the GLC method [12]. The hydrolyzate was found by PC in the butan-1-ol–benzene–pyridine–water (5 : 1 : 3 : 3) system [13] to contain glucose, arabinose, xylose, and rhamnose.

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α-AMYRIN ACETATE FROM Apocynum

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When ethanolic extracts of the roots of various species of dogbane are concentrated, a light grayish precipitate consisting mainly of triterpene sapogenins usually deposits [1]. Their yield not infrequently amounts to more than 2% of the weight of the air-dry raw material.

The nature of the petroleum-ether-soluble terpenoids of Apocynum cannabinum L. has been studied previously [2]. Oleanolic acid, α-amyrin, and lupeol were isolated in crystalline form.

We have now studied the triterpenoid sapogenins of A. androsaemifolium L. and, again, those of A. cannabinum. Thin-layer chromatography on silica gel [benzene–petroleum ether (3 : 1)] showed that in addition to the compounds mentioned the mixture of triterpenoids contained another substance less polar than the others. Its amount was considerably greater than those of the others. This main component of the triterpenoids of A. androsaemifolium L. and A. cannabinum was separated from the accompanying compounds by chromatography on silica gel. The column was eluted with benzene. As a result, from 2 g of the combined sapogenins we isolated 1.4 g of a crystalline substance with mp 154-156°C [from chloroform–ethanol (4 : 1)], $[\alpha]_D^{20}$ + 59.0 ± 2° (c 1.75; benzene).

The IR spectrum of this substance lacked the absorption band of a hydroxy group (3300-3600 cm^{-1}), while the bands of a carbonyl group (1740 cm^{-1}), of a double bond (1645 cm^{-1}), and of a C–O–C bond (1250 cm^{-1}) were distinct. The mass spectrum of the sapogenin had an intense molecular peak, M^+ 468, and the presence of peaks of the fragmentary ions 425 ($M - CH_3CO$) and 408 ($M - CH_3COOH$) permitted the assumption that the product $C_{32}H_{52}O_2$ that we were investigating was the acetate of lupeol or of α-amyrin. In addition to the fragment

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mentioned, the mass spectrum of the compound also contained the peaks of ions with m/e 453 (M − CH_3), 393 (M − CH_3COOH −CH_3), 368, 357, 272, 257, 249, 218 (maximum), 203, and 189.

In 10 ml of dioxane, 0.2 g of the acetate was heated with 10 ml of a 10% solution of KOH in methanol at the boiling point of the dioxane for 4 h. The completeness of hydrolysis was checked by the TLC method. The solution was evaporated in vacuum, and the residue was dissolved in 50 ml of water and extracted with chloroform. The yield of hydrolysis product was 0.14 g. After repeated recrystallization from acetone, it had the composition $C_{30}H_{50}O$, mp 176-178°C, $[\alpha]_D^{24}$ +97.0 ± 2° (c 1.48; benzene).

The mass spectrum of the sapogenin showed the peak of the molecular ion, M^+ 426, and also the peaks of ions with m/e 218 (maximum), 207, 203, and 189. The peaks mentioned correspond, respectively, to fragments a, g, c, and d of the mass-spectroscopic fragmentation of triterpene compounds of the Δ^{12}-ursene series [3], and the mass spectrum as a whole was characteristic for α-amyrin.

It was previously [4] concluded erroneously that the compound described in the present paper was lupeol acetate.

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IDENTIFICATION OF PENNOGENIN OBTAINED IN THE ENZYMATIC CLEAVAGE OF POLYGONATOSIDES C^1 AND C^2 FROM THE RHIZOMES OF Polygonatum stenophyllum

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We have reported previously that when polygonatoside C (a mixture difficult to separate of two steroid glycosides C^1 and C^2) is incubated with the digestive juice of the snail Eulota maackii, an aglycone with mp 226-231°C (I) is formed [1]. The aglycone (I) was identified as pennogenin (17α-hydroxydiosgenin) on the basis of the identity of the IR, ^1H NMR, and mass spectra of (I) with the corresponding spectra of pennogenin [2, 3] and the absence of a depression of the melting point of mixtures of (I) and its acetate (II) with authentic samples of pennogenin and its acetate, supplied by Prof. Gonzales (Spain).

By using the method of out-of-resonance decoupling and literature information [4, 5] we have for the first time made a complete assignment of the signals of the C atoms in the ^{13}C NMR spectrum of (I) taken in $CDCl_3$ (with TMS as standard) on a Bruker HX-90 E instrument at a working frequency of 22.63 MHz. A comparison of the chemical shifts of the C atoms in the spectrum of (I) and of diosgenin [4] showed differences only for rings C, D, and E: δ ($\Delta\delta$ pennogenin−diosgenin) C-8, 31.6 (0.2); C-9, 49.8 (−0.3); C-11, 20.7 (−0.2); C-12, 31.6 (−8.2); C-13, 43.9 (3.7); C-14, 52.9 (−3.6); C-15, 30.9 (−0.9); C-16, 90.9 (10.2); C-17, 90.1 (28.0); C-18, 17.1 (0.8); C-20, 44.6 (3.0); C-21, 8.1 (−6.4); C-22, 110.0 (0.9); the sign (−) shows an upfield shift.

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[*] Deceased.

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