ISOLATION OF CYCLOCOLORENONE FROM THE ESSENTIAL OIL OF *Ledum palustre*

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From a carbon dioxide extract and also from the essential oil of the leaves of *Ledum palustre* L. we have isolated a sesquiterpene ketone (I) not previously described for this medicinal plant with the composition $C_{15}H_{22}O$ — a colorless mobile liquid with mp 140-143°C/4 mm Hg, n_D^{20} 1.5270, d_{20}^{20} 1.0031, $[\alpha]_D^{20}$ −390° (c 6.0; ethanol). In the IR spectrum there are the following absorption bands, ν_{max}, cm^{-1}: 1695 ($O=C-C=C$) and 1625 ($C=C$); IR spectrum: λ_{max} 264 nm (ε 12,813); the NMR spectrum is given in Fig. 1.

The ketone forms an oxime and reacts with a solution of bromine in chloroform to give an emerald-green coloration, which shows the azulene skeleton of the ketone, and this was then confirmed by the production of guaiazulene when the compound was dehydrogenated over selenium.

The composition of the ketone and also the absence of vinyl protons from its NMR spectrum and the presence of two quaternary methyls — two singlets at 1.0 and 1.2 ppm — permitted the assumption that the ketone, like the sesquiterpene alcohol ledol isolated previously from this plant [1, 2] belongs to the group of sesquiterpene compounds of the aromadendrane type.

On comparing the results obtained with information in the literature, we found that they were identical with those given for cyclocolorenone — a sesquiterpene ketone from the essential oil of *Pseudowintera colorata*. For this, structure (I) has been suggested as the most probable on the basis of chemical transformations and the results of IR and UV spectroscopy [3].

The NMR and mass spectra given (see Figs. 1 and 2) confirm the proposed structure.

The mass spectrum of (I) shows an intense peak of the molecular ion with m/e 218 (100%), corresponding to the empirical formula of the compound. The presence in the molecule of a gem-dimethyl grouping is responsible for the appearance of the ions $(M - C_3H_6)^+$ with m/e 176 (16%) and $(M - C_3H_7)^+$ with m/e 175 (43%). The fragment $(M - CH_3)^+$ with m/e 203 (24%), with a medium intensity, is probably formed through the splitting out of a CH_3 radical from the gem-dimethyl grouping. The absence of an ion $(M - H_2O)^+$ from the mass spectra of (I) must be noted. This fact confirms the presence of the carbonyl group in the C_2, and not the C_1, position of the 5-membered ring [4].

It is interesting to note that the hydrogenation of cyclocolorenone in acetic acid over a Pt catalyst formed — in addition to hydrocarbons with the compositions $C_{15}H_{24}$ and $C_{15}H_{26}$ containing a cyclopropane ring, which agrees with information in the literature [1, 2] — substance (II) with the composition $C_{17}H_{28}O_3$; its IR spectrum has ν_{max} 1740 cm^{-1} (OCO) and 1726 cm^{-1} (C=O); in its NMR spectrum there are the signals of the protons of a hemi-acetyl methyl (singlet, 1.95 ppm) and another methyl (1.4 ppm) and also of the protons of an isopropyl group (doublets, 0.90-1.1 ppm). It follows from these facts that on hydrogenation the addition of a molecule of acetic acid to the double bond and the opening of the cyclopropane ring took place. This interesting fact has not been reported previously.

EXPERIMENTAL

The NMR spectra were taken on a Varian JNM-4H-100 MHz instrument in chloroform solution with TMS as internal standard, and the mass spectra were recorded on a Varian CH-8 spectrometer at an ionizing voltage of 75 V and a recording temperature of 30°C.

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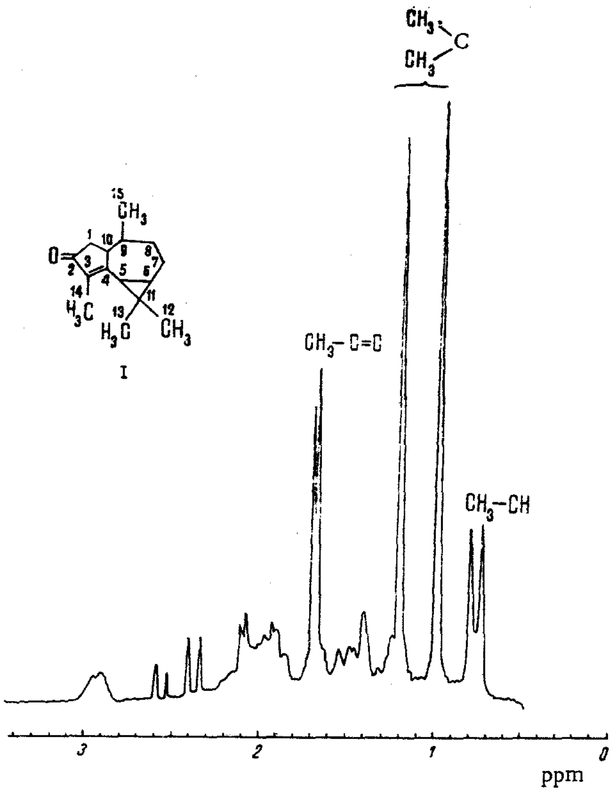

Fig. 1. NMR spectrum of cyclocolorenone.

