UDC 547.918+547.597

STRUCTURE OF SAPONASIDE A

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 3, p. 188, 1969

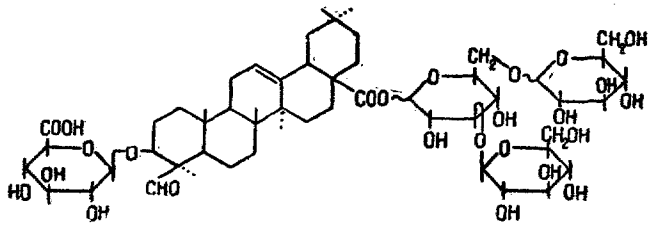
The fractions containing mainly saponaside A (remaining after the isolation of the main saponin from Saponaria officinalis—bouncingbet, fullers' herb [1]), were combined and chromatographed in the butanol—ethanol—water (10 : 2 : 5) system. Saponaside A with mp 132–134° C, $[\alpha]_D^{20}$ +35° (c 2; methanol) was obtained.

On acid hydrolysis, the aglycone obtained was identified by its melting point, specific rotation, and chromatographic behavior as gypsogenin, while glucose and glucuronic acid were identified by paper chromatography of the hydrolysate.

Treatment of the saponin with 10% aqueous ethanolic alkali (80° C, 5 hr) yielded the β-glucuronoside of gypsogenin [2] with mp 203–205° C (decomp.), $[\alpha]_D^{20}$ +16° (c 1.6; ethanol).

To elucidate the structure of the carbohydrate component, the saponin was methylated by Kuhn's method [3] and the product was subjected to cleavage. 2,3,4,6-Tetra-O-methyl-D-glucose and methyl 2,3,4-tri-O-methyl-D-glucuronate and also 2,4-di-O-methyl-D-glucose, were identified by chromatography on paper and in a thin layer of silica gel. The dimethyl ether mentioned was isolated in preparative amount and was identified as described previously [4]. When the permethylated saponaside A was cleaved with aluminum hydride and the resulting fragments were subjected to methanolysis, it was found that the 2,4-di-O-methyl-glucose, to which two glucose residues were attached, was bound directly to the carboxyl group of the aglycone and glucuronic acid was bound to the hydroxyl group of the gypsogenin. These results were confirmed by the periodate oxidation of the saponin.

The final structure of saponaside A can be represented in the following way:



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15 January 1969

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UDC 547.92+615.711.5

CARDENOLIDES OF CHEIRANTHUS ALLIONI

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 3, pp. 188–189, 1969

From Cheiranthus allioni Hort (Erysimum asperum, plains erysimum) N. P. Maksyutina and one of us [1–3] has obtained the cardiac glycosides allioside A (erysimin, helveticoside), desglucoerycordin, erycordin, allionin, and fiolin [1–3]. The structures of the last two compounds have been investigated partially.

Continuing a study of the seeds of the plant mentioned, we have established that it contains not less than 18 cardenolides. In accordance with the method of preparation described below, the latter have been divided provisionally into two groups: moderately and highly polar cardenolides. A chemical study of the substances of the first group has begun.

The comminuted seeds, after being defatted with petroleum ether, were exhaustively extracted with 96% and 70% ethanol. The ethanolic extracts were evaporated in vacuum. The still residue was dissolved in water and purified with petroleum ether and then with alumina. The glycosides were extracted from the purified aqueous solution three times with an equal volume of a mixture of chloroform and ethanol (2 : 1). After evaporation in vacuum, these extracts yielded the combined moderately polar cardenolides. The aqueous solution was saturated with sodium chloride and the remaining glycosides were extracted completely by repeated treatment with the mixture of ethanol and chloroform (1 : 2). The extracts were evaporated, giving the combined highly polar glycosides.

The cardenolides of the first group were chromatographed on alumina (activity grade III) and were eluted with mixtures of chloroform and ethanol (95 : 5–70 : 30). The following compounds were isolated in the individual crystalline state and identified by direct comparison: allioside A [1] (erysimin [4], helveticoside [5]), desglucoerycordin [6], glucodigifucoside [7, 8], erysimoside [9], and erycordin [6] and, in addition, two new cardenolides were isolated which we have called alliside and allotoxin.

Alliside, $C_{29}H_{44}O_{10}$ crystallizes from acetone–benzene, mp 180–183° C; $[\alpha]_D^{23}$ – 47.7 ±5° (c 0.5; methanol); with concentrated H_2SO_4 it gives a coloration changing with time: 0 min, yellow-brown; 60 min, violet.

Alliotoxin $C_{29}H_{44}O_9$ crystallizes from methanol–water; mp 262–272° C; $[\alpha]_D^{24}$ – 40.0 ±7° [c 0.35; chloroform–ethanol (2 : 1)]; with 84% H_2SO_4 it gives a coloration changing with time: 0 min; yellow-brown; 6 min, red-violet; 20 min, violet.

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16 December 1968

Khar'kov Chemical and Pharmaceutical Scientific-Research Institute

UDC 547.92+615.711.5

ALLIOTOXIN AND ALLIOTOXIGENIN

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 3, pp. 189–190, 1969

Alliotoxin is a new cardiac glycoside isolated [1] from the seeds of Cheiranthus allioni Hort.; it has the composition $C_{29}H_{44}O_9$. It exhibits biological activity at 0.25 mg/kg bodyweight of the cat (determined by S. I. Lutokhin). UV spectrum: $\lambda_{max}^{ethanol}$ 217 mμ (log ε 4.18). The optical rotatory dispersion spectrum (recorded by I. P. Kovalev) shows a smooth positive curve (for the other properties of the glycoside, see [1]).

The hydrolysis of alliotoxin gave the aglycone (II), which we have called alliotoxigenin and a monosaccharide (III). The aglycone (II) has mp 295–301° C; $[\alpha]_D^{22}$ + 25.8° ±5° (c 0.5; pyridine); it dissolves in 84% H_2SO_4 giving a coloration changing with time: 10 sec, yellow; 15 sec, yellow-red; 7 min, brown; 30 min, blue.

Found, %: C 71.02; H 8.93; mol. wt. 395 (spectroscopic method). Calculated for $C_{23}H_{34}O_5$, %: C 70.74; H 8.77; mol. wt. 390.5.