Dipsacoside A, $C_{41}H_{66}O_{12} \cdot H_2O$ (elementary analysis), is a diglycoside with mp 240–245° C (from ethanol), $[\alpha]_D^{20}$ +12.5 ± 3° (c 2.40; ethanol). On being heated in a mixture of 6% H_2SO_4 and methanol (1 : 1) it hydrolyzed, giving an aglycone with mp 324–326° C (from ethanol), $[\alpha]_D^{20}$ +75.5 ± 2° (2.96; pyridine) and two monosaccharides, identified by paper chromatography in system 1 as L-arabinose and L-rhamnose. The diacetate of the aglycone had mp 164–166° C (from aqueous ethanol) and $[\alpha]_D^{20}$ +65.5 ± 2° (c 3.27; chloroform). A chromatogram on silica gel in chloroform–ethanol (10 : 1) (system 2) and in ether–benzene (34 : 1) (system 3) showed the identity of the sapogenin of dipsacoside A and hederagenin obtained by the hydrolysis of the glycosides of Leontice eversmanii [1]. The IR spectra of the compounds compared coincided. From the composition of the aglycone and the sugars, dipsacoside A is similar to kalopanax saponin A [2], but possibly differs from it in the arrangement of the bonds between the monosaccharides.

The bulk of the combined saponins consisted of the amorphous but chromatographically homogeneous dipsacoside B with mp 198–202° C, $[\alpha]_D^{22}$ +11 ± 3° (c 0.20; water). The glycoside gave an amorphous polyacetate with mp 140–144° C (from benzene–petroleum ether). From the behavior of the substance on silica gel in systems 2 and 3 it may be concluded that dipsacoside B is an acyloside [1]. When the glycoside was hydrolyzed with 6% H_2SO_4, hederagenin, L-arabinose, L-rhamnose, and D-glucose were obtained. Alkaline hydrolysis on the anion-exchanger AV-17 (OH form), carried out under the conditions for the hydrolytic cleavage of patrinoside C [3], led to dipsacoside A, identified chromatographically on silica gel in the butan-1-ol–ethanol–25% ammonia (10 : 2 : 5) system and on paper in system 1. D-Glucose was detected in the sugar fraction after acid hydrolysis. Consequently, dipsacoside B differs from dipsacoside A by the presence of an acylglycosidic moiety consisting of one or more molecules of D-glucose.

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21 April 1969

Institute of the Physiology and Experimental Pathology of High Altitudes ASKirgSSR

UDC 547.597

SOME RESULTS ON THE STRUCTURE OF THE GENIN OF THE GLYCOSIDE OF POLEMONIUM COERULEUM

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 5, pp. 452–453, 1969

On hydrolysis, polemoniosides B and C formed one and the same aglycone. Since in this process the product underwent pronounced resinification, it was converted into the acetyl derivative, which was purified on silica gel and was then deacetylated by being heated with alkali. The genin obtained in this way with mp 198–200° C and $[\alpha]_D$ +50° (c 1; ethanol) had a neutral character and was soluble in only chloroform, ethyl acetate, and ethanol. According to the elementary analysis, the substance contained no nitrogen and its most probable empirical formula was $C_{30}H_{48}O_5$. The IR spectrum exhibited strong absorption maxima in the 1650, 1725, and 3300–3500 cm^{-1} regions. The band at 1725 cm^{-1} shows the presence of a carbonyl group of some kind. This is not an aldehyde group, since there are no characteristic frequencies in the 2700–2730 cm^{-1} region and the NMR spectrum has no signals of protons at 9–10 ppm. The aglycone gave a crystalline 2,4-dinitrophenylhydrazone $C_{36}H_{54}O_8N_4$ with mp 155–157° C.

When the aglycone was hydrogenated over Raney Ni in acetic acid, it consumed 1 mole of hydrogen. When the IR spectrum of the product was obtained, with mp 181-183°C, and $[\alpha]_D$ +40° (c 1; ethanol), the carbonly absorption band had disappeared.

