THE NATURE OF THE POLAR RESIN ACIDS IN FIR OLEORESINS

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It was reported long ago that the oleoresin of the Siberian fir Abies sibirica Ledeb. contains a considerable amount of resin acids insoluble in petroleum ether [1, 2]. According to Piguleveskii [2], they make up about 30% of the weight of the initial oleoresin. Their chemical nature has remained unknown. In order to investigate these compounds, an ethereal solution of the oleoresin was treated successively with saturated aqueous sodium bicarbonate and with 1% aqueous sodium hydroxide. By this method, which we have used previously for isolating the "strong" and "weak" acids from an extract of the oleoresin of the Japanese stone pin [3], it was possible to obtain the corresponding mixtures of acids of the oleoresin of the Siberian fir. The yield of "strong" acids was 11% and that of the "weak" acids 40%. According to TLC, all the usual resin acids were present ony in the "weak" acid fraction.

The mixture of "strong" acids was obtained in the form of a pale yellow powder. Their mean molecular weight determined by vapor-phase osmometry was 756, which is more than twice that for the common diterpene acids and their derivatives. A portion of these acids was methylated with an ethereal solution of diazomethane and the methyl derivatives were chromatographed on silica gel (with elution by petroleum ether containing increasing amounts of diethyl ether). The molecular weight of the least polar component eluted in the first fractions was 510 (mass spectrometry). It was obtained with a yield of 8% on the fraction taken in the form of colorless crystals with mp 93-94°C (from acetonitrile), $[\alpha]_D^{20}$ −37.3° (c 4.84; $CHCl_3$); empirical formula $C_{32}H_{50}O_5$ (high-resolution spectrometry). Four of the oxygen atoms in its molecule were present in two methoxycarbonyl groups (PMR spectrum, δ scale, ppm; 364 and 379, singlets, 3 H each, $2COOCH_3$), and the fifth in the form of an α-enone grouping [IR spectrum: 1695 cm^{-1}; UV spectrum: λ_{max} 238 nm (log ε 3.54)]. We have found no compound with such an empirical formula and with such constants and spectral characteristics in the literature. The corresponding ketodicarboxylic acid has been given the name abiesonic acid.

The methylation and subsequent chromatography of a portion of the "weak" acids gave a mixture of methyl esters of resin acids described previously (48% on the initial fraction) [4] and a mixture of methyl esters of resin acids described previously (48% on the initial fraction) [4] and a mixture of methyl esters of polar "weak" acids (52%). Rechromatography of the latter led to the isolation of one of its main components, which also proved to be a new compound. It has mp 154-155°C and $[\alpha]_D^{21}$ +10.3° (c 3.86; $CHCl_3$); empirical formula $C_{31}H_{48}O_4$. Its molecule contains one methoxycarbonyl group (PMR spectrum: 3.64 ppm, singlet, 3H; IR spectrum: 1730 cm^{-1}), a γ-lactone ring (IR spectrum: 1770 cm^{-1}), and an exomethylene group (IR spectrum: 915, 1650, and 3080 cm^{-1}). The initial lactonic acid has been given the name of abiesolidic acid.

Abiesolidic acid was also isolated (in the form of the methyl ester) from the oleoresin of Abies mayriana Maybe et Kudo and from the silver fir (Abies alba Mill), containing, according to TLC, analogous mixtures of highly polar acids. The oleoresin of the latter fir yielded, in the form of its methyl ester, one more compound, with mp 225-228°C (from acetone); empirical formula $C_{31}H_{46}O_4$. Its molecule contained a hydroxy group (IR spectrum: 3610 cm^{-1}), a methoxycarbonyl group (PMR spectrum: 3.67 ppm, singlet, 3H), and, apparently, a methoxy group (3.46 ppm, singlet, 3H),

In the light of the results obtained and known facts concerning the presence in the bark of various species of fir of neutral lanostane and cycloartane triterpenoids [5, 6],

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it may be assumed that the petroleum-ether-insoluble resin acids of fir oleoresin are mainly highly oxidized compounds of this type. Triterpenoids have previously been found in fir oleoresins. The investigation of the compounds isolated is continuing.

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ALKALOIDS OF THE EPIGEAL ORGANS OF Crinum giganteum

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From the sum of the bases obtained by chloroform extraction from the bulbs with roots of Crinum giganteum L. (Family Amaryllidaceae) – 750.0 g of air-dried raw material collected on an experimental plot of the Transcaucasian zonal experimental station of VILR [All-Union Scientific-Research Institute of Medicinal Plants] (Kobuleti) in the flowering period –, after treatment with acetone, 3.54 g of lycorine has been isolated [2].

When the remainder of the total bases was chromatographed on a column of type KSK silica gel (1:30) using mixtures of chloroform and methanol in various proportions (99:1, 98:2, 97:3, 96:4, 95:5, ..., 9:1), lycorine (1.14 g), hippeastringe (1.17 g) [2], galanthamine (0.21 g), crinidine (0.45 g), tazettine (0.37 g), and base (I) with mp 240°C (methanol) [1, 2] (0.0143 g) were isolated.

The crinidine was identified on the basis of its physicochemical properties, and the lycorine, hippeastrine, tazettine, and galanthamine on the basis of their physicochemical properties and the absence of melting point depressions in mixtures of the alkaloids isolated with authentic samples.

Because of its small amount, base (I) could not be identified. Thus, six substances have been isolated from Crinum giganteum introduced into the conditions of Transcaucasia, and five known alkaloids have been identified.

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