GROUP COMPOSITION OF THE OLEORESIN OF THE SIBERIAN STONE PINE

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For the oleoresin of the Siberian Stone Pine (*Pinus sibirica* R. Mayr.), which is produced on the industrial scale, information is given in the literature on the quantitative and qualitative compositions of its mono- and sesquiterpene [1] and resin acids [2]. The remaining components have been characterized only in the qualitative aspect [3-6]. In order to determine the composition of this oleoresin more accurately, we have reanalyzed it using the scheme for the group separation of conifer oleoresins [7].

The isolation of the only "strong" (dicarboxylic) acid [8] of the oleoresin under investigation — 15-O-succinylisocupressic acid — was effected by the extraction of an ethereal solution of the oleoresin with a saturated solution of sodium bicarbonate, and it was characterized in the form of its dimethyl ester, $[\alpha]_D^{20}$ +38.9° (c 4.63; chloroform), yield 0.04%. Subsequent treatment of the ethereal solution of the oleoresin by the scheme mentioned [7] yielded its neutral (30.6%) and acidic (68.0%) fractions. The latter was methylated with diazomethane and subjected to chromatography, giving a mixture of methyl esters of resin acids (91.8% of the total acids) and of oxidized resin acids (8.2%). The main component (∿80%) of the mixture of methyl esters of the oxidized resin acids was methyl isocupressate [3], isolated by chromatography on silica gel.

The separation of 7.78 g of the neutral fraction of the oleoresin according to the scheme being followed [7] yielded 5.38 g of total hydrocarbons, 0.32 g of a fraction of carbonyl compounds and oxides, 1.40 g of a fraction of tertiary nonpolar alcohols (∿95% consisting of isocembrol and 4-epiisocembrol [4], the remainder being bisabolol with traces of unidentified alcohols), 0.20 g of a fraction of polar monohydric alcohols (from which 0.08 g of acetates of acetylated alcohols [7] and 0.10 g of δ-cadinol [5] were obtained), and 0.43 g of a fraction of polyfunctional compounds. Rechromatography of the latter gave 0.30 g of a mixture of pinusolide [3], isoagatholal, and methyl isocupressate (3:3:1 according to the PMR spectrum), and 0.10 g of agathadiol [6].

By means of the given scheme [7], the fraction of carbonyl compounds and oxides (a mixture of aldehydes, methyl esters of resin acids, and oxides) yielded 0.20 g of alcohols from aldehydes, 0.02 g of alcohols from methyl esters (∿95% lambertianol according to GLC and PMR spectroscopy), and 0.08 g of an oxide fraction. Rechromatography of the oxides on silica gel gave 0.02 g of the methyl ether of thymol, 0.03 g of 3,5-dimethoxystilbene [6], and 0.03 g of unidentified oxides.

The alcohols from the aldehyde were converted into the acetates and they were analyzed, like the acetylated alcohols, by GLC (5% of SE-30/Chromaton N-AW, DMCS, 210°C) with the addition of authentic samples. The presence of the compounds identified by GLC was confirmed by the PMR spectra (200.13 MHz) of the fractions under investigation. It was found that the aldehydes of the oleoresin consisted of isopimara-8,15-dien-18-al (9.8%), sandaracopimarinal (3.3%), palustral and isopimarinal (48.6% ∿1:1 according to the PMR spectrum), dihydroabietinal (11.0%), abietinal (26.0%), and neoabietinal (1.3%).

The alcohols that were acetylated consisted of isopimarinol (40.0%), 13E-labd-8(20),13-dien-15-ol (31.5%), abietinol (6.5%), dehydroabietinol (3.5%), and other alcohols (18.5% — traces of neoabietinol, of sandaracopimarinol, and unidentified alcohols).

According to GLC (5% SE-30/Chromaton N-AW, DMCS, 90-240°C/2°C; for the dieterpenes, 120-240°C/2°C) the hydrocarbons consisted of monoterpenenes (89.1%), sesquiterpenes (9.8%), and diterpenes (1.2%). The latter consisted of cembrene (26.9%), isocembrene (15.6%), neocembrene (30.1%), isopimaradiene (21.0%), dehydroabietane (1.7%), and abietadiene (4.7%).

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