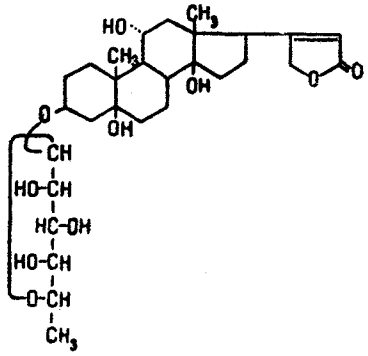
The aglycone crystallizes from acetone and ethanol; it has a double mp—232–235° C/294–301° C, $[\alpha]_D^{23}$ + 29, 3 ± 3° (c 1.0; methanol). UV spectrum: $\lambda_{max}^{ethanol}$ 217 mμ (log ε 4.20), and it dissolves in 84% H_2SO_4 giving a coloration changing with time: 1 min, yellow-orange; 25 min, violet; 140 min, lilac.

Found, %: C 68.32; H 8.61; mol. wt. 410 (spectroscopic method). Calculated for $C_{23}H_{34}O_6$, %: 67.95; H 8.43; mol. wt. 406.5.

Among the known cardiac aglycones with the composition $C_{23}H_{34}O_6$, the closest in properties to that described is the comparatively rarely found bipindogenin [3]. The results of a direct comparison (chromatography and IR spectra, taken by I. P. Kovalev) of the aglycone from alliside with bipindogenin (a sample of the latter was kindly supplied to us by N. F. Komissarenko) shows their identity.

The monosaccharide of alliside forms a phenylosazone melting at 180–182° C, $[\alpha]_D^{24}$ + 48.8 ± 6° (c 0.42; ethanol). The phenylosazone of the monosaccharide, as the result of a mixed melting point test, paper chromatography, and the IR spectrum shows, is identical with the phenylosazone of L-rhamnose. Nevertheless, the monosaccharide obtained is not L-rhamnose, as is shown by paper chromatography. This permits the assumption that the monosaccharide of alliside is 6-deoxy-L-glucose, which differs from L-rhamnose only by the configuration at C_2 and must give the same phenylosazone as L-rhamnose. On a direct comparison by paper chromatography of the monosaccharide and 6-deoxy-L-glucose (obtained by the demethylation of L-thevetose), their identity was established.



An analysis of the molecular rotations of the glycoside and the aglycone in accordance with Kline's rule [4] showed that the 6-deoxy-L-glucose (L-glucomethylose) is attached by an α-glycosidic bond. Thus, alliside is bipindogenin 3-α-L-glucomethyloside. This is apparently the first time that 6-deoxy-L-glucose has been found in cardiac glycosides.

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NEW DIGOXIGENIN GLYCOSIDES

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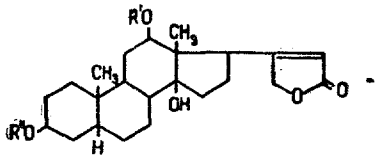
Khimiya Prirodnykh Soedinenii, Vol. 5, No. 3, pp. 191–192, 1969

We have previously reported the synthesis of digoxigenin 3-α-L-rhamnose [1]. In the same work it was shown that the reaction of acetylrhamnosyl bromide with digoxigenin takes place only at the C_3 hydroxyl group. Continuing a search for methods of obtaining diglycosides in which the monosaccharides are attached to two positions—at C_3 and C_{12}—, we have synthesized glucosides and xylosides of digoxigenin. This led to the desired result. The synthesis was carried out by the Königs-Knorr method [2] in Chernobai's modification [3]. The acetylglycosides were saponified with ammonia

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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INHIBITION OF PLANT GLUCOSIDE HYDROLASES

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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.