

Cephalaroside E was saponified with 10% alkali, and the glycoside formed was extracted with n-butanol. After acid hydrolysis of the progenin, D-glucose, L-arabinose, and L-rhamnose were detected. The acid hydrolysis of the oligosaccharide split off yielded L-arabinose.

The IR spectrum of cephalaroside showed an absorption band at 1755 cm^{-1} (ester grouping), which confirms the O-acyl glycosidic nature of cephalaroside E [5]. The results of alkaline hydrolysis and of the characteristics of its IR spectrum show that cephalaroside E is an O-acyl glycoside. The O-acyl moiety contains several molecules of L-arabinose. The study of cephalaroside E is continuing.

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METHODS OF ANALYZING CUCURBITACINS IN CUCUMBERS

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The bitter principle of cucumbers, as of other plants of the family Cucurbitaceae, consists of substances belonging to the class of tetracyclic triterpenoids and having the general name "cucurbitacins." Having the same carbon skeleton as lanostane, they are distinguished only by the number and positions of oxygen-containing functional groups. More than 20 individual cucurbitacins have been described, and information on the pharmacological activity of these compounds obtained from various plants of the family Cucurbitaceae is known [1-3]. As has been shown by Chembliss and Jones, the cucurbitacins play the part of attractants for insects [4]. The peculiar properties of the cucurbitacins make it necessary to seek accurate and rapid methods for their determination in plants.

The Moldavian Scientific-Research Institute of Vegetable Growing has presented chemists with the task of developing a method of analyzing plants for their content of cucurbitacins which is sufficiently sensitive and is suitable for use in micromodifications and for routine determinations.

We have proposed and subjected to practical testing two methods of determining cucurbitacins in plants. First, two representatives of this group of triterpenoids — cucurbitacins B [2] and C [5] — were isolated from cucumber leaves and identified.

The first method of analysis is based on the fact that the cucurbitacins fluoresce in UV light, particularly in the presence of formaldehyde. About 100 mg of the fresh plant is heated in a test tube with 1 ml of a 33% solution of formaldehyde in the boiling-water bath for 3 min. After this, a 0.01-ml sample is taken from the reaction mixture, deposited on chromatographic paper, and dried. The spot begins to fluoresce in UV light. For comparison, a standard consisting of a sheet of paper upon which cucurbitacins B and C in various concentrations have been deposited is examined under the same conditions.

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The method is recommended for routine analyses for which it is unnecessary to determine the percentage content of the cucurbitacins accurately. In the selection and screening of shoots it is sufficient to group them according to three arbitrary characteristics: very bitter (rich in cucurbitacins), moderately bitter, and not bitter (poor in cucurbitacins).

The second method, which is based on the property of the cucurbitacins of giving a characteristic maximum in the UV spectrum at λ 202-207 nm, has been used for their quantitative determination. The spectra of individual cucurbitacins obtained from cucumber leaves have been obtained on a Specord UV-IS spectrophotometer, and a calibration curve has been plotted for them.

When the conditions of extraction are strictly observed, it is possible to obtain satisfactorily reproducible results showing the relative amount of the total cucurbitacins.

Samples of the fresh plant (100 mg) were each placed in a test tube and covered with 2 ml of ethanol. The series of test tubes was placed in the water bath heated to 70°C and kept there for 5 min. Then from each test tube 0.01 ml of the extract was removed by means of a micropipette and transferred to the cell of a spectrophotometer to which 2 ml of the pure solvent used in the given experiment was also added. On the spectrum recorded, the height of the maximum at λ 202-207 nm was determined with an accuracy of 1 mm. The amounts of cucurbitacin in the samples were calculated from the calibration curve.

Impurities present in the ethanolic extract do not absorb in this region of the spectrum and therefore do not interfere with the determination. This fact is extremely important, since it has proved unnecessary to free the extract from ballast substances.

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STRUCTURE OF THE PRODUCT OF THE REDUCTION BY BARTON'S METHOD OF METHYL 3 β ,23-DIACETOXY-16-OXOLEAN-12-EN-28-OATE

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Previously, during a determination of the structure of the new triterpenoid caulophyllogenin (3 β ,16 α ,23-trihydroxyolean-12-en-28-oic acid) we reduced methyl 3 β ,23-diacetoxy-16-oxolean-12-en-28-oate by Barton's method [1, 2]. After the treatment of the reaction product with diazomethane, we isolated a compound which, from its R_f value on TLC and its melting point, was considered to be the methyl ester of hederagenin. However, on the basis of an analysis of its IR, PMR, and mass spectra it has been established that the reduction product actually has the structure of 28-norolean-12-ene-3 β ,23-diol (I).

The decarboxylation of triterpene β -oxo acids under the conditions of Wolff-Kishner reduction is known [3, 4]. The information which we give is an additional confirmation of the fact that caulophyllogenin is a β -hydroxy acid. The IR spectrum of (I), mp 207-210°C (MeOH): $[\alpha]_D^{22} +17.2^\circ$ (c 0.13; CHCl₃), lacks the absorption of an ester group.

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