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A STUDY OF THE CHEMICAL COMPOSITION OF THE ESSENTIAL

OIL OF *Ledum palustre*

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Eight substances have been isolated by preparative chromatography on silica gel from the essential oil of *Ledum palustre* L., collected in the Kostroma oblast in August. Six of them have been described previously for this essential oil (myrcene, palustrol, ledol, allocaromadendrene, 6-methyl-2-methylenecycloocta-5,7-dien-3-ol, and cyclocolorone) and two are new substances not described in the literature: a colorless liquid with a pleasant smell having the composition $C_{10}H_{14}O_2$, mp 108-111°C/4 mm Hg, n_D^{20} 1.4925, d_4^{20} 1.002, $[\alpha]_D^{20}$ 0°C, which has been called lepalol, and a colorless liquid with a pleasant smell having the composition $C_{10}H_{12}O$, bp 91-93°C/4 mm Hg, n_D^{20} 1.5175, d_4^{20} 0.9444, $[\alpha]_D^{20}$ 0°C, which have been proposed for lepalin and lepalol on the basis of their IR, UV, and NMR spectra. The physical constants of all the substances isolated and the characteristics of their IR, NMR, and mass spectra are given.

The chemical composition of the essential oil of crystal tea *Ledum palustre* L. varies considerably. Some authors connect this with the growth site [1-3] and others with botanical varieties [4, 5].

The composition of the essential oil of crystal tea *Ledum palustre* L. growing in the USSR has been studied by N. P. Kir'yalov. He established that the essential oil of crystal tea *Ledum palustre* L. from

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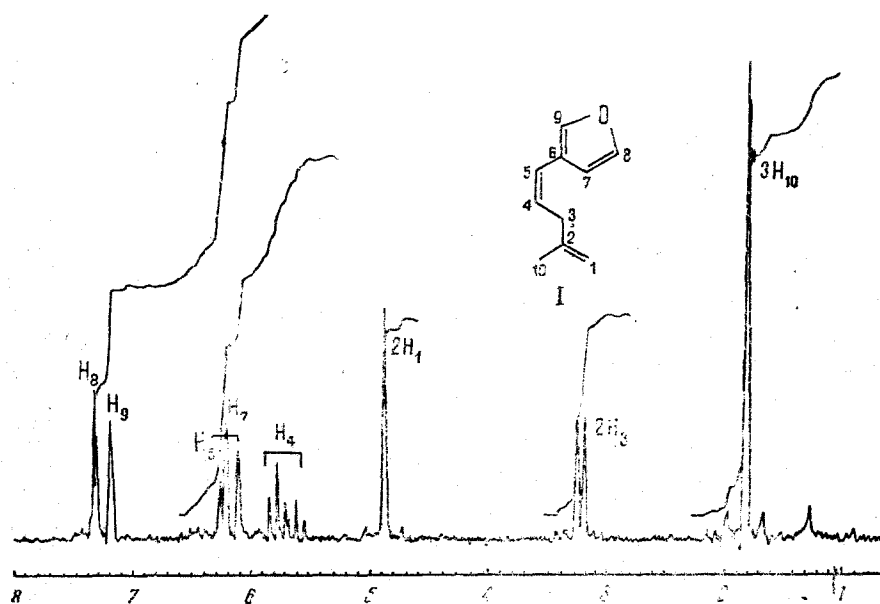


Fig. 1. NMR spectrum of lepalin.

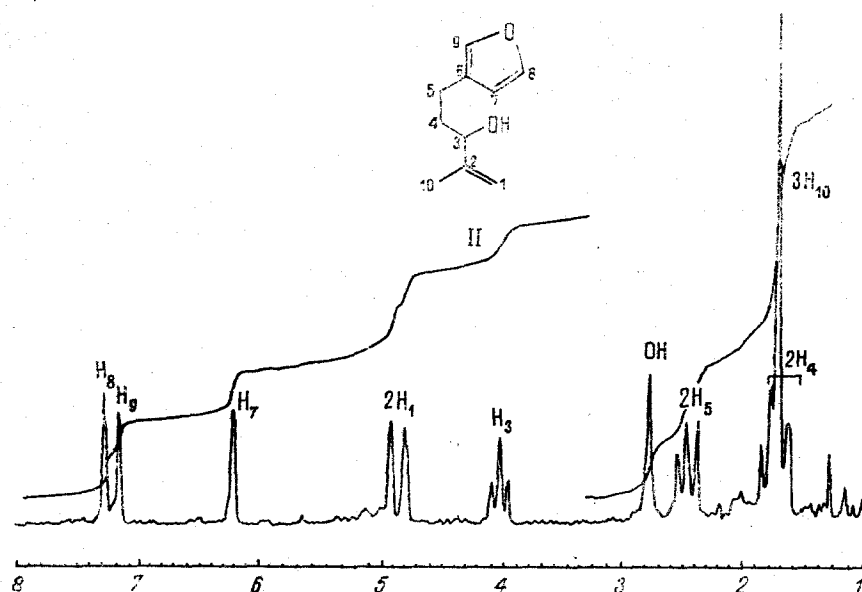


Fig. 2. NMR spectrum of lepalol.

