hydroxide solution was boiled at 130°C for 1.5 h and was then neutralized with 10% H_2SO_4 solution to pH 4-5. The degradation products were extracted with ethyl ether. The ethereal extract was evaporated and the residue was dissolved in 1 ml of ethanol and chromatographed in systems 1 and 2. Gallic acid (VI) and chloroglucinol (VII) were detected.

SUMMARY

The leaves of Azara microphylla Hook., have yielded a new flavonoid glycoside which has been called azamicroside. From its physicochemical and spectral characteristics its most probable structure has been established as myricetin 3-O-α-L-dirhamnoside.

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TERPENOIDS OF THE ESSENTIAL OIL OF Ledum palustre

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The chemical composition of the essential oil of crystal tea ledum of the ordinary variety growing in Western Siberia has been studied. Eighteen terpenoids have been isolated and identified from their spectral characteristics. Linalyl acetate, α-terpenyl acetate, carvone, geraniol, β-farnesene, calamenene, p-mentha-1(7)-8-dien-2α-ol, and p-mentha-1(7)-8-dien-2β-ol have been isolated from the essential oil of crystal tea ledum for the first time. Compounds of the p-menthane and aromadendrane series were found as the main components.

The officinal medicinal plant Ledum palustre L. (crystal tea ledum) (family Ericaceae) is widely distributed in the territory of the Soviet Union [1]. The main active principle, possessing an antitussive action, is the sesquiterpene ledol [2]. For medical purposes, the preparation of the raw material (leafy shoots) is carried out mainly in Belorussia and in the north of the European part of the USSR. In order to expand the raw materials basis, we have studied the composition of the mono- and sesquiterpenoids of the essential oil of Ledum palustre L. var. vulgare Ledeb. (crystal tea ledum, common variety), which grows widely in the territory of Western Siberia [3].

The composition of the monoterpene hydrocarbons (19.6%) was determined by gas–liquid chromatography (GLC); the main component was limonene (17.6%). From the fraction of sesquiterpene hydrocarbons (4.0%) we isolated and identified from their spectral characteristics α-humulene, alloaromadendrene, calamenene, β-farnesene, and δ-cadinene, and we also isolated an unidentified hydrocarbon with a molecular weight of 204.

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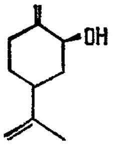
The main component of the sesquiterpene hydrocarbon fraction was alloaromadendrene.

In the fraction of oxygen-containing mono- and sesquiterpene compounds (59.1%) of the essential oil of crystal tea ledum, we detected linalyl acetate, α-terpenyl acetate, bornyl acetate, carvone, geraniol, palustrol, ledol, and a mixture of three isomeric secondary alcohols (I), (II), and (III), which were separated into the individual components after acetylation. According to PMR spectroscopy, all the alcohols contained an isopropenyl group while one contained a $-CH=C(CH_3)-$ and each of the other two a $>C=CH_2$ group.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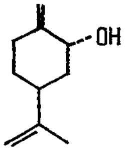
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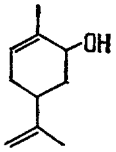
III

When the ^{13}C NMR spectra of the alcohols with the exocyclic double bonds were compared with the spectra of a large group of monoterpene compounds [4], and also with the calculated spectra using substituent increments [5], it was seen that they agreed with the structures of p-mentha-1(7)-8-diene-2α-ol (I) and p-mentha-1(7)-8-diene-2β-ol (II). These two compounds differ only by the fact that in alcohol (I) the hydroxy group is equatorial, and in alcohol (II) it is axial. Alcohol (III) had in place of the exomethylene group a trisubstituted double bond. This assignment of the structures agrees well with the presence of limonene and carvone in the essential oil.

This is the first time that linolyl acetate, α-terpenyl acetate, carvone, geraniol, β-farnesene, calamenene, and alcohols (I) and (II) have been isolated from the essential oil of crystal tea ledum. It must be mentioned that limonene and the products of its oxidation – alcohols (I) and (II) and carvone – predominated among the monoterpene compounds. The amount of the main biologically active component – ledol – in the essential oil of the Siberian sample of crystal tea ledum was low (about 4%) in comparison with the amount in European specimens (23.0-37.0%) [6]. The qualitative compositions of the mono- and sesquiterpenoids of the essential oil of the sample investigated differed considerably from the composition of the essential oils of crystal tea ledum growing in the European part of the Soviet Union [7-9] and some areas of Finland [10, 11], where myrcene, palustrol, and ledol have been found as the main components.

EXPERIMENTAL

IR spectra were taken on a UR-20 instrument. PMR spectra were recorded in CCl_4 on a Varian A-56/60 instrument with HMDS as internal standard, the chemical shift of which was taken as δ 0.05 ppm, and the ^{13}C NMR spectra on a Bruker-Physik AG HX-90 instrument. Mass spectra were taken on a MS 902 instrument with a glass inlet system (120°C), 70 eV.

