TRITERPENE GLYCOSIDES OF *Zygophyllum obliquum*

I. AGLYCONES

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Continuing a study of the family Zygophyllaceae [1, 2] we have investigated four species of the genus *Zygophyllum* (*Z. obliquum*, *Z. rosovii*, *Z. kegense* and *Z. megacarpum*) that grow in Kirghizia. A preliminary chemical analysis has shown that they all contain saponins of triterpene nature.

In the present communication we give the results of an investigation of the saponins of the epigeal part of *Z. obliquum* collected in July, 1975 in the Boom gorge, Issyk-Kul' oblast, in the fruit-bearing phase. The saponins were extracted with ethanol from the raw material that had previously been treated with chloroform. The isolated total saponins, according to TLC on silica gel in butan-1-ol–formic acid–water (4:1:5) and chloroform–methanol–water (65:30:6.5) systems contained six glycosides of triterpene nature which we have called, in order of increasing polarity glycosides A, B, C, D, E, and F.

The total saponins were hydrolyzed with 20% sulfuric acid on the water bath for 5 h. The total genins liberated were separated on a column of KSK silica gel with elution by chloroform–ethanol in various ratios (99:1, 98:2, 97:3). Zones were eluted that contained individual genins having R_f 0.67 and 0.40 in the chloroform–ethanol (25:1) system which have provisionally been designated genins A and B.

Genin A had mp 294-296°C, $[\alpha]_D^{20}$ +71.6° ($CHCl_3$). The mass spectrum* of the genin under investigation has a strong peak of the molecular ion with m/e 456 and the peaks with the lower m/e ratios of 248, 207, and 189 that are characteristic for triterpene compounds [3]. The IR spectrum of the substance showed bands with frequencies of 3440 cm^{-1} (OH) and 1680 cm^{-1} (C=O). NMR spectrum: signals of methyl groups in the 0.75-1.15 ppm region and of a vinyl proton at 5.3 ppm. The acetate of the genin had mp 256-259°C. The latter spectrum contained the peak of the molecular ion with m/e 498 and the main characteristic peaks with m/e 248, 249, and 189. The IR spectrum lacked the absorption band of a hydroxy group. NMR spectrum: the signals of an acetyl group were detected in the 2.0 ppm region.

Genin B, mp 315-318°C, $[\alpha]_D^{20}$ +77.54±16.47° (c 1.64; pyridine). The mass spectrum of the genin contained the peak of the molecular ion with m/e 472 and peaks with m/e 248, 223, 207. IR spectrum: 3450, 3320 cm^{-1} (OH), 1700, 1690 cm^{-1} (C=O). In the NMR spectrum of genin B the signals of methyl groups appeared in the region from 0.92 to 1.12 ppm and the signals of a proton at C_3 in the 3.16 ppm region, of a C_{23} proton at 3.62 to 4.0 ppm and of a vinyl proton at 5.36 ppm. The mp of the acetate of the genin was 156-159°C. Mass spectrum (M^+556): m/e 307, 223, 187. IR spectrum: 1690 cm^{-1} (C=O). The NMR spectrum of the acetate had the signals of methyl groups in the 0.89-1.12 ppm region and of acetyl groups in the 2.00 ppm region.

On the basis of the physicochemical properties and the characteristics of their mass, NMR, and IR spectra, genins A and B were identified as oleanolic acid and hederagenin. The acid hydrolyzate, after treatment with barium carbonate, was found by paper chromatography to contain glucuronic acid and glucose.

LITERATURE CITED

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QUANTITATIVE DETERMINATION OF SPHAEROPHYSINE BENZOATE

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Sphaerophysine — an alkaloid obtained from the plant salt globe-pea (*Sphaerophysa salsula*) is produced by the domestic pharmaceutical chemistry in the form of sphaerophysine benzoate.

The determination of sphaerophysine benzoate by acid–base titration in a nonaqueous medium [1] is characterized by low sensitivity and inconvenient execution. A method is known for the quantitative analysis of sphaerophysine by the colorimetric examination of a sample obtained in the chromatographic separation of the alkaloids of the globe-pea and its treatment with ninhydrin [2]. A defect of this method is its low selectivity, since ninhydrin is used in the analysis of many drugs belonging to various classes of compounds [3].

The object of the present investigation was to increase the sensitivity of the determination of sphaerophysine benzoate. For this purpose we have studied the possibility of using alloxane hydrate for the quantitative analysis of this drug by a spectrophotometric method in the visible region. It has been established that alloxane hydrate reacts with sphaerophysine benzoate in dimethyl formamide with the formation of a crimson solution. The optimum conditions for the reaction are heating in the boiling water bath, the use of alloxane hydrate in the form of a 10% solution in dimethylformamide, and the use of kh. ch. ["chemically pure"] dimethylformamide as solvent.

The figures given below show the high sensitivity of the reaction of alloxane hydrate with sphaerophysine benzoate

Analytical index	Numerical values
Absorption maximum, nm	479
Molar absorption coefficient	12,050
Specific absorption	0.0272
Sandell coefficient	0.0367
Koch and Koch–Dedic coefficient	1.835
Minimum detectable concentration, μg/ml	1.836

The absorption spectrum of the product of the interaction of the drug with the reagent has λ_{max} 479 nm. We have calculated the specific absorption index ($E^{1\%}_{1cm}$) for this wavelength. The basic law of light absorption is obeyed within the concentration of 1.2-3.6 mg of sphaerophysine per 100 ml of solution.

The quantitative determination of sphaerophysine benzoate in the substance was carried out in the following way. An accurately weighed sample of between 0.0124 and 0.0229 g was dissolved in dimethylformamide in a 50-ml measuring flask and was made up to the mark with dimethylformamide. To 2 ml of this dilution was added 2 ml of a solution of alloxane hydrate in dimethylformamide. The reaction mixture was heated on the boiling water bath for 5 min and was then artificially cooled, and the solution was transferred quantitatively to a 25-ml measuring flask and was made up to the mark with dimethylformamide. The optical density of the colored solution was measured in a SF-4A spectrophotometer in quartz cells with a layer thickness of 1 cm at an analytical wavelength of 479 nm.

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