CARDENOLIDES OF Adonis amurensis

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Adonis amurensis Regel (Amur adonis), family Ranunculaceae Juss. belongs to the cardenolide-containing plants [1]. Cymarin has been obtained from its roots [2].

The present paper gives the results of a study of the cardenolides contained in this plant.

In purified extracts of the roots and herbage of Amur adonensis we have found no less than 11 substances of cardenolide nature by paper chromatography in the benzene–formamide, chloroform–formamide, tetrahydrofuran–chloroform–formamide (50:50:6.5), and toluene–butan-1-ol (3:1)–water (35%) systems. To isolate these compounds, the comminuted raw material was treated with a mixture of chloroform and ethanol (1:1). Then the extract was purified as described previously [3], with the subsequent separation of the cardenolides into fractions by means of benzene–chloroform (8:2), chloroform, and chloroform containing 20% of ethanol. The residues from the evaporation of each fraction were separated into individual substances by partition chromatography on silica gel or by adsorption on alumina. Eight substances were obtained (I, III-V, VI, VIII, X, and XI), and of them (I), (III), (IV), (VIII), and (XI) gave a positive xanthydrol reaction [4], which shows the presence of 2,6-dideoxysugars in their molecules. They were readily hydrolyzed by dilute (0.05 N) sulfuric acid. The substances were identified by their physicochemical properties, their transformation products, their UV and IR spectra, their colorations with sulfuric acid, their R_f values, and the melting points of mixtures with authentic samples.

Substance (I) (somalin), $C_{30}H_{44}O_7$, mp 126-131°C, $[\alpha]_D^{22}$ +6.8° (ethanol). On acid hydrolysis with 0.05 N sulfuric acid, it split into cymarose and digitoxigenin [$C_{23}H_{34}O_4$, mp 242-247°C, $[\alpha]_D^{22}$ +18° (ethanol)]. A comparison of the properties of this glycoside with those known in the literature showed that it was identical with somalin [5, 6].

Substance (III) (cymarin), $C_{30}H_{44}O_9$, mp 137-139°C, $[\alpha]_D^{23}$ +37° (ethanol). As in the case of somalin, it was hydrolyzed by dilute solutions of acids to D-cymarose and strophanthidin, $C_{23}H_{32}O_6$, mp 138-142°C, 223-225°C, $[\alpha]_D^{22}$ +43° (ethanol) [3]. The glycoside was identified as cymarin [2, 7, 8].

Substance (IV) (cymarol), $C_{30}H_{46}O_9$, mp 225-229°C, $[\alpha]_D^{23}$ +24° (ethanol). On acid hydrolysis it split into D-cymarose and strophanthidol, $C_{23}H_{34}O_6$, mp 137-144°C/222-224°C, $[\alpha]_D^{23}$ +37° (ethanol). Cymarin reduced by sodium tetrahydroborate at the aldehyde group was identical with substance (IV).

Substance (V) (strophanthidin) and substance (VI) (strophanthidol) were identical with the aglycones of cymarin (III) and of cymarol (IV).

Substance (VIII) (corchoroside A), $C_{29}H_{42}O_9$, mp 160-164°C, $[\alpha]_D^{23}$ +13° (ethanol). This glycoside hydrolyzed to strophanthidin and D-boivinose. A parallel comparison of substance (VIII) and an authentic sample of corchoroside A [9] showed their identity.

Substance (X) (convallatoxin), $C_{29}H_{42}O_{10}$, mp 245-247°C, $[\alpha]_D^{22}$ −4° (ethanol). Hydrolysis showed [10] that the substance contained the aglycone strophanthidin and the sugar L-rhamnose. It was reduced by sodium tetrahydroborate to convallatoxol [11]. The investigations performed showed that this glycoside is authentic convallatoxin [3].

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Substance (XI) (k-strophanthin-β), $C_{36}H_{54}O_{14}$, mp 187-193/205-210°C, $[\alpha]_D^{22}$ +32° (ethanol). Under the action of acids, (XI) hydrolyzed to strophanthidin (V), D-cymarose, and D-glucose, and under the action of the enzymes of the grape snail it hydrolyzed to cymarin and D-glucose. By its physicochemical properties and transformation products, glycoside (XI) was identified as k-strophanthidin-β [8, 12].

Somalin has not previously been found in the herb Adonis amurensis, and cymarol and strophanthidol have been determined only chromatographically.

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