SOME TERPENOID COMPONENTS OF THE NEEDLES OF THE SIBERIAN STONE PINE

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The needles of *Pinus sibirica* R. Mayr. (Siberian stone pine), which from a waste of the timber-felling industry have long attracted the attention of research workers. The GLC method has been used to study the mono- and sesquiterpene hydrocarbons [1, 2], the oxygen-containing monoterpene compounds [1], the phenols [2], and the fatty and resinous acids of the needles and lopping litter of the Siberian stone pine [1-3].

We have investigated the air-dry (23% moisture) needles of the Siberian stone pine collected in September, 1979, in the Tomsk province. A petroleum ether extract obtained in a Soxhlet apparatus (yield 5.5%) was separated by treatment with 1% sodium hydroxide solution into acidic and neutral fractions (yields 52 and 45% on the extract, respectively). By methylation of the acid fraction with diazomethane and chromatography on silica gel, we isolated a mixture of methyl esters of nonpolar resin acids and fatty acids (30% of the total amount of methyl esters; in TLC on Silufol, this mixture gave a single extended spot the boundaries of which coincided with the spots of the markers methyl isopimarate and methyl dehydroabietate).

According to GLC (5% of XE-60 on Chromaton N-AW, DMCS, 2.5 m × 3 mm, glass, 140-250°C/4°C), this mixture contained not less than 28 components, of which the following were identified by the method of additives: methyl lambertianate (62.5%), methyl dehydroabietate (6.2%), methyl isopimarate (3.3%), methyl levopimarate + methyl palustrate (2.8%), methyl arachidate (1.5), methyl stearate (1.0%), and methyl palmitate (1.5%). Methyl abietate coincides with methyl lambertianate under the GLC conditions used, but the identification of the latter was confirmed by its PMR spectrum [4]. According to the spectrum, the amount of methyl abietate did not exceed the amount of methyl isopimarate (evaluated from the relative integral intensities of the H_{14} signal of methyl abietate) and, therefore, lambertianic acid is the main resin acid of the needles studied.

Chromatography of the neutral fraction of the needle extract (5.64 g) on silica gel gave, successively, 2.21 g of combined hydrocarbons, 0.49 g of waxes, 0.12 g of a mixture of waxes and methyl lambertianate (GLC, PMR spectrum), and 0.43 g of a mixture of two substances which were then separated by chromatography on silica gel with 5% of silver nitrate. One of them (yield 0.15 g) was identified from its constants and spectral characteristics as 5S,8S-germacra-1E,6E-diene-5-ol (n_D^{18} 1.4945, $[\alpha]_D^{18} - 178°$), which has been isolated previously from the oleoresin of the Yeddo spruce [5]. The second, with mp 83-84°C, proved to be nonacosan-10-ol, a usual component of conifer needles [6]. It was identified from its mass spectrum, which corresponded to that given in the literature [6].

According to GLC, the total hydrocarbons consisted of a mixture of mono- and sesquiterpenes [1, 2] with traces of diterpenes. The hydrocarbon with the smallest R_f value (TLC on Silufol, pentane) was isolated by chromatography on silica gel (with pentane as eluent) in a yield of 0.15 g. It was identified by its IR, UV, and PMR spectra as germacrene D [7], n_D^{20} 1.5100, $[\alpha]_D^{20} - 279°$ (c 1.9; chloroform); according to the literature [7]: $[\alpha]_D - 240°$. This hydrocarbon has not been detected previously in the needles studied.

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MASLINIC ACID FROM THE LEAVES OF *Eucalyptus viminalis*

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According to the literature, the leaves of the ribbon eucalyptus contain cineol, β-sitosterol, 5-hydroxy-4',7-dimethoxy-6,8-dimethylflavone, 4',5-dihydroxy-7-methoxy-6,8-dimethyl flavone [1], and quercitrin [2].

When the total acidic components of a chloroform extract of the leaves of the ribbon eucalyptus were chromatographed on silica gel 40/100 mμ, we obtained a fraction (eluent ethyl acetate—petroleum ether (15 : 85)) containing, according to GLC, a triterpene compound (R_f 0.65, Silufol, chloroform—methanol (4 : 1), visualization with a 20% ethanolic solution of tungstophosphoric acid). From a concentrated ethereal solution of this fraction previously washed with 0.5% aqueous sodium bicarbonate and with water, a precipitate deposited, and from an ethanolic solution of this, by repeated purification on a column with acidic activated carbon of type B and silica gel 40/100 mμ, we obtained a compound $C_{30}H_{48}O_4$, mp 265-268°C (from aqueous ethanol).

Its mass spectrum showed that this substance belonged to the pentacyclic triterpenes. The spectrum contained the following characteristic peaks: M^+ 472 (2.76%), m/z 248 (93.98%), 223 (25.84%), 203 (100%). The nature of the retrodiene breakdown indicates the presence of a double bond in the 12,13 position. The peak with m/z 248 is characteristic for ion **a** [3], including rings D and E of a pentacyclic triterpene and containing a carboxy group, the splitting off of which led to the ion with m/z 203. The presence in the mass spectrum of the peak of an ion with m/z 223 including rings A and B shows the position of the two hydroxy groups in rings A and B (or only in ring A) [3].

The PMR spectrum (pyridine-d_5, TMS) contained a doublet at 3.35 ppm, J = 9 Hz, and a sextet at 4.02 ppm, $J_1 = 9$ Hz, $J_2 \approx 9$ Hz, and $J_3 \approx 4$ Hz, 1 H each. These signals are due to two vicinal hemihydroxylic protons, H-3 and H-2, respectively. A multiplet at 5.44 ppm, 1 H, is due to an olefinic H-12 proton. The PMR spectrum (CD_3OD, TMS) contains in the 0.8-1.1 ppm region five singlets with an intensity ratio of 1 : 2 : 1 : 1 : 2, which shows that the substance belongs to the β-amyrin derivatives.

Thus, on the basis of its physical constants and spectral characteristics, the compound isolated can be identified as maslinic acid, or 2,3-dihydroxyolean-12-ene-28-carboxylic acid [4, 5]. This conclusion was confirmed by the production on the methylation of the substance described with diazomethane of a compound $C_{31}H_{50}O_4$, mp 227-229°C, in the mass spectrum of which the mass of ion **a** [3] had been increased by 14 mass units, while the IR spectrum proved to be identical with that of methyl maslinate [4].

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