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 3β,23-DIACETOXY-16-OXOOLEAN-12-EN-28-OATE

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UDC 547.918+547.597

Previously, during a determination of the structure of the new triterpenoid caulophyllogenin (3β,16α,23-trihydroxyolean-12-en-28-oic acid) we reduced methyl 3β,23-diacetoxy-16-oxoolean-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-3β,23-diol (I).

The decarboxylation of triterpene β-oxo acids under the conditions of Wolff–Kizhner 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° (c 0.13; $CHCl_3$), lacks the absorption of an ester group.

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The mass spectrum contains the peak of the molecular ion with M^+ 428 and the main peaks of ions with m/e 223, 204, and 189 corresponding to the fragments obtained as a result of the retro-Diels–Alder fragmentation of a triterpenoid from which a carboxy group is absent. The PMR spectrum (90 MHz, $CDCl_3$) has the signals of six methyl groups at (ppm) δ 0.78 (3 H), 0.89 (3 H), 0.91 (6 H), 0.95 (3 H), 1.03 (3 H); and the signals of protons on the corresponding carbon atoms and on a double bond: δ 3.59 ($C_{(3)}H{-}OH$); $\Delta\delta_{AB}$ 0.13 ppm, $J_{AB} = 7.2$ Hz, δ_A 3.52 ppm, δ_B 3.39 ppm ($C_{(23)}{-}H_2$); δ 5.24 ppm ($C_{(12)}{-}H$).

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STEROID SAPONINS.

XII. PRELIMINARY CHARACTERIZATION OF STEROID GLYCOSIDES FROM *Funkia ovata*

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Cases of the presence in one plant of the glycosides of the spirostanol and furostanol series have been described in the literature [1, 2]. *Funkia ovata* (*Hosta caerulea*; blue plantain lily) has not previously been studied for the presence of steroid glycosides.

We isolated the total saponins from the leaves of this plant, and they were separated by repeated chromatography into nine individual compounds called in order of their increasing polarity funkiosides A, B, C, D, E, F, G, H, and I. The positive reaction of the compounds obtained with the Sannié reagent [3] enabled us to assign them to the steroid glycosides. By means of the Ehrlich reagent [4], the glycosides were separated into furostanol compounds (funkiosides B and I) and spirostanol compounds (all the others). The NMR spectra of the compounds mentioned confirmed that they belong to the furostanol series since their spectra showed the signal of a methoxy group at 3.15 ppm which is characteristics for a C-22 methyl ketal [5] and is absent from the spectra of the spirostanol glycosides.

After acid hydrolysis, diosgenin was identified for all the funkiosides from its melting point, specific rotation, chromatographic mobility in a thin layer of silica gel in the presence of markers, and also its IR and mass spectra. However, in view of the fact that funkiosides B and I belong to the furostanol series, it can be stated that their aglycone is actually (25R)furost-5-en-3β,22α,26-triol. The monosaccharide compositions were determined by gas–liquid and paper chromatography, as shown on the following page.

Funkiosides A and B were methylated by Kuhn's method [6] followed by the methanolysis of the permethylated compounds. In both cases, methyl 2,3,4,6-tetra-O-methyl-D-glucoside was found in the reaction products by GLC and TLC.

On the basis of the results of hydrolysis, methylation, determinations of the melting points and values of $[\alpha]_D$, and its chromatographic mobility on TLC, funkioside A was identi-

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