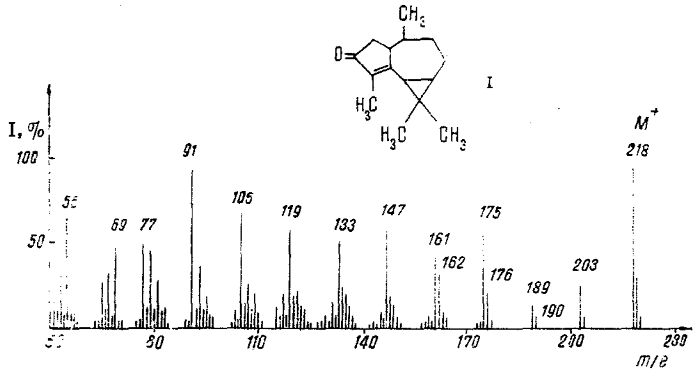

Fig. 2. Mass spectrum of cyclocolorenone.

The analyses of all the compounds corresponded to the calculated figures.

Isolation of Cyclocolorenone. The essential oil of *L. palustre* was subjected to fractional distillation. The residue after the elimination of the myrcene, 6-methyl-2-methyleneocta-5,7-dien-3-ol, palustrol, and ledol [5, 6] was subjected to chromatography on silica gel L 100/250 μ, elution being performed with petroleum ether and petroleum ether—diethyl ether. Petroleum ether—diethyl ether (6:4) eluted a faintly colored liquid which was then subjected to distillation. A colorless mobile liquid was obtained with bp 140-143°C/4 mm Hg, n_D^{20} 1.5270, d_{20}^{20} 1.0031 $[\alpha]_D^{20}$ −390° (c 6.0; ethanol) which was shown by TLC in the petroleum ether—diethyl ether (8:2) system to be an individual substance with R_f 0.57.

Cyclocolorenone was also isolated from a carbon dioxide extract by chromatography under similar conditions.

Hydrogenation of (I). Hydrogen was passed through a solution of 1 g of cyclocolorenone in 50 ml of glacial acetic acid to which 0.35 mg of still moist freshly prepared PtO_2 had been added until its absorption ceased. After the elimination of the platinum, the acetic acid was distilled off on the water bath in vacuum, the residue was dissolved in 50 ml of ether, the ethereal solution was washed with water to neutrality, the ether was distilled off, the residue was distilled, and a colorless mobile liquid was obtained giving on TLC in the petroleum ether—diethyl ether (1:1) system two spots with R_f 0.70 and 0.62.

The mixture was chromatographed on silica gel. Petroleum ether eluates yielded 0.7 g of a colorless mobile liquid with n_D^{20} 1.4480. IR spectrum (in $CHCl_3$), ν_{max}, cm^{-1}: 1380, 1455, 2880, 2940 (CH_3—C; CH_2—C). Mass spectrum: mixture of hydrocarbons with M^+ 204 ($C_{15}H_{24}$) and M^+ 206 ($C_{15}H_{26}$). The NMR spectrum also showed the presence of a mixture of these substances: broadened singlet at 1.7 ppm (CH_3—C=C); four singlets at 0.85, 0.9, 1.0, 1.1 (four quaternary methyls), doublets at 0.8-1.0 ppm.

Petroleum ether—diethyl ether (1:1) eluted 0.15 g of (II) in the form of a viscous liquid; IR spectrum (in $CHCl_3$), ν_{max}, cm^{-1}: 1742 (OCO), 1726 (C=O), 1370, 1455, 2870, 2950 (CH_3—C; CH_2—C). Mass spectrum: M^+ 280. The NMR spectrum is given above.

SUMMARY

From a carbon dioxide extract and also from the essential oil of the leaves of *Ledum palustre* L. the sesquiterpene ketone cyclocolorenone, hitherto unreported for this medicinal plant, has been isolated. The structure proposed for it previously has been confirmed by NMR and mass spectroscopy and also by the production of hydrogenation products.

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PHYTOECDYSONES OF *Ajuga turkestanica*

VI. 22-ACETYLCYASTERONE

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Continuing a study of the phytoecdysones of *Ajuga turkestanica* (Rgl.) Briq. (family Labiatae), in addition to cyasterone, ecdysterone, turkesterone [1], ajugalacterone, and ajugasterone-B [2], which have been isolated previously, we have detected a new phytoecdysone. After the determination of its structure, it has been given the name of 22-acetylcyasterone (I).

The ecdysone from *A. turkestanica* has the elementary composition $C_{31}H_{46}O_9$. The UV spectrum of this compound contains an intense maximum at 240 nm (log ε 4.07), which is characteristic for Δ^7-6-oxo steroids. In the IR spectrum, in addition to absorption bands at 3440 cm^{-1} (OH), 1745 cm^{-1} (γ-lactone), and 1655 cm^{-1} (conjugated ketone), which are close to those for ecdysones for the cyasterone type [3, 4], bands are also observed at 1755 and 1255 cm^{-1} showing the presence of an ester grouping.

Quantitative oxidation of the new ecdysone with sodium periodate showed that its molecule includes one free diol group.

The ORD curve of compound (I) shows a positive Cotton effect: $[M]_{361}$ +2822°; $[M]_{260}$ −2515°; $a = +53^\circ$. On the CD curve, Cotton effects are observed at 340 nm ($\Delta\varepsilon = +1.27$) and 288 nm ($\Delta\varepsilon = -0.66$).

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