

ether, α -terpinyl acetate, and bornyl acetate. To confirm the results obtained, we isolated the main components from the sesquiterpenoid fraction of the oleoresin of L. amurensis by preparative GLC (Tween-60, 5 m \times 6 mm): longifolene, thymol methyl ether, bornyl acetate, and α -terpinyl acetate, which were identified from their IR spectra. The main component of both oleoresins is longifolene (30-35%).

In their chemical compositions, the mono- and sesquiterpenoids of the oleoresins of L. dahurica and L. amurensis are very similar. In their sesquiterpene fractions a large number of oxidized monoterpenoids was found. In addition, by GLC two labile sesquiterpene compounds were detected in both oleoresins the amounts of which fell when the oleoresins were stored. Attempts to isolate them by column chromatography were unsuccessful, since on the sorbents used (SiO_2 , $\text{SiO}_2 + \text{AgNO}_3$) these compounds were converted into a complex mixture of sesquiterpene hydrocarbons from which we succeeded in isolating α -amorphene and α -muroloene.

In the compositions of their mono- and sesquiterpenoids, the oleoresins studied differed considerably from the oleoresin of L. sibirica L. [3]. Thus, in contrast to far-eastern species of larch, in oleoresin of L. sibirica we found only a small number of oxidized monoterpenoids. The main component of the sesquiterpene fraction was not longifolene but γ -elemene.

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SESQUITERPENE LACTONES OF Handelia trichophylla

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UDC 547.314

We have continued a study of the lactones of the inflorescences of Handelia trichophylla Heimerl [1]. The fraction of a chloroform extract that was soluble in 60% ethanol was separated on a column of type KSK silica gel. The components were eluted with mixtures of benzene and methyl ethyl ketone with increasing proportions of the latter.

The first fractions of the eluate yielded cumambrin A, and from the eluates germacranolide with mp 191°C crystallized.

The recrystallization from ethyl acetate of fraction 17 yielded colorless rhombic crystals (I) with the composition $\text{C}_{15}\text{H}_{20}\text{O}_4$, mp 224°C (preheated metal block), $[\alpha]_D^{22} +46^\circ$ (c 0.4; chloroform). IR spectrum (cm^{-1}): $\nu_{\text{max}}^{\text{KBr}}$ 3500 (OH), 1750 (carbonyl of an α -methylene- γ -lactone ring), 1700 ($\text{C}=\text{O}$ in a six-membered ring).

This compound formed an adduct with dimethylamine (according to Michael) with mp 127°C and M^+ 309 (mass spectrometry), which confirms the presence of an exomethylene group in the lactone ring and the composition of (I).

The hydroxy group is readily acetylated by acetic anhydride in pyridine. The acetate of (I) has the composition $\text{C}_{17}\text{H}_{22}\text{O}_5$ with mp 210°C (acetone).

The NMR spectrum of (I) (JNM-H-4, H-100 MHz instrument, in deuteropyridine, δ scale, internal standard

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HMDS) showed the following signals (ppm): singlet at 1.12 and doublet with its center at 1.28 ($J = 6$ Hz, 3H each), and in the weak field two doublets at 6.0 (1H, $J = 3$ Hz) and 5.3 (1H, $J = 3$ Hz), which are characteristic for an exocyclic methylene group conjugated with the lactone carbonyl. The proton on the carbon atom connected with the lactone oxygen appears in the form of a triplet with its center at 3.83 ($J = 11$ Hz), the hydroxyl is represented by a doublet at 6.72 ($J = 5$ Hz), and the proton in the geminal position to the hydroxyl by a quartet with its center at 3.66 ($J_1 = 6$ Hz; $J_2 = 11$ Hz).

The results obtained show that compound (I) belongs to the eudesmane series. By reducing the exocyclic methylene group of lactone (I) (Pd/C in ethanol) we obtained a dihydro derivative (II), $C_{15}H_{22}O_4$, mp 195–197°C. IR spectrum (cm^{-1}): 3500 (OH), 1780 (γ -lactone), 1710 ($C=O$). By a mixed melting point and a comparison of IR spectra, compound (II) was identified as the lactone arsanin, of the eudesmane type [2].

Arsanin differs from artecalin [3] by the fact that at C_{11} in artecalin there is an exomethylene group conjugated with the lactone carbonyl. Consequently, the lactone (I) that we isolated is artecalin.

The subsequent eluates yielded two compounds with mp 245 and 212°C, the study of which is continuing.

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3,18-O-ISOPROPYLIDINELAGOCHILIN FROM *Lagochilus pubescens*

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Continuing a study of the plant *Lagochilus pubescens* [1], we have isolated a substance of the diterpene series. The comminuted air-dry raw material (1.2 kg) was extracted with chloroform (40 liters) and the chloroform extract was concentrated to small volume and diluted with water, after which it was extracted successively with petroleum ether, hexane, benzene, and ether. The benzene extract (40 g) was chromatographed on Al_2O_3 and eluted with benzene-ether (2:1). The first fractions contained hydrocarbons, flavonoids, and sterols, and the later fractions contained lagochilin and other diterpenes. The last fractions, with R_f 0.05, 0.025, and 0.9 (TLC, SiO_2 ; ether system) were rechromatographed on type KSK silica gel. Elution with chloroform-acetone (30:1) gave a crystalline substance with the composition $C_{23}H_{40}O_5$, mp 150–151°C (from ether), R_f 0.25 (TLC, SiO_2 ; ether system), $[\alpha]_D^{25} - 42^\circ$ (c 1; ethanol), yield 1.5 g (0.12%) (I).

Substance (I) was readily soluble in acetone and dioxane, sparingly soluble in benzene and ethanol, and insoluble in water. The IR spectrum of (I) showed the absorption band of a hydroxy group (3450 cm^{-1}). The presence of a hydroxy group was confirmed by the preparation of a di-O-acetyl derivative (II) with mp 120–121°C (from methanol). The IR spectrum of the diacetate lacked the absorption band at 3450 cm^{-1} but a new band had appeared at 1735 cm^{-1} which is characteristic for an ester group.

The oxidation of (I) with manganese dioxide gave substance (III), $[\alpha]_D^{28} - 15.6^\circ$ (c 1; ethanol) the IR spectrum of which contained a strong band at 1790 cm^{-1} (carbonyl group). A high value of the stretching vibrations of the carbonyl group is characteristic for five-membered lactones. The formation of a lactone showed that the hydroxy groups were present in the γ position relative to one another. This arrangement of the hydroxy groups was confirmed by the formation of an acetonide (IV) with mp 117–118°C (from ether), $[\alpha]_D^{28} - 50^\circ$ (c 1; ethanol).

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