the Leningrad oblast and other oblasts of the European part of the USSR consists of myrcene, ledol, and palustrol while the essential oil of crystal tea ledum from the Sayan mountains includes p-cymene, α -pinene, and germacrene although no morphological differences whatever were found between these plants.

We have studied the chemical composition of the essential oil of crystal tea ledum collected in the Kostroma oblast in August. Eight substances were isolated by preparative chromatography on the silica gel: the myrcene, palustrol, and ledol mentioned above; alloaromadendrene and 6-methyl-2-methylenoocta-5,7-dien-3-ol, which have been isolated previously from the essential oil of crystal tea ledum growing in Finland; cyclocolorenone [6], isolated for the first time from the essential oil of crystal tea ledum; and two substances not previously described in the literature, $C_{10}H_{12}O$, and $C_{10}H_{14}O_2$, which we have called lepalin (I) and lepalol (II).

Lepalin and lepalol each contain a furan ring, as is shown by the signals of the protons in the NMR spectra (Figs. 1 and 2): w.res.m 6.15 (H_7), 7.12 (H_9) and 7.25 ppm (H_8) in (I) and br.s 6.33 (H_7), 7.18 (H_9), and 7.28 ppm (H_8) in (II), and also by a positive Ehrlich test:

with an ethanolic solution of p-dimethylaminobenzaldehyde in the presence of hydrochloric acid, lepalol gives a red coloration and lepalin a red-violet one [7, 8]. The presence of furan rings in (I) and (II) is also in harmony with their IR and UV spectra. The IR spectra of lepalol has absorption bands at (cm^{-1}) 3420-3370 (OH), 3080, 3140, 3110, 1650, 1600, 1505 (furan ring), 1450, and w 1800 (vinyl methylene). The IR spectrum of lepalin has (ν_{max} , cm^{-1}): 3140, 3090, 3030, 1650, 1610, and 1510 (furan ring), 1440, and w 1780 (vinyl methylene).

The UV spectrum of lepalol has λ_{max} (in ethanol) 203 and 210 nm, 6200 and 6000, respectively (furan ring), and that of lepalin has λ_{max} (in ethanol) 225, 230, and 274 nm, ϵ 25,000, 25,200, and 4000, respectively, i.e., in the UV spectrum of (I) the absorption bands of the furan ring appear at longer wavelengths than in the spectrum of (II). Furthermore, there is an additional absorption band at 274 nm. Thus, unlike lepalol, lepalin contains no hydroxyl, but it has one additional double bond which forms a conjugated system with the double bonds of the furan ring, i.e., it is between C_4 and C_5 . In the NMR spectrum of lepalin (Fig. 1), the signals of the protons of this double bond are located at 5.62 ppm ($J_{4,5} = 16.0$ Hz), sextet (H_4) and 6.11 ppm ($J_{5,4} = 16.0$ Hz), d (H_5), which is also in harmony with the conjugation of the double bond with the furan ring, and the position of the signal of the H_5 proton is explained by the influence of the currents of the furan ring.

The NMR spectrum of (I) also has the signals of the protons of two methylene groups, one of them being a vinyl methylene, as is confirmed by the presence of a singlet (2 H) in the 4.78 ppm region, while the second methylene group is located between double bonds. Both its protons interact only with H_4 , giving a doublet in the spectrum at 3.23 ppm ($J_{3,4} = 7$ Hz). A 3 H singlet at 1.72 ppm is the signal of the protons of a methyl group attached to a carbon atom with a double bond. Since there are olefinic protons at C_4 - C_5 , only the position at C_2 remains for the methyl. These facts permit the assumption of structure (I) for lepalin. The suggested structure agrees with the isoprene rule, where two isoprene units are joined in the "head" to "tail" manner.

Lepalol also contains a vinyl methylene group and a methyl on a double bond, but as mentioned above, it does not contain a double bond in the C_4 - C_5 position. Furthermore, the NMR spectrum of lepalol has a 1 H triplet in the 4.15 ppm region ($\Sigma J = 14$ Hz), which is the signal of a proton in the geminal position to a hydroxyl. It follows from this that lepalol contains a secondary hydroxy group.