The analytical GLC of the monoterpene hydrocarbons was carried out on a Chrom-32 instrument using a 3.75 m × 0.3 mm column with TCEP at a rate of flow of carrier gas (nitrogen) of 30 ml/min and a column temperature of 76°C.

Preparative GLC was performed on a Pye-105 instrument with a 5 m × 6 mm column containing 10% of Tween-65 on Celite-22 (0.16-0.20 mm), rate of flow of carrier gas (nitrogen) 100 ml/min, column temperature 130°C.

The essential oil (2.85%) was obtained by steam distillation of leafy shoots of crystal tea ledum of the common variety collected in July, 1981, in the fruit-bearing phase in a sphagnum bog in a pinewood in the environs of Tomsk.

Isolation of the Hydrocarbons. The essential oil (58.78 g) was chromatographed on Al_2O_3 (neutral, activity grade II) at a ratio of substance to sorbent of 1 : 15. Petroleum ether eluted hydrocarbons (15.39 g) and ethanol eluted oxygen-containing compounds (34.72 g).

Fractionation of the Hydrocarbons. The hydrocarbon fraction (15.39 g) was subjected to vacuum distillation into monoterpene hydrocarbons (11.52 g) (bp 70-110°C/10 mm Hg) and sesquiterpene hydrocarbons (2.37 g) (the still residue).

Analysis of the Monoterpenes. The monoterpene hydrocarbons were analyzed by the GLC method. From the relative retention times, in all the monoterpene fractions, we identified limonene and traces of α- and β-pinenes. Quantitative determination was carried out by the simple normalization method.

Identification of the Sesquiterpene Hydrocarbons. The fraction of sesquiterpene hydrocarbons from the essential oil (2.37 g) was chromatographed on SiO_2 at a ratio of substance and sorbent of 1 : 25. Petroleum ether eluted eight fractions (1-8). The first fraction (0.22 g) contained an unidentified compound. IR spectrum: 765, 1380, 460 cm^{-1}, M^+ 204. From the results of PMR spectroscopy, alloaromadendrene was identified in the third fraction (0.52 g), δ-cadinene in the fourth (0.29 g), calamenene in the fifth (0.05 g), β-farnesene in the sixth (0.01 g), and α-humulene in the eighth (0.09 g).

Identification of the Oxygen-Containing Mono- and Sesquiterpenoids. The fraction of oxygen-containing terpenoids (18.60 g) was chromatographed on SiO_2 at a ratio of substance and sorbent of 1 : 15. Gradient elution (petroleum ether–diethyl ether) yielded fractions 1-6. Ethanol eluted a fraction of more polar compounds (3.16 g) which was not investigated. Fraction 1 (0.85 g) consisted of linolyl acetate (IR, PMR). Palustrol was identified (IR, PMR; n_D^{20} 1.4910) in fraction 2 (2.27 g). Fraction 3 (1.74 g) consisted of a mixture of α-terpenyl acetate, bornyl acetate, and geranyl acetate (PMR). From fraction 4 (0.35 g) by chromatography on SiO_2 geranyl acetate and carvone (IR, PMR) were isolated. Fraction 5 (1.23 g) consisted of a crystalline mass and after fractional recrystallization from petroleum ether ledol was identified (IR, PMR), mp 104-106°C. By rechromatography on SiO_2 impregnated with 20% of $AgNO_3$, fraction 6 (2.76 g) yielded geraniol (0.14 g) (PMR) and a mixture of alcohols (I), (II), and (III) (2.5 g).

The mixture of alcohols (1.6 g) was acetylated with 3 ml of acetic anhydride and 10 ml of pyridine at 0°C for 12 h. The reaction products were extracted with petroleum ether, and the solvent was distilled off to give 1.5 g of a mixture of acetates. By preparative GLC, the acetates of alcohols (I), (II), and (III) were obtained in the individual form (0.42, 0.60, and 0.02 g, respectively).

PMR spectrum of (I), ppm: 1.70 (singlet, 3 H); 1.95 (singlet, 3 H); 4.65 (singlet, 2 H); 4.80 (singlet, 1 H); 4.91 (singlet, 1 H); 5.33 (triplet, 1 H, J = 5.0 Hz).

PMR spectrum of (II), ppm: 1.70 (singlet, 3 H); 2.03 (singlet, 3 H); 4.70 (broadened singlet, 4 H); 5.10 (doublet of multiplets, 1 H, width at half-height 20 Hz).

PMR spectrum of (III), ppm: 1.87 (singlet, 3 H); 2.13 (singlet, 3 H); 4.68 (singlet, 2 H); 5.18 (broadened singlet, 1 H); 5.65 (broadened singlet, 1 H).

