CHEMICAL CHARACTERISTICS OF PROTOYUCCOSIDE E. IX

I. P. Dragalin and P. K. Kintya

UDC 547.917 + 547.918

By a method described previously [1], we have isolated from the roots of Yucca filamentosa L. (Adam's needle yucca) a new steroid glycoside of the furostanol series with mp 150-152°C, $[\alpha]_D^{20}-29°$ (c 2.75; MeOH), which is a prototype of the sarsasapogenin glycoside yuccoside E [2], and we have called it protoyuccoside E (I).

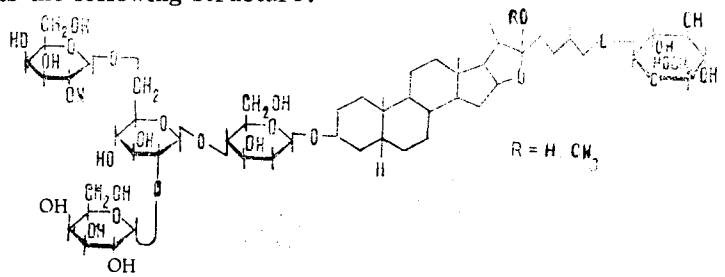
The Ehrlich's reagent (I) gives a positive reaction [3], while yuccoside E does not react with this reagent. Its enzymatic hydrolysis with the β-glucosidase from Helix pomatia yielded yuccoside E (II). Peracetylated (I) was subjected to oxidative cleavage [4] and a tetraacetylglucoside of methyl δ-hydroxy-γ-methylvalerate was obtained. The mass spectrum of the latter had characteristic peaks with m/e 331, 243, 242, 200, 169, 157, 145, 141, 140, 115, 109, 103 and 98 for tetraacetylglucose, and also for fragments with m/e 129 ($C_7H_{13}O_2$) and 97. These results show that (I) has the furostanol structure. In methanol systems, (I) behaves in the same way as glycosides of the furostanol series [4].

The acid hydrolysis of (I) formed an aglycone which was identical with sarsasapogenin in its specific rotation $[\alpha]_D^{20}-74°$ (c 0.95, $CHCl_3$), its mp of 199°C, its mass spectrum (M^+ 416), its IR spectra (912 and 892 cm^{-1} with an intensity of 3 :1), and its chromatographic behavior. Analysis of the monosaccharides isolated by the GLC of the acetates of their aldononitrile derivatives showed that (I) contains galactose and glucose in a ratio of 2 :3.

When (I) was methylated by Kuhn's method [5] followed by methanolysis of the products obtained with 72% $HClO_4$, methyl 2,3,4,6-tetra-O-methyl-D-galactopyranoside, methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside, methyl 2,3,6-tri-O-methyl-D-glucopyranoside, and methyl 3,4-di-O-methyl-D-glucopyranoside, were identified by GLC and TLC in the presence of markers. The presence of the latter two was also shown by mass and NMR spectrometry, as in the case of yuccoside E [2].

When (I) was subjected to periodate oxidation followed by hydrolysis, not one of the sugars named, was unaffected, which is in agreement with the results of methylation. The partial hydrolysis of (I) gave the same progenins as yuccoside E. The methanolysis of the permethylated progenins showed the same methyl glycosides as the progenins of yuccoside E [4]. The configurations of the glycosidic centers were determined by Klyne's rule [6] taking into account the molecular rotations of (I) itself and its progenins.

Protoyuccoside E has the following structure:



LITERATURE CITED

1. P. K. Kintya, I. P. Dragalin, and V. Ya, Chirva, Khim. Prirodn. Soedin., 615 (1972).
2. I. P. Dragalin, A. P. Gulya, V. V. Krokhmalyuk, and P. K. Kintya, Khim. Prirodn. Soedin., 747 (1975) [in this issue].
3. S. Kiyosawa and M. Huton, Chem. Pharm. Bull., 16, 6, 1162 (1968).

Institute of Chemistry, Academy of Sciences of the Moldavian SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 806-807, November-December, 1975. Original article submitted November 14, 1974.

4. R. Tschesche, G. Lüdke, and G. Wulff, Chem. Ber., 102, 1253 (1969).
5. R. Kuhn and H. Trischmann, Chem. Ber., 96, 284 (1963).
6. W. Klyne, Biochem. J., 47, No. 4, xli (1950).

PHENETHYL β-D-GLUCOPYRANOSIDE FROM THE FLOWERS OF Rosa gallica

V. N. Mel'nikov, P. S. Bugorskii, and V. V. Medvedkova

UDC 547.918

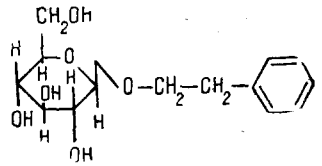
The essential oil of the rose consists mainly of monoterpene alcohols and β-phenylethanol. There is information in the literature of the presence of only monoterpene glycosides in rose flowers [1].

An aqueous ethanolic extract of fresh flowers of Rosa gallica L. (French rose; of the essential-oil variety Krymskaya Krasnaya) was separated by chromatography of silica gel; elution of the column with the solvent mixtures 1) benzene–ethanol (7 :3) and 2) ethyl acetate–ethanol–water (10 :2 :3) yielded a crystalline substance with the composition $C_{14}H_{20}O_6$, mp 38-39°C $[\alpha]_D^{20}$ −33.5° (c 3.0; water), calculated according to Klyne– 23.3° [2], soluble in water and ethanol and, on heating, in benzene.

UV spectrum λ_{max} (in ethanol) 253, 256 mμ (log ε 2.56, 2.57). IR spectrum (cm^{-1}): 706, 750 (monosubstituted aromatic nucleus); 1460, 1500, 1579 (C = C of an aromatic nucleus) [3]; 780, 1022, 1050, 1078 (pyranose ring); 904 (β-glycosidic bond); 3623 (OH group) [4, 5]; mol. wt. 278 (cryoscopically).

On acid and enzymatic hydrolysis of the substance with β-glucosidase in acetate buffer, pH 5.8, a monosaccharide was obtained which was identified chromatographically as D-glucose. The aglycone was identified as β-phenylethanol by GLC comparison with an authentic sample, and also by their IR and UV spectra [6].

Thus, the substance isolated is phenethyl β-D-glucopyranoside, and its structure can be represented by the following formula:



LITERATURE CITED

1. M. Francis and C. Allcock, Phytochem., 8, 1339 (1969).
2. W. Klyne, Biochem. J., 47, xli (1950).
3. Y. R. Naves, Perfum. Record, 49, 290 (1958).
4. N. K. Kochetkov and A. F. Bochkov, Chemistry of the Carbohydrates [in Russian], Moscow, Part I (1967), pp. 58-62.
5. A. T. Troshenko and G. A. Kutikov, Khim, Prirodn. Soedin., 244 (1967).
6. M. J. Kland-English, J. Amer. Chem. Soc., 75, 3709 (1953).

All-Union Scientific-Research Institute of Essential-Oil Crops. Translated from Khimiya Prirodnykh Soedinenii, No. 6, p. 807, November-December, 1975. Original article submitted May 5, 1975.