To determine the position of the OH group in lepalol we used a chemical shift reagent — $\text{Eu}(\text{fod})_3$. The greater downfield shift of the protons of the methyl group and of the vinyl methylene group as compared with the other signals, including the signal from 2 H_5 , shows the position of the hydroxyl at C_3 . Thus, lepalol has the structure (II).

EXPERIMENTAL

The NMR spectra were recorded on a Varian JNM-4H-100 MHz spectrometer in CCl_4 solution with TMS as internal standard using the δ scale, and the mass spectra on a Varian CH-8 spectrometer at an ionizing voltage of 75 V and a temperature of 30°C. Thin-layer chromatography was performed on Silufol plates in the petroleum ether-diethyl ether (1:1) system, the spots being revealed with a 0.5% solution of KMnO_4 in 0.5% H_2SO_4 .

The percentages of the components are given relative to the initial essential oil.

Preparation of the Essential Oil. The essential oil was obtained from 100 kg of leaves and thin branches of *Ledum palustre* by steam distillation in an industrial apparatus. The oil obtained (1.3 kg of a grease-like mass) was kept at -5°C for two days, after which the solid part was separated off by filtration in vacuum and was recrystallized from ethanol to give colorless needles with the composition $\text{C}_{15}\text{H}_{26}\text{O}$, mp 104 – 106°C , identified from their NMR spectrum as ledol.

The liquid fraction of the oil was separated by vacuum distillation into three fractions: fraction I, 50 – $80^\circ\text{C}/4$ mm Hg; fraction II, 80 – $100^\circ\text{C}/4$ mm Hg; and fraction III, residue.

Isolation of Myrcene. When 100 ml of fraction I was chromatographed on silica gel L 100/160 μ , petroleum ether eluted a liquid substance with R_f 0.53 containing a small amount of a second substance with R_f 0.41 (petroleum ether system), and after rechromatography followed by steam distillation, a pure substance with R_f 0.50 was obtained in the form of a colorless mobile liquid having a peculiar pleasant smell, with the composition $\text{C}_{10}\text{H}_{16}$, d_4^{20}

0.7900, n_D^{20} 1.4690. The constants of the substance correspond to those given in the literature for myrcene [9]. The NMR spectrum corresponds to the structure of β -myrcene (natural myrcene). Yield 23%.

Isolation of Alloaromadendrene and Lepalin. Fraction II (100 ml) was chromatographed on silica gel of type L 100/160 μ . Petroleum ether eluted two substances, and after their rechromatography and distillation we obtained:

a) an odorless colorless mobile liquid with R_f 0.83 and the composition $C_{15}H_{24}$, d_4^{20} 0.9232, n_D^{20} 1.5000. The constants and IR spectrum corresponded to those given for alloaromadendrene [10, 4]. The NMR spectra agreed with this structure; and

b) a second substance, which we called lepalin, with R_f 0.72, also a colorless liquid but with a sharp pleasant smell, composition $C_{10}H_{12}O$, M^+ 148, mp 91-93°C/4 mm Hg, d_4^{20} 0.9444, n_D^{20} 1.5715, $[\alpha]_D^{20}$ 0°C.

The yield of alloaromadendrene was 2.1% and of lepalin 1%.

Isolation of Palustrol and of 6-Methyl-2-methyleneocta-5,7-dien-3-ol. When fraction II was chromatographed with a mixture of petroleum ether and ether (9:1), two substances were isolated. After their rechromatography and purification by vacuum distillation, we obtained:

a) a colorless mobile liquid with the composition $C_{15}H_{26}O$, d_4^{20} 0.9647, n_D^{20} 1.4910. From its constants, the substance corresponded to palustrol [11]. The NMR spectrum agreed with the structure suggested for it. On TLC, the method of detection under the conditions described above does not show up palustrol; and

b) a colorless mobile liquid with the composition $C_{10}H_{14}O$, d_4^{20} 0.8985, n_D^{20} 1.4870, R_f 0.47. In its composition and NMR spectrum, the substance isolated corresponded to 6-methyl-2-methyleneocta-5,7-dien-3-ol [5].

Isolation of Lepalol. When fraction II was chromatographed in petroleum ether-diethyl ether (8:2 and 7:3), ledol was isolated, while petroleum ether-diethyl ether (1:1) gave lepalol. After rechromatography and purification by distillation, a colorless mobile liquid (2.4%) with a pleasant smell having the composition $C_{10}H_{14}O_2$, M^+ 166 (mass spectrometrically), bp 108-111°C/4 mm Hg, n_D^{20} 1.4925, d_4^{20} 1.002, $[\alpha]_D^{20}$ 0°C, R_f 0.37, was obtained. NMR spectrum of (II): s 1.80 ppm (3 H_{10}); m 1.85 ppm (2 H_4); m 2.55 ppm (2 H_5); t 4.15 ppm ($\Sigma J = 1.40$ Hz) (H_3); br.s 4.92 and 5.04 ppm (2 H_1); br.s 6.33 ppm (H_7); br.s 7.28 ppm (H_8); br.s 7.18 ppm (H_9).

