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, $[\alpha]_D^{24} + 97.0 \pm 2°$ (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.

*Deceased.

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The previously undescribed 3-O-methylpennogenin was obtained by Purdie's method [6] and had mp 203-207°C $[\alpha]_D^{20}$ −71.17° (chloroform); mass spectrum, M^+ 444.

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CARDENOLIDES OF Erysimum repandum

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It is known that Erysimum repandum L. (spreading erysimum) contains cardenolides. Three glycosides have been isolated from it: erysimin, erysimoside, and cheirotoxin [1].

We have studied the seeds of this plant collected in the experimental field of the Institute in Sofia [2].

The chromatography of ethanolic extracts of the seeds in a thin layer showed the presence of no less than 12 substances of cardenolide nature, which were isolated by the method described previously [3]. In the present paper we discuss the identification of two substances.

Glucoperiplorhamnoside, $C_{35}H_{54}O_{14}$, mp 192-195°C (from ethanol), $[\alpha]_D^{20}$ −12° (c 0.5; methanol); $\nu_{max}^{C_2H_5OH}$ 217 nm (log ε 4.17); IR spectrum, cm^{-1}: 1812, 1780, 1680, 1640 (butenolide ring). With concentrated sulfuric acid, the glycoside formed colorations changing with time: 1 sec-2 min − orange; 5-25 min − orange-brown; 30-120 min − brownish yellow; up to 24 h − violet.

On acid hydrolysis [4], the glycoside decomposed into D-glucose, L-rhamnose, and periplogenin [$C_{23}H_{34}O_5$, mp 232-234°C, $[\alpha]_D^{20}$ +27.6° (c 0.1; methanol)]. The enzyme of the grape snail hydrolyzed it to D-glucose and periplogenin 3-rhamnoside, $C_{29}H_{44}O_9$, mp 222-230°C (from ethanol−water), $[\alpha]_D^{24}$ −11.6° (c 0.38; methanol), identical with an authentic sample of periplogenin 3-O-α-L-rhamnopyranoside [5].

Glucoperiplorhamnoside forms an acetonide, which shows the attachment of the D-glucose to the L-rhamnose by a 1 → 4 bond [6]. In the bioside, β and α glycosidic bonds in the D-glycosidic and L-rhamnosidic residues, respectively, were found by Klyne's rule. The stability of the glycoside to hydrolysis by a 0.1 N solution of sulfuric acid [8] confirmed the pyranose forms of the oxide rings in its sugars.

Glucoperiplorhamnoside has been isolated previously from Antiaris toxicaria Lesch. [9].

Periplorhamnoside from E. repandum was shown to be identical with the periplogenin 3-O-α-L-rhamnopyranoside obtained by the enzymatic hydrolysis of the glucoperiplorhamnoside.

These cardenolides have not previously been found in plants of the genus Erysimum.

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