.2; C_{X_2}–0.3; $C_{15:0}$–0.4; $C_{15:1}$–0.3; $C_{16:1}$–15.7; $C_{16:1}$–1.3; $C_{17:0}$–0.8; $C_{17:1}$–0.6; $D_{18:0}$–5.9; $C_{18:1}$–11.0; C_{X_3}–1.6; $C_{18:2}$–47.2; C_{X4}–1.2; $C_{20:0}$–4.7; $C_{20:1}$–1.6; $C_{20:2}$–1.2; $C_{22:1}$–0.3; $C_{22:1}$–0.1. The main acids were linoleic, palmitic, and oleic. The presence of acids with even and odd numbers of carbon atoms is characteristic for Parmelia and other lichens [4].

After petroleum ether, the raw material was treated with acetone and the extract obtained was chromatographed on a column of silica gel, with elution by petroleum ether and then by petroleum ether–chloroform (9:1). The latter eluate yielded yellow-orange crystals with the composition $C_{18}H_{16}O_7$, mp 168-169°C $[\alpha]_D^{20}$ +500° (chlf), R_f 0.55. From its spectral characteristics (UV, IR, PMR, and mass spectra) the substance was identified as isousnic acid [5, 6], detected for the first time in the genus Parmelia.

Thus, the neutral lipids of Parmelia form a complex mixture of substances including usnic, isousnic, and fatty acids.

When the acetone extract was concentrated, a grey precipitate containing labile phenolic compounds was obtained. The fraction was acetylated and chromatographed on silica gel, giving an acetate with the composition $C_{26}H_{20}O_{14}$, mp 223-225°C, UV spectrum ν_{max}, nm: 234, 270, 342, and 354 (shoulder), R_f 0.36. Its IR, PMR and mass spectra showed that this substance was depsidone tetraacetate – salazinic acid [7]. The chromatography of the grey precipitate on silica gel with elution by methanol yielded a brown crystalline substance with mp 153-155°C which, according to its UV, IR, and PMR spectra was salazinic acid monorhamnoside.

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