A NEW LABDANE ACID FROM THE NEEDLES OF *Pinus sylvestris*

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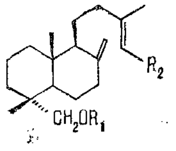
In view of the detection in the needles of *Pinus sylvestris* L. (Scotch pine) of new labdane acids of the 4-epiagathic (dehydropinifolic [1]) and 4-epiimbricatolic (pinifolic [2, 3]) types, we have begun a more detailed investigation of its chemical composition.

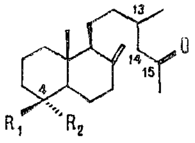
The sum of the acids obtained by the usual method [4] from the petroleum-ether-soluble fraction of an isopropanol extract of the needles was chromatographed on silica gel. The fractions eluted before pinifolic acid were methylated with diazomethane and rechromatographed on silica gel. The methyl esters of two new acids were isolated with yields of 0.32 and 0.27% on the total amount of free acids.

The first ester was an oil with $[\alpha]_D^{23}$ +34.2° (c 2.17; chloroform). According to its PMR spectrum (60 MHz, HMDS, CCl_4, δ scale), its molecule contained the fragment $-C(CH_3)=CH-COOCH_3$ (2.08 and 3.50 ppm, 3H, each, singlets; 5.54 ppm, 1H, broadened singlet) and the fragment $>C-CH_2OAc$ (1.94 ppm, 3H, singlet, 3.54 and 3.83 ppm, 1H each, AB system with J_{AB} = 11 Hz). Mass spectrum, m/z (%): M^+ 376 (3), 135 (39), 107 (51), 93 (38), 81 (57), 54 (39), 42 (100). When the compound under investigation was reduced with lithium tetrahydroaluminate in diethyl ether, the known 4-epiagathadiol (I, R_1 = H, R_2 = CH_2OH) was obtained with mp 107-109°C, $[\alpha]_D^{22}$ +37.4° (c 2.4; chloroform); according to the literature [1]: mp 107-109.5°C $[\alpha]_D$ +41.5°. Its PMR spectra agreed with that given in the literature [1]. Consequently, the initial ether was methyl 18-acetoxyanticopulate (I, R_1 = OAc, R_2 = $COOCH_3$).

The second ester was an oil with $[\alpha]_D^{20}$ +14.7° (c 8.86; chloroform), $C_{22}H_{36}O_3$ (high resolution mass spectrometry). Its PMR spectrum differed from that of dimethyl pinifolate by the displacement of the doublet signal of Me_{13} downfield by 0.03 ppm, and also by the fact that it contained, in place of the signal of one methoxycarbonyl group, the singlet of a methyl ketone group (2.00 ppm). These facts, in the light of the empirical formula, permit us to suggest for the compound under investigation structure (II), differing only by the configuration at C_4 from the keto ester (III) obtained by Zinkel et al. [5] from the needles of *Pinus elliotii*. In the mass spectrum of the compound obtained, as in the mass spectrum of its C_4 epimer [5], the main peak was that of the ion with m/z 121.



I



II, III

II. $R_1 = CH_3$, $R_2 = COOCH_3$

III. $R_1 = COOCH_3$, $R_2 = CH_3$

The isolation of the ester (II) indicates the possible presence in the initial mixture of acids of 15-formyllabd-8(17)-en-18-oic acid (by analogy with [5]). However, the possibility that the acid isolated in the form of the ester (II) was present in the native form cannot be excluded, since in our case the time of methylation of the acids with diazomethane did not exceed 15 min, and the formation of the methyl ketone (III) from the corresponding C_{15} aldehyde is complete only after 15 h [5].

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TERPENOIDS OF THE OLEORESIN OF *Abies semenovii*

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The oleoresin of *Abies semenovii* B. Fedtsch. (Semenov's fir) (1000 g), collected in the Aflatun gorge in the Tian-Shan was separated into neutral (520 g) and acidic (400 g) components by treatment with an 80% solution of caustic soda. Fractional distillation of the neutral part of the oleoresin yielded 196 g of monoterpenes (bp 60-100°C/10 mm Hg), 53 g of mono- and sesquiterpenoids (bp 70-130°C/0.1 mm Hg), and 248 g of diterpenoids.

The following hydrocarbons were identified in the monoterpene fraction by GLC [1]: α-pinene (7.2%), camphene (3.6%), β-pinene (10.1%), 3-carene (55.7%), β-phellandrene (21.2%), limonene (2.5%), myrcene (1.0%), and γ-terpinene (traces). The mono- and sesquiterpene fractions were separated by chromatography on Al_2O_3 (neutral, activity grade II) into sesquiterpene hydrocarbons (16 g) and oxygen-containing compounds (35 g). The hydrocarbons were analyzed by GLC (Biokhrom-01; glass capillary column 52 m long, OV-101); the following were determined from their relative retention times and by the method of additives: sibirene (11.2%), β-bisabolene (45.6%), γ-bisabolene (11.5%), α-bisabolene (3.0%), δ-cadinene (7.0%), β-selinene (2.5%), caryophyllene (0.9%), and an unidentified hydrocarbon (9.5%), and, in very small amounts, α-longipinene, longicyclene, α-copaene, α-ylangene, and α-humulene. Isolated by column chromatography on SiO_2 and SiO_2 + 20% $AgNO_3$, and identified by their PMR spectra, were α-ylangene, sibirene, β-selinene, δ-cadinene, and β- and γ-bisabolenes. The unidentified hydrocarbon was also isolated: it had $[\alpha]_D^{20}$ −9.1°. PMR ($CDCL_3$, ppm): 0.84 (3H, doublet, J = 7 Hz); 1.60, 1.63, and 1.70 (singlets, 3H each); 5.38 (1H, multiplets); 1.21 (1H, multiplet); 1.43 (1H, multiplet); 1.75-2.42 (9H). ^{13}C NMR spectrum (ppm): singlets at 143.3, 133.1, 122.2, and 45.5; doublets at 121.8 and 44.4; triplets at 33.0, 31.7, 31.1, 30.3, and 28.4; and quartets at 23.8 (two), 20.7, and 17.6. The mass spectrum had the peak of M^+ at 204 and strong peaks corresponding to ions with masses of 121 and 136. Of the sesquiterpenes described in the literature, the hydrocarbon isolated is closest, in relation to these properties, to β-alaskene [2].

By chromatography of the oxygen-containing mono- and sesquiterpenes on SiO_2 and SiO_2 + 20% of $AgNO_3$ we isolated bisabolol (∿30% fraction), bornyl acetate, geranyl acetate, geraniol, borneol, cubebol, epicubebol, and nerolidol.

The diterpenoids were represented mainly by the bicylic labdane alcohol cis-abienol (mp 40-41°C, 90% fraction), identical with an authentic sample according to melting point and spectral characteristics. Not only cis-abienol, but also palustral, abietinal, and abietinol were isolated chromatographically and identified.

The acids of the oleoresin of Semenov's fir were studied in the form of the methyl esters by the GLC method [1]. The main components were abietic acid (64.5%) and neoabietic acid (25%), with smaller amounts of sandaracopimaric acid (1.2%), dehydroabietic acid (1.1%), palustric or levopimaric acid (8%), and isopimaric acid (traces).

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