The acetate of alcohol (I) (0.3 g) was saponified with a 10% solution of KOH in ethanol at 50°C for 3 h. Chromatography on SiO_2 (10 g with 20% diethyl ether as the eluent) led to the isolation from the reaction mixture of alcohol (I) (0.15 g), $[\alpha]_D^{20}$ – 74.7° (in the pure form).

IR spectrum, cm^{-1}: 880, 905, 1050, 1460, 3070, 3615.

PMR spectrum, ppm: 1.70 (singlet, 3 H); 3.27 (triplet, 1 H), J = 3 Hz; 4.65 (singlet, 3 H); 4.78 (singlet, 1 H).

^{13}C NMR spectrum: 20.85 – quartet; 29.81, 32.45, 38.92, 108.78, 109.48 – triplets; 37.95, 72.15 – doublets; 149.13, 149.78 – singlets.

By similar treatment, 0.3 g of the appropriate acetate yielded 0.2 g of the alcohol (II) $[\alpha]_D^{20}$ –5° (in the pure form).

IR spectrum, cm^{-1}: 900, 1095, 1455, 1650, 3090, 3630.

PMR spectrum, ppm: 1.60 (singlet, 3 H); 3.83 (doublet of multiplets, 1 H, width at half-height 20 Hz); 4.51 (singlet, 3 H); 4.78 (singlet, 1 H).

^{13}C NMR spectrum: 20.53 – quartet; 32.51, 33.58, 41.84, 103.82, 108.19 – triplets; 43.94, 71.83 – doublets; 148.37, 150.85 – singlets.

SUMMARY

1. The composition of the mono- and sesquiterpenoids of the essential oil of Ledum palustre L. var. vulgare Ledeb. has been studied.

2. It has been established that the composition of the essential oil of a Siberian specimen of crystal tea ledum differs from those of European specimens.

3. The predominating components of the monoterpenoids of the essential oil studied were compounds of the para-menthane series: limonene, p-mentha-1(7)-8-dien-2-ols (I) and (II); and, among the sesquiterpenoids, allo-aromadendrene, palustrol, and ledol.

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STRUCTURE AND STEREOCHEMISTRY OF LAPIFERIN*

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Lapiferin, $C_{22}H_{34}O_6$, mp. 137-138°C, $[\alpha]^{21}_{D}$ +63 (c 1.3; chloroform), a diester of the new carotane alcohol lapiferol with angelic and acetic acids, has been isolated from the roots of *Ferula lapidosa* Eug. Korov. On the basis of chemical transformations and spectral characteristics, the structure of 10α-acetoxy-6α-angeloyloxy-8α,9α-epoxy-trans-carotan-4β-ol has been proposed for it.

Continuing the separation of the neutral components of the roots of *Ferula lapidosa* Eur. Korov. [1], we have isolated a new compound with the composition $C_{22}H_{34}O_6$ (mass-spectrometrically), which we have called lapiferin (I).

The IR spectrum of lapiferin is typical for sesquiterpene esters, containing strong absorption bands of ester carbonyl groups of saturated (1740 cm^{-1}) and unsaturated (1715 cm^{-1}) acids and bands of a trisubstituted double bond (1655, 970 cm^{-1}) [2], of a hydroxy group (3540 cm^{-1}), and of ester–C–O bonds (1230-1260 cm^{-1}) [1].

A maximum in the UV spectrum with λ_{max} 218 nm (log ε 3.96) confirms the presence of an α,β-unsaturated ester carbonyl in the molecule of (I) [2].

The results of the fragmentation of lapiferin under the action of electron impact show that it belongs to the group of esters of sesquiterpene alcohols. In the mass spectrum there are the peaks of ions corresponding to a fragment of the molecule without an isopropyl group having m/z 351 $(M - C_3H_7)^+$, the residue of a sesquiterpene alcohol with m/z 234, and also peaks due to the ejection of residues of angelic and acetic acids with m/z 294 $(M - C_5H_8O_2)^+$ and 251 $(M - C_5H_8O_2 - CH_3CO)^+$ and of a molecule of water with m/z $(M - C_5H_8O_2 - 17)^+$.

In the PMR spectrum of (I) ($CDCl_3$) in the strong-field region the signals of the methyl groups of an isopropyl residue appear in the form of a doublet (6 H) at 0.85 ppm with $^3J = 7$ Hz, of an angular methyl group in the form of a singlet at 1.26 ppm (3 H), and of a methyl attached to a carbon atom bearing oxygen at 1.42 ppm (s, 3 H). In addition, there are the signals of an epoxide proton at 2.86 ppm (d, $^3J = 5.5$ Hz) [1], of two gem-acyl protons at 4.83 ppm (d, $^3J = 5.5$ Hz) and 5.18 ppm (sx, $^3J = 10.0; 10.0; 3.0$ Hz), and of acetic and angelic acid residues.

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