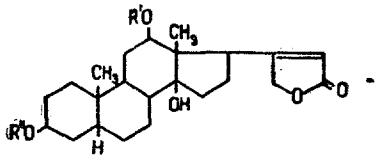
Substance	Empirical formula	Mp, °C	$[\alpha]_D$, deg (in methanol)	Biological activity	
				Mg/kg body wt. in the cat	Determined by
Digoxigenin-3-β-D-glucoside (I)	$C_{36}H_{44}O_{10}$	204—207	+2.1 ∓2	0.17	Zh. A. Lyubetskaya
Digoxigenin-3,12-di-β-D-glucoside (II)	$C_{35}H_{54}O_{15}$	amorphous	−9.8 ±3	0.19	
Digoxigenin 3-β-D-xyloside (III)	$C_{28}H_{42}O_9$	245—250	+5.2 ±2	0.16	N. A. Kisten
Digoxigenin-3,12-di-β-D-xyloside (IV)	$C_{33}H_{50}O_{13}$	154—159	−4.5 ±3	Not determined	

in methanolic solution. Substances I-IV were isolated in the pure state by partition chromatography in the solvent system toluene—butan-1-ol (1 : 1–1 : 2)/water. The stationary-phase carrier was a column of water-saturated alumina. The glycosides I-IV were crystallized from acetone and acetone—water (5 : 1). The properties of the substances synthesized are given in the table. As was to be expected, the diglycosides II and IV proved to be considerably more polar than the monoglycosides I and III.



I. $R' = H$; $R'' = \beta$-D-glucopyranose
II. $R' = R'' = \beta$-D-glucopyranose
III. $R' = H$; $R'' = \beta$-D-xylopyranose
IV. $R' = R'' = \beta$-D-xylopyranose

The yield of the monoglycosides I and III was about 40%, while the diglycosides II and IV were obtained with a yield of only 3%. The structure of the glycosides I-IV was confirmed by elementary analyses, molecular weights (determined spectroscopically from the absorption in the UV region), and by analyses of the molecular rotations in accordance with Klyne's rule [4]. The position of attachment (at C_3 of the aglycone) of the monosaccharide residues in the monoglycosides I and III was also known as described previously [1].

Pharmacological investigations of the cardenolides obtained have shown that they possess a high biological activity (see table). The introduction of a monosaccharide into position 12 not only does not lower the cardiotonic effect but, on the contrary, is capable of raising it, since the calculated molar coefficient of the activity (μM/kg body weight of the animal) is 0.266 for the diglycoside II and 0.307 and 0.306, respectively, for the monoglycosides I and III.

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16 December 1968

Khar'kov Chemical and Pharmaceutical Scientific-Research Institute

UDC 547.918+577.152

INHIBITION OF PLANT GLUCOSIDE HYDROLASES

P. I. Gvozdyak

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 3, p. 193, 1969

To prevent the hydrolysis of glycosides during their isolation from plants, it has been proposed to suppress the enzymes by both chemical [1–4] and physical [2,3,5] methods.

We have found that the δ-lactone of gluconic acid specifically inhibits the process of the cleavage of flavonoid [6] and anthraquinone [7] glucosides by enzymes of fungal origin. It was of interest to study the influence of the inhibitor on the enzymes of glucoside-containing plants. We investigated the roots of Frangula alnus, which contain very powerful hydrolytic enzymes [8, 9]. The process of extraction of the hydroxymethylanthraquinones from the roots of Frangula by 70% ethanol was studied by percolation, with the addition to the extractant of from 0 to 5% (of the weight of the roots) of δ-gluconolactone. The contents of glucofrangulin, frangulin, and emodin were determined photocolorimetrically after their separation in a thin layer of silica gel. It was found that as little as 0.1% of the lactone appreciably inhibits the enzymatic decomposition of glucofrangulin and about 1% of the inhibitor is sufficient for the practically complete suppression of the action of the glucoside hydrolases.

To obtain the gluconolactone, an aqueous solution of calcium gluconate was passed through a column of the cation exchange resin KU-2-8 (H^+ form), and the gluconic acid was evaporated to a sirup from which the final product crystallized on standing.

The simplicity of the preparation of the lactone, its physiological inertness, and its fairly high inhibiting capacity permits the hope that it will find wide use as an inhibitor of the glucoside hydrolases of plants during the isolation of various glycosides from them, and also in the production of medicinal substances.

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Khar'kov Chemical and Pharmaceutical Scientific-Research Institute

UDC 547.92+615.711.5

GLUCOEVONOGENIN AND GLUCOEVONOLOSIDE

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 3, pp. 193-194, 1969

As reported previously, from the seeds of Evonymus europaea auct. (Central Russian variety of the European euonymus) we have isolated the cardenolides evonomonoside, evonoloside, and evonogenin. In this paper we give the results of an investigation of two new cardiac glycosides from native seeds of the plant mentioned.

Comminuted euonymus seeds were defatted with petroleum ether and extracted with 70% ethanol. The ethanolic extracts were evaporated to an aqueous residue. The aqueous solution was purified with petroleum ether and alumina. The cardenolides were extracted with chloroform and then with a mixture of chloroform and ethanol (2 : 1). The ethanolic-chloroformic extracts were evaporated and the mixture of cardenolides was separated by partition chromatography in the toluene–butan-1-ol (3 : 1–1 : 2)/water system. The stationary-phase carrier was alumina saturated with water. The combined fractions yielded evonoloside and two unknown cardenolides which we have called glucoevonogenin (I) and glucoevonoloside (II). Substance I has mp 212–220° C; $[\alpha]_D^{22}$ + 1.9 ± 2° (c 0.7; methanol; UV spectrum: $\lambda_{max}^{ethanol}$ 218 mμ (log ε 4.16). The biological activity, determined by P. I. Bezruk and Zh. A. Lyubetskaya is 0.14 mg/kg body weight in the cat.

Found, %: C 61.64; H 7.80; mol. wt. 563.5 (spectroscopic method). Calculated for $C_{29}H_{44}O_{11}$, %: C 61.25; H 7.79; mol. wt. 568.67.