ERYCHROSOL – A NEW TYPE OF CARDIAC GLYCOSIDE

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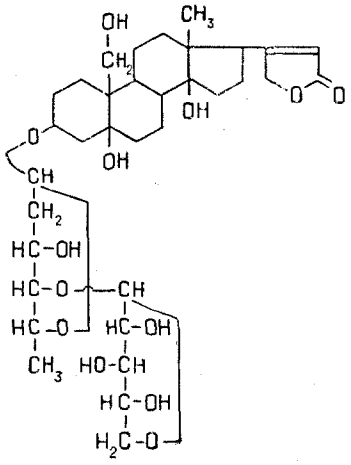
From the herbage plant Erysimim cheiranthoides L. (treacle erysimum), in addition to the other cardenolides which we have described in previous communications, we have isolated a new cardiac glycoside called erychrosol. Its isol t was associated with certain difficulties. The polarity of the glycoside is close to that of some other erysimim cardenolides. Attempts to isolate it in the individual state by means of adsorption chromatography on alumina proved unsuccessful. Only by partition chromatography on cellulose in long columns was it possible to obtain the glycoside in the individual crystalline state.



Erychrosol gives positive Legal, Raymond, and Kedde cardenolide reactions, and also a positive reaction with the Webb-Levy reagent [1], which shows the presence of a 2-deoxysugar. The molecular weight of 670. 1 and the empirical formula $C_{34}H_{52}O_{13}$ correspond to a steroid diglycoside. The UV spectrum exhibits only one absorption maximum at 220 mμ (log ε = 4. 16) which, in addition to the qualitative reactions, shows the presence of a butenolide ring. The hydrolysis of erychrosol with an enzyme preparation obtained from the pancreatic juice of the grape snail Helix pomatia in the crystalline state yielded a monoglycoside and a monosaccharide which were identified, respectively, as helveticosol and D-xylose. The acid hydrolysis of erychrosol under mild conditions has given the aglycone strophanthidol and the disaccharide erychrobiose [2]. Consequently, the second monosaccharide contained in erychrosol is D-digitoxose.

A comparison of the molecular rotations of erychrosol, helveticosol, and strophanthidol in accordance with Klyne's rule [3] shows that the D-digitoxose and D-xylose are connected by β-glycosidic bonds. The pyranose form of the oxide rings of the monosaccharide residues in the glycoside and also the 1-4link of the xylose with the digitoxose are determined by the structure of erychrobiose which we established previously [2]. Erychrobiose is 4-(β-D-xylopyranosyl)-D-digitoxose. Thus, erychrosol is 5, 14, 19-trihydroxy-5β-card-20(22)-enolide-(3)-D-digitoxopyranosido-(4)-β-D-xylopyranoside; its structure can be represented by the formula shown above.

The preparative isolation of erychrosol from erysimum confirms our suggestion [4] that erychrosol is present in this plant.

Experimental

The substances for analysis were dried in vacuum (0. 01 mm Hg) at 100° over phosphorus pentoxide for 2 hr. The following systems of solvents were used in the identification of the sugars by paper chromatography: n-butanol-acetic acid-water (4: 1: 5) and n-butanol-ethanol-ammonia-water (40: 10: 1: 49). The cardenolides were chromatographed on paper in the following systems: toluene-n-butanol-water (2. 5: 1. 5: 1)/water, and tetrahydrofuran-chloroform-formamide (50: 50: 6. 5)/formamide. The column (5 · 120 cm) was filled with moist cellulose in the form of a suspension in the "organic" phase of the toluene-n-butanol-water (2. 5: 1. 5: 1) system. Four grams of the glycosidic fraction obtained as waste products from the production of erychroside and consisting of erychrosol, erychroside, and glucodigifucoside was dissolved in 30 ml of the "organic" phase and the solution was transferred to the column. Elution was carried out with the same solvent. Erychroside was eluted first and then erychrosol and, finally, glucodigifucoside. The fractions containing the erychrosol were combined and evaporated in vacuum. The glycoside was crystallized from isopropanol-ether solution. The crystals obtained (0. 4 g) melted at 228-232°, $[\alpha]_D^{22}$ + 18. 7 ± 3° (c 0. 924; methanol). The glycoside dissolved in 84% sulfuric acid with a brown coloration changing after 10 min into red-brown.

Found %: C 60. 77; H 7. 92; molecular weight 672. 1 (lactone titration).

Calculated for $C_{34}H_{52}O_{13}$: C 61. 06; H 7. 84%; molecular weight 668. 79.

The enzymatic and acid hydrolyses of erychrosol were carried out by the method described previously [5]. After enzymatic hydrolysis, a monoglycoside and a monosaccharide were obtained. The monosaccharide crystallized from alcohol-ether in the form of long prisms melting at 145-147° which proved to have the same R_f on paper chromatography as D-xylose. The osazone of the sugar was prepared; it melted at 162-163°. The monoglycoside crystallized from aqueous methanol in the form of prisms melting at 147-151°; $[\alpha]_D^{21}$ + 27. 1 ± 3° (c 0. 839; methanol). It dissolved in 84% sulfuric acid with a brown coloration. The acid hydrolysis of erychrosol gave the crystalline aglycone and the amorphous disac-

charide. The R_f of the disaccharide on paper chromatography proved to be identical with the R_f of erychrobiose. The aglycone melted at 139-142°; $[\alpha]_D^{20}$ + 34.2° ± 5° (c 0.424; methanol). It dissolved in 84% sulfuric acid with a yellow coloration changing to red after 10 min. On paper chromatography, it exhibited an R_f value identical with that of strophanthidol.

Summary

A new glycoside called erychrosol has been isolated from the herbage plant Erysimum cheiranthoides L., and its chemical structure has been established. Erychrosol is strophanthidol-(3)-β-D-digitopyranosido-(4)-β-D-xylopyranoside.

REFERENCES

1. I. M. Webb and H. B. Levy, J. Biol. Chem., 213, 107, 1955.
2. I. F. Makarevich, Author's Abstract of Dissertation, Kharkov, 1962.
3. W. Klyne, Biochem. J., 47, no. 4, 1950.
4. I. F. Makarevich and I. G. Zoz, Med. prom., SSSR, no. 5, 19, 1964.
5. I. F. Makarevich, M. Ya. Tropp, and D. G. Kolesnikov, Med. prom., SSSR, no. 7, 38, 1961.

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