The genin gave a positive color reaction with tetranitromethane and it added bromine in chloroform solution forming a crystalline dibromide [acetyl derivative $C_{36}H_{58}O_8Br_2$, mp 102–105° C, $[\alpha]_D$ +30° (c 1; ethyl acetate)].

The double bond is apparently tetrasubstituted, since the NMR spectrum lacks signals of protons in the 5–6.8 ppm region and the substance does not hydrogenate over PtO_2 in acetic acid. When the aglycone was boiled with lithium

aluminum hydride in benzene, the carbonyl group and the double bond were reduced. In the IR spectrum of the product obtained, with mp 207–208° C ($C_{30}H_{52}O_5$), the absorption bands at 1650 and 1725 cm^{-1} had disappeared. It is known that such hydrogenation of a double bond is possible only in the case of the conjugation C=C–C=O [1, 2].

The IR spectrum also confirms the presence of such conjugation in the aglycone, since there are two absorption maxima at 220 mμ (log ε 4.8, 4.1). When treated with acetic anhydride in pyridine, the aglycone formed an acetate $C_{36}H_{54}O_8$ with mp 108–109° C, $[\alpha]_D$ +30° (c 1.5; ethanol), mol. wt. 540–580 (cryoscopy), % $OCOCH_3$ 21 (titration). The percentage of acetyl groups corresponds to three hydroxyls in the genin. However, the absorption band at 3400 cm^{-1} had not disappeared from the IR spectrum of the acetate, which may show the presence of a nonacetylatable OH group.

The genin gave negative Legal and Liebermann-Burchard reactions. The shifts in the absorption maximum in the UV spectrum of the aglycone under the action of 94% sulfuric acid according to Walens were completely different in this case from the shifts characteristic for steroid sapogenins [3].

The IR spectrum of the aglycone is extremely similar to the spectra of triterpene compounds as is also indicated by the empirical formula given above.

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2 December 1968

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UDC 547.92+615.711.5

DIGITOXIGENIN 3-α-L-ARABINOSIDE

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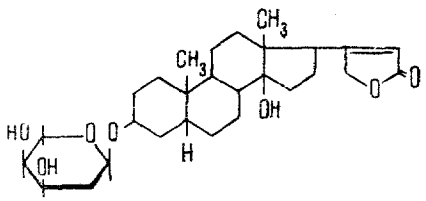
Khimiya Prirodnykh Soedinenii, Vol. 5, No. 5, pp. 453–454, 1969

Bliss and Ramstand [1], using preparative paper chromatography, have isolated from Evonymus atropurpurea Jacq. in the amorphous state a cardiac glycoside evatroside and have characterized it as digitoxigenin L-arabinosido-D-glucoside. The enzymatic hydrolysis of this compound yielded the monoglycoside digitoxigenin L-arabinoside (evatromonoside). However, evatromonoside was not obtained in the crystalline state. The work of the authors mentioned induced us to synthesize digitoxigenin L-arabinoside in order to decide the presence or absence of this glycoside in the central Russian geographic race of European euonymus (Evonymus medirossica Klok.), the cardenolide composition of which we are engaged in studying [2, 3].



Digitoxigenin 3-α-L-arabinopyranoside was synthesized by the Königs-Knorr method [4] by the reaction of the aglycone digitoxigenin with O-acetyl-L-arabinosyl bromide. The glycoside triacetate formed was saponified with ammonia in methanol. After being freed from accompanying substances by chromatography on alumina and crystallization from water, the glycoside was obtained in the pure state. It melted at 165–168° C; $[\alpha]_D^{23}$ +13.8 ± 5° (c 0.4; methanol). It dissolved in concentrated sulfuric acid giving colorations, min: 0) brown; 1) yellow; 15) yellow-orange; 45) red. On acid hydrolysis by Mannich's method [5], it formed digitoxigenin and L-arabinose. The configuration of the glycosidic bond was established by a comparison of molecular rotations using Klyne's rule [6], and the size of the oxide ring for the carbohydrate component on the basis of the stability of the glycoside to hydrolysis with dilute acids [7, 8].