Cyclocolorenone [6] was isolated from the still residue.

SUMMARY

1. Myrcene, palustrol, ledol, alloaromadendrene, 6-methyl-2-methyleneocta-5,7-dien-3-ol, and cyclocolorenone, and also two new substances which have been called lepalol and lepalin, have been isolated from the essential oil of *Ledum palustre* L. collected in the Kostroma oblast.

2. On the basis of spectral characteristics, structural formulas (I) and (II) have been suggested for lepalin and lepalol.

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A NEW SESQUITERPENE LACTONE — ALKHANOL FROM *Artemisia fragrans*

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The structure of the new sesquiterpene lactone alkanol from *Artemisia fragrans* has been studied. On the basis of spectral and chemical characteristics a most probable structure has been suggested for alkanol.

A sesquiterpene lactone alkanin isolated from *Artemisia fragrans* Willd. has been reported previously [1]. The present paper gives information on a new sesquiterpene lactone also isolated from this plant which has been called alkanol.

Alkanol has the composition $C_{15}H_{22}O_4$, mp 179–181°C. The IR spectrum (Fig. 1) shows, in the region of characteristic frequencies, bands of an OH group (3360 cm^{-1}), of a CO group of a γ -lactone ring ($1775, 1760\text{ cm}^{-1}$), and of a double bond (1665 cm^{-1}). Acetylation led to a diacetyl derivative $C_{19}H_{26}O_6$ with mp 194–196°C, the IR spectrum of which contained the band of the CO group of a γ -lactone ring (1775 cm^{-1}) and the bands of acetyl CO groups ($1725, 1270$ and 1240 cm^{-1}). There was no band of OH groups in the spectrum. Thus, of the four oxygen atoms of the alkanol molecule, two form a lactone ring and two are present in two hydroxy groups.

The following signals appeared in the strong field in the NMR spectrum of alkanol (Fig. 2): a singlet from an angular methyl group at 1.06 ppm ($\text{CH}_3-\text{C}-$), a doublet from a secondary methyl group with its center at 1.23 ppm ($J = 7\text{ Hz}$, $\text{CH}_3-\text{CH}-$), a doublet from a vinyl methyl group at 2.04 ppm ($J = 2\text{ Hz}$; 3 H, $\text{CH}_3-\text{C}=\text{C}$).

One-proton signals at 3.59 and 3.92 ppm belong to two protons in the geminal positions to hydroxy groups. Consequently, these groups are secondary. The fact that these signals are those of hemihydroxylic protons is confirmed by the PMR spectrum of the diacetyl derivative of alkanol, in which they undergo a paramagnetic shift and appear at 4.62 and 5.16 ppm in the form of a triplet ($J = 3\text{ Hz}$) and an unresolved quartet ($J_1 = 3\text{ Hz}$, $J_2 = 6\text{ Hz}$), respectively. The singlet of the angular methyl group in the spectrum of the diacetate also shifts

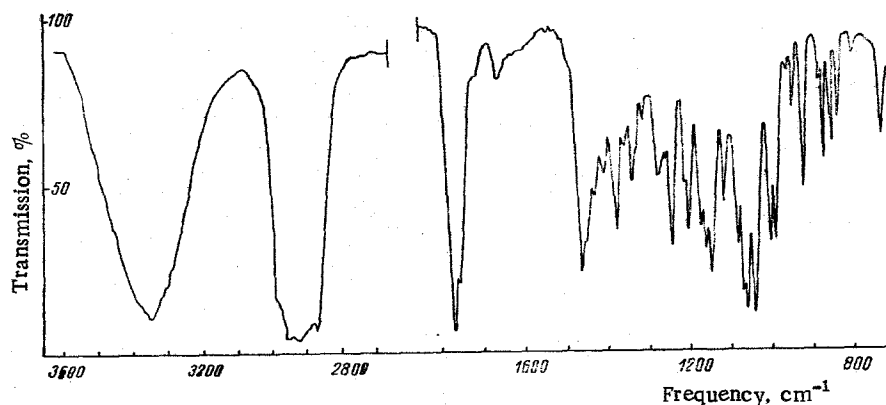


Fig. 1. IR spectrum of alkanol.

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