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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UDC 547.9+547.599.4

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), $[\alpha]^{25}_D -42°$ (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), $[\alpha]^{28}_D -15.6°$ (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), $[\alpha]^{28}_D -50°$ (c 1; ethanol).

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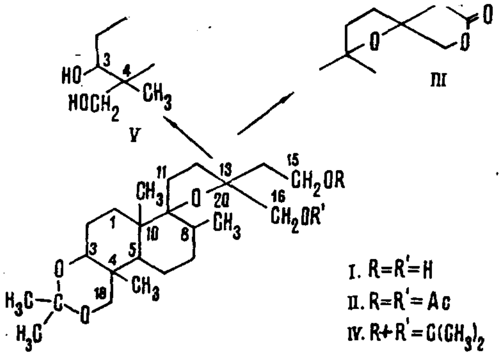

The acid hydrolysis of (I) gave lagochilin (V) with mp 167-168°C (from ether) $[\alpha]_D -9.63°$ (c 1; ethanol).

The NMR spectrum of (I) taken in pyridine (Varian XL-100, HMDS scale) showed triplets at 3.98 and 2.26 ppm belonging to the methylene protons at C_{15} and C_{14}; the signals of the methylene protons at C_{16} form an AB spin system and their signals have the following parameters: δ_A 3.80 ppm, δ_B 3.66 ppm (J_{AA} = 10 Hz). The signals of the C_3 proton resonate at 3.48 ppm and, judging from the great width of the signal, this proton occupies the axial position in the ring. Doublets at 3.37 and 3.15 ppm (J = 10.5 Hz) relate to the methylene protons at C_{18}. The signals of the methyl groups of the main skeleton are arranged in a similar way to those of lagochilin [2]. Signals at 1.34 and 1.16 ppm correspond to the two methyls of an isopropylidene group.

The mass spectrum of (I) shows the peak of a molecular ion at 396 and strong peaks of ions at m/e 198, 185, and 172 which are characteristic for diterpenes of the labdane group with the grindelane skeleton [3].

On the basis of the results obtained, for the diterpene isolated we propose the structure of 3,18-O-isopropylidenelagochiline (I) [2]. To prove the native nature of the substance isolated, we studied various extracts (aqueous, acetonic, ethanolic, benzene, heptane, and ethereal) by chromatography. 3,18-O-Isopropylidenelagochilin was found in all the extracts.

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