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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N-PHENYL-β-NAPHTHYLAMINE FROM Centaurea salonitana

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We obtained a resinous residue from the epigeal part of Centaurea salonitana Vis. collected in the flowering phase in the region of the town of Pyatigorsk by its leaching with hot water followed by extraction with chloroform. By chromatographing this resin on silica gel with elution by petroleum ether—benzene (99:1) we isolated colorless crystals with the composition $C_{16}H_{13}N$, M^+ 219, mp 108-109°C.

The substance had a bright blue fluorescence in UV light and with diazotized sulfanilic acid it gave a stable bright crimson coloration. The maxima of the UV spectrum in methanol and on the addition of sodium methoxide were, nm (log ε): 272 (4.32), 310 (4.26), 350 (3.2). The NMR spectrum taken in CCl_4 has a multiplet consisting of the signals of 12 aromatic protons (6.8-7.7 ppm) and a broadened singlet at 5.65 ppm (1H), due to a NH group. The IR spectrum (paraffin oil) contained narrow absorption bands at (cm^{-1}) 3395, 1630 (N—H), 1600, 1500 (C=C bond) and 1305 cm^{-1} (C—N).

The elementary analysis, mass and NMR spectra, and melting point of the compound isolated corresponded to N-phenyl-β-naphthylamine; the second possible isomer — the α-naphthylamine derivative — has mp 62°C [1].

The isolation of N-phenyl-β-naphthylamine from plant sources has been reported [2], but this is the first time that this substance has been obtained from plants of the genus Centaurea.

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