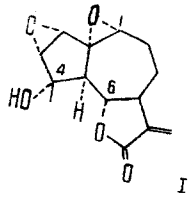
and the vicinal protons interacting with it are represented by a doublet (^3J = 10.5 Hz) and by a multiplet with their respective centers at 2.77 and 3.20 ppm.

The characteristics given are similar to those of the sesquiterpene lactone chrysartemesin B from Chrysanthemum parthenium [2] and only the melting points show some difference. But the melting point (225°C, from ethanol) and IR spectrum of the dihydro derivative with the composition $C_{15}H_{20}O_5$ obtained by the reduction of (I) with 5% Pd/C in ethanol are similar to those for dihydrochrysartemin B, which confirms the identity of (I) with chrysartemin B.

The orientation of the substituents at C-4 in the latter remained undetermined. To answer this question we used measurements of the intramolecular nuclear Overhauser effect. Additional irradiation with a strong radio frequency field of the resonance frequency of the protons of the methyl group geminal to a hydroxy group (0.89 ppm) led to an increase in the intensity of the doublet at 3.58 ppm by 30%, which shows that it is due to the proton at C_3. Under these conditions the intensity of the doublet at 2.77 ppm remained unchanged. These facts enable the assignment of the signals of the protons of the epoxy ring at C-2 and C-3 to be refined and show that the proton at C-3 and the methyl group at C-4 both have the β orientation, as shown in structure (I):



I

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ISOLATION OF DIOSGENIN FROM Solanun laciniatum

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UDC 547.944.3

Diosgenin (I) is one of the most important starting materials for the synthesis of cortisone and its analogs [1]. It is usually found in the form of glycosides of steroid sapogenins of plants of the genus Dioscorea [2].

We have investigated the xylene mother solution after the extraction of solasodine from Solanum laciniatum Ait. By thin-layer chromatographic analysis we found in the mother liquor, apart from diosgenin, traces of solasodine and solasodiene. To isolate the diosgenin, the xylene was distilled off with steam from 5 liters of the mother solution, the residue was washed in benzene, and the solution was washed successively with 3% NaOH solution and 5% H_2SO_4 solution, and then with water to neutrality. The solvent was evaporated off and the dry residue (10.6 g) was purified by chromatography on alumina (activity grade (III) with elution with benzene. The yield of diosgenin was 8.2 g (77.3% on the dry residue), mp 206-208°C (from ethanol), $[\alpha]_D^{20}$ −121.5°, ν_{max}^{KBr} 3440 cm^{-1} (OH).

The presence of a 3-hydroxy group and a double bond at C_5-C_6 in the diosgenin molecule was established by its Oppenhauer oxidation [3].

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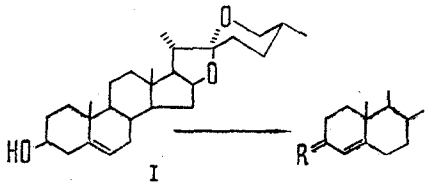

I

II. R=O
III. R=NOH
IV. R=N—NH—$C_6H_3(NO_2)_2$

The oxidation product – 3-oxo-Δ^4-diosgenin (II) – had mp 203-204°C (from methanol), $\lambda_{max}^{ethanol}$ 242 nm (log ε 4.36), which is the characteristic maximum for α,β-unsaturated ketone [4]. The IR spectrum showed absorption bands at 1685 cm^{-1} (C = O) at 1632 cm^{-1} (C = C). The absence of the broad absorption band of a hydroxy group (3400-3440 cm^{-1}) also confirmed the formation of a 3-oxo-Δ^4 grouping in compound (II). The PMR spectrum of 3-oxo-Δ^4-diosgenin contains a signal at 5.74 ppm (δ) (C_4-vinyl proton).

The ketone obtained was characteristized in the form of the oxime (III), mp 218-220°C (from ethanol) and the 2,4-dinitrophenylhydrazone (IV), mp 241-243°C (from ethanol). The elementary analyses of all the substances (I-IV) obtained corresponded to the calculated figures.

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ISOLATION AND IDENTIFICATION OF ERGOSTEROL PEROXIDE FROM Cetraria richardsonii AND Ganoderma applanatum

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UDC 547.926+661.729

The dry comminuted lichen Cetraria richardsonii Hook. (905 g) collected in August in the environs of the village of Stokovyi, Ten'kinskii region, Magadan oblast, was extracted with boiling petroleum ether (70-100°C). The extract obtained (weight of the dry residue 5.04 g) was chromatographed on a column of silica gel L (100-250 μ). The petroleum ether–chloroform system (4:1 → 3:1) eluted 0.33 of a compound (I) which, after rechromatography on KSK silica gel (175-200 mesh) and recrystallization had mp 179.5-181°C (hexane), $[\alpha]_D^{21}$ −29° (c 0.45; chloroform); acetate of (I): mp 199-201.5°C (ethanol), $[\alpha]_D^{21}$ −22.9 (c 0.43 chloroform).

Compound (I) was shown to be identical with the ergosterol peroxide (II) isolated from Thamnolia subuniformis (Ehrh.) W. Culb. [1] on the basis of the identity of the TLC behavior and NMR, IR, and mass spectra of (I) and (II) and the absence of a depression of the melting point of mixtures of (I) and (II) and of their acetates.

Compound G_2 [2] isolated previously from the basidiomycete Ganoderma applanatum (Fr.) Pat., after additional chromatography and crystallization, had mp 181-182°C (hexane), $[\alpha]_D^{21}$ −27.3° (c 0.48; chloroform); acetate of G_2: mp 200-202°C (methanol–ethanol) $[\alpha]_D^{21}$ −21.3° (c 0.48; chloroform). On the basis of their TLC behavior and the identity of the NMR, IR, and mass spectra of G_2 and (II) and the absence of a depression of the melting point of mixtures of G_2 and (II) and of their acetates, G_2 was also identified as ergosterol peroxide.

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