the coleoptiles of wheat of the Saratovskaya 29 variety. At a concentration of 0.5%, britanin exhibited 100% repellance for the imago of the yellow mealworm beetle, and the degree of protection of a leaf was 85%.

LITERATURE CITED

1. K. S. Rybalko, Natural Sesquiterpene Lactones [in Russian], Moscow (1978).
2. H. Yoshioka, T. J. Mabry, and B. N. Timmermann, Sesquiterpene Lactones. Chemistry, NMR, and Plant Distribution. University of Tokyo Press, 544 (1973).
3. N. H. Fischer, E. J. Olivier, and H. D. Fischer, "The biogenesis and chemistry of sesquiterpene lactones," Fortsch. Chem. Org. Naturst., 38, 47 (1979).
4. K. S. Rybalko, V. I. Sheichenko, G. A. Maslova, E. Ya. Kiseleva, and I. A. Gubanov, Khim. Prir. Soedin., 251 (1968).
5. M. N. Mukhmetzhanov, S. M. Adenov, and O. A. Abdurakhmanov, in: Theoretical Principles of the Processing of Organic and Mineral Raw Material [in Russian], Karaganda, No. III (1976), p. 104.

THE MAIN TRITERPENE COMPOUNDS OF VINE LEAVES AND RACHISES

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We have investigated the neutral triterpene components of hexane extracts of the leaves and rachises of the vine *Vitis vinifera* L. s., of the Rkatsiteli variety. The corresponding extracts, obtained with yields of 5 and 4%, respectively, were saponified by the usual method [1]. The unsaponifiable part contained 49.5% in the case of the extract from the leaves and 23.8% in the case of the extract from the rachises.

Chromatography on silica gel (the eluent being petroleum ether, containing increasing concentration of diethyl ether) yielded from both products a fraction of dimethyl- and methylsterols which were identified by using authentic compounds of these classes as markers in TLC. Since the fractions isolated proved to be complex mixtures of compounds (GLC), they were acetylated with acetic anhydride in pyridine and the acetates obtained were rechromatographed on silica gel impregnated with 5% of silver nitrate, using the same eluting system. Then the dimethylsterol fraction from the leaves yielded the acetates of taraxerol, of taraxasterol, and of β-amyrin, which were identified from their melting points and their PMR and mass spectra. These compounds were the main ones, and they were accompanied by small amounts of the acetates of β-amyrin, lupeol, and methyl oleanolate, which were identified from their mass spectra with the use of chromato-mass spectrometry (CMS) (for conditions, see [2]).

It was established by the CMS methed that the main components of the acetylated fraction of the methylsterols from the leaves were the acetates of citrostadienol and of 24-ethyllophenol.

Similarly, from the mixture of acetates of the dimethylsterols from the vines rachises we isolated the acetates of α- and β-amyrins and of lupeol, and by the CMS method we identified the acetates of taraxerol, tarazasterol, germanicol, cycloartenol, and 24-methylenecycloartanol. By the CMS method, the fraction of methylsterols from the rachises were found to contain citrostadienol, obtusifoliol, and oleanic and ursolic aldehydes.

This is the first time that any of the compounds identified apart from the last two [3] have been identified in *Vitis vinifera* L.s.

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0009-3130/84/2006- 0758$08.50

LITERATURE CITED

1. T. Hilditch and P. Williams, The Chemical Constitution of Natural Fats, 4th edn., Chapman and Hall, London (1964).
2. V. L. Salenko, V. N. Sidel'nikov, M. L. Troshkov, V. A. Raldugin, and V. A. Pentegova, Khim. Prir. Soedin., 328 (1982).
3. C. H. Brieskorn and G. Blosczuk, Z. Lebensmittel-Untersuch. Forsch., 172, 201 (1981).

STRUCTURE OF CUCUMARIOSIDE A_2-2 — A TRITERPENE GLYCOSIDE FROM THE HOLOTHURIAN *Cucumaria japonica*

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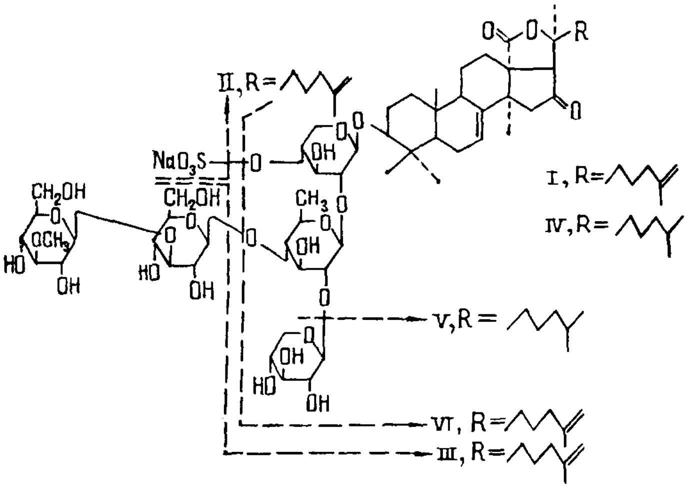
Continuing our investigation of the glycosides of the holothurian *Cucumaria japonica* Semper, we have isolated a new triperpene glycoside — cucumarioside A_2-2 (I) and have determined its structure. It had been shown previously that the native aglycone of (I) was 3β-hydroxyholosta-7,25-dien-16-one [1].

Cucumarioside A_2-2, mp 245-247°C (from ethanol), $[\alpha]_D^{20}$ −68° (c 2.0; pyridine) was isolated from a methanolic extract of the holothurian by successive chromatography on silica gel in the $CHCl_3$—C_2H_5OH—H_2O (100:100:17) system and on Polikhrom-1 ($H_2O \rightarrow 13\%\ C_2H_6OH$).



The acid hydrolysis of (I) gave a mixture of D-quinovose, D-xylose, 3-O-methyl-D-glucose, and D-glucose in a ratio of 1:2:1:1, and sulfuric acid. The monosaccharides were identified by GLC and by the chromato-mass-spectrometric method (GLC-MS) in the form of the peracetates of the corresponding aldononitriles. In the ^{13}C NMR spectrum of (I) signals at 105.6 (double), 105.1, 104.9, and 102.4 ppm of the anomeric carbon atoms of the carbohydrate chain showed the β-configurations of all the glycosidic bonds.

When glycoside (I) was heated in a mixture of pyridine and dioxane the desulfated derivative (II) was obtained with mp 283-285°C, $[\alpha]_D^{20}$ −76.5° (c 1.7; pyridine). The Hakomori [2] methylation of (II) followed by methanolysis and acetylation of the methanolysis products led to the formation of methyl 2-O-acetyl-3,4-di-O-methyl-α- and -β-xylopyranosides, methyl 2,3,4-tri-O-methyl-α- and -β-xylopyranosides, methyl 2,4-di-O-acetyl-3-O-methyl-α- and -β-quinovopyranosides, methyl 3-O-acetyl-2,4,6-tri-O-methyl-α- and -β-glucopyranosides, and methyl 2,3,4,6-tetra-O-methyl-α- and -β-glucopyranosides. The results obtained showed that the carbohydrate chain of glycoside (I) had a branched structure. The center of branching was a quinovose residue, and 3-O-methylglucose and xylose residues were terminal.

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