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A GLYCOSIDE OF MERISTOTROPIC ACID

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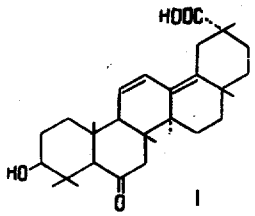
From an extract of the roots of Meristotropis triphylla Fisch. et Mey. we have isolated meristotropic acid [1], the structure [2, 3] of which corresponds, probably, to (I). In view of the possibility of the formation in the acid hydrolysis of triterpene compounds of heteroannular dienes, we made an attempt to obtain meristotropic acid or a suitable derivative of it by omitting the stage of acid hydrolysis. An extract of the roots of M. triphylla was boiled with ethanol or methanol. The alcoholic extract was evaporated and cooled. The precipitate that deposited was chromatographed on silica gel. Colorless needle-like crystals with mp 208–210° C (from ethanol) were obtained.

IR spectrum: 3200 (OH group), 1700 (CO group of a carboxyl), and 1695 cm^{-1} (CO group of a ketone). UV spectrum: λ_{max} 258, 250, and 242 mμ (1.5 mg of substance in 80 ml of 70% ethanol). It is known that these maxima are also characteristic for meristotropic acid. The substance isolated is perhaps an insufficiently pure glycoside consisting of meristotropic acid and two molecules of uronic acids.



I

The acid hydrolysis of the glycoside formed meristotropic acid.

The isolation from the roots of M. triphylla of a glycoside with mp 208–210° C and a characteristic UV spectrum shows that the conjugated system of double bonds in meristotropic acid is created in the plant itself.

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A SAPONIN OF PRIMULA TURKESTANICA

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We have studied the subterranean organs of the plant (roots and rhizomes) collected in 1966 in the region of the Chon-Ashu pass (Kirgiz SSR) at a height of 3600 m above sea level.

From a methanolic extract of the defatted raw material (1.2 kg), after threefold precipitation with acetone from methanol, we obtained 87 g of a purified mixture containing about eight compounds.

When this mixture was filtered through inactivated alumina, about 60% of substances not containing flavonoids was obtained. From the results of chromatography on a thin layer of hydrated silica in the chloroform—methanol—water (62 : 31 : 7) system, the mixture contained three substances (A, B, and C), of which only A was a saponin.

Substance A was isolated with a yield of 15% from the combined A, B, and C by column chromatography on hydrated silica in the system mentioned above. Substance A gave a single spot on chromatography in a thin layer of KSK silica gel and hydrated silica in neutral, acid, and alkaline systems: chloroform—methanol—water (62 : 31 : 7), 1-butanol—acetic acid—water (4 : 1 : 2); and n-propanol—17% ammonia (8 : 2). The R_f values of substance A, its melting point (about 250° C), the melting point of the acetate (160–163° C), and the IR spectrum were identical with the same figures for samples of Primula saponin given to us by N. I. Libizov (VILR [All-Union Scientific-Research Institute for Medicinal and Aromatic Plants]).

The full tridecaacetate of substance A, recrystallized from a mixture of petroleum ether and ether had mp 160.5–163° C.

Found, %: C 58.20; H 7.17. Calculated for $C_{80}H_{114}O_{36}$, %: C 58.17; H 6.96.

The melting point of the full acetate that we obtained from a sample of Primula saponin was 157–150° C. A mixture of the acetates gave no depression of the melting point. The IR spectra were identical.

The thin-layer chromatogram on silica gel G of the water-insoluble products of hydrolysis of substance A corresponded to that reported for Primula saponin [1]. The monosaccharides obtained on hydrolysis were identified by means of paper chromatography as galactose, glucose, rhamnose, and uronic acid. An analysis of the monosaccharides formed during hydrolysis shows that uronic acid split off last. This shows that it is attached directly to the genin.

All these data correspond to those reported previously for Primula saponin and, thus, the saponin from Primula turkestanica is also 3{[β-D glucopyranosyl-(1 → 6)-β-D-galactopyranosyl(1 → 4)]-[α-L-rhamnopyranosyl(1 → 2)]-β-D-galacturopyranosyl-(1)} primulagenin A.

When a mixture of substances A, B, and C was chromatographed together with substance A, a mixture of B and C was obtained from which recrystallization from methanol gave substance B with mp 183.5–185° C, which was identified as sucrose.

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A STUDY OF THE ALKALOIDS OF SENECIA KRYLOVII

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The epigeal part of Senecia krylovii was collected by V. B. Kubaev in Transbaikal at the end of the vegetation phase of the plant. The alkaloids were extracted from 450 g of raw material with a 4% solution of sulfuric acid with simultaneous reduction by means of zinc dust. The alkaloids were extracted with chloroform from the sulfuric acid extract after it had been made alkaline with ammonia. The chloroform extract was treated with a small amount of sulfuric acid solution. When the sulfuric acid extract was alkalized with ammonia to pH 8, a white crystalline precipitate deposited. Yield 0.03%. It was shown by thin-layer chromatography on silica gel in the systems 1) methanol, and 2) diethyl ether—chloroform—diethylamine (8 : 2 : 1) that it consisted of a single base with R_f values 0.60 and 0.50, respectively. After recrystallization from methanol, the melting point of the base was 214–212° C; $[\alpha]_D^{20}$ −139° (c 0.71; chloroform); composition $C_{18}H_{25}O_5N$; melting point of the picrate 180–181° C and of the picrolonate 187–189° C. A mixture of the substance was obtained with an authentic sample of seneciphylline gave no depression. The IR spectrum of the base was identical with that of seneciphylline.

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