CARDIAC GLYCOSIDES OF Cheiranthus allioni. X

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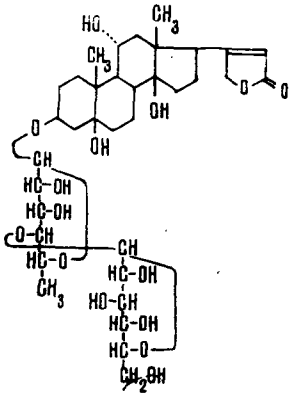
From the seeds of Cheiranthus allioni hort. (plains erysimum), family Cruciferae, we have obtained another two cardiac glycosides previously denoted by the symbols M-66A and M-81Ch. The first was obtained by the partition chromatography of a highly polar fraction of glycosides on cellulose in the toluene–butan-1-ol (1:2)/water system, and the second by adsorption chromatography on alumina of the "moderately polar" fractions [1].

Glycoside M-66A, named, after its structure had been established, glucobipindogulomethyloside, is one of the most important cardenolides of the plant investigated. The elementary analysis and the molecular weight found (for method, see [2]) agree well with the composition $C_{35}H_{54}O_{15}$. The IR spectrum is characterized by the presence of the following functional groups: a band with its maximum at 3390 cm^{-1}, OH group; 2940 and 2880 cm^{-1}, $-\underset{|}{\overset{|}{CH}}-$, $>CH_2$ and $-CH_3$ groups; 1734 cm^{-1}, $-C=O$ of a butenolide ring; 1624 cm^{-1}, $>C=C<$ of a butenolide ring.

Under the influence of an enzyme preparation obtained from the pancreatic juice of the grape snail, glucobipindogulomethyloside hydrolyzed, forming a monoglycoside and D-glucose. From the products of acid hydrolysis, and also by a direct comparison with a sample, the monoglycoside was identified as bipindogulomethyloside [3], which is bipindogenin 3β-O-β-D-gulomethylopyranoside.

In view of the comparative ease of hydrolysis of D-gulomethylosides, we attempted to isolate a biose from the diglycoside. Hydrolysis with 0.22 N sulfuric acid at 100°C led to the formation of D-glucose, D-gulomethylose, and a disaccharide, with the predominance of the latter. By preparative chromatography on paper, the disaccharide was obtained in the pure state and proved to be identical with erycordinobiose which, as has been established previously is 4-O-β-glucopyranosyl-D-gulomethylose [4]. On the basis of the facts obtained, glucobipindogulomethyloside (M-66A) can be characterized as 5β,11α,14β-trihydroxycard-20(22)-enolide-3β-O[O-β-D-glucopyranosyl-(1→4)-β-D-gulomethylopyranoside], and its structure can be expressed by the following formula:



The considerable amount of the diglycoside glucobipindogulomethyloside in plains erysimum has suggested the possibility of the existence of the native monoglycoside corresponding to it, bipindogulomethyl-

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cside. A directed search confirmed this hypothesis. The glycoside M-81Ch was found in individual fractions obtained previously in the isolation of alliside [1]. By being chromatographed twice on alumina, it was isolated in the pure state and was identified both from the products of its hydrolysis and by direct comparison with an authentic sample.

The cardiac glycoside uzarigenin 3β-O-[O-β-D-glucopyranosyl-(1→4)β-D-glucopyranoside] (M-64) isolated previously from Cheiranthus allioni hort. and described previously [8] we have compared with a sample of uzarin kindly given to us by Prof. T. Reichstein. As was assumed, these glycosides proved not to be identical, obviously differing in the sites of attachment of the terminal D-glucose. We consider it desirable to call the new glycoside M-64 neouzarin.

EXPERIMENTAL

The methods of isolating bipindogulomethyloside and glucobipindogulomethyloside were similar to those described previously [1, 5].

Bipindogulomethyloside (M-81Ch). The glycoside was crystallized from isopropanol–ether, mp 150-154/168-170°C, $[\alpha]_D^{23} -16.0 \pm 3°$ (c 0.45; methanol). In the chloroform–tetrahydrofuran (1 : 1)/formamide system, $R_{bipindogulomethyloside} = 1.00$. In concentrated H_2SO_4 it formed colors similar to the colorations of a sample of the cardenolide.

The glycoside (15 mg) was hydrolyzed by the Mannich–Siewert method for 47 h [6]. The aglycone fraction contained a cardenolide identical, according to paper chromatography, with bipindogenin. The sugar component and the phenylosazone obtained from it were identical, according to their R_f values with D-gulomethylose and its phenylosazone.

Glucobipindogulomethyloside (M-66A). The melting point of the glycoside was 192-195°C (from butanol), $[\alpha]_D^{21} -31.0 \pm 3°$ (c 1.00; methanol). In concentrated H_2SO_4 it gave the following colorations changing with time: 0 min – orange; 1 min – orange-brown; 60 min – violet; 180 min – blue-violet. In the toluene–butan-1-ol (1 : 2)/water system, $R_{glucoalliside} = 0.68$. Molecular weight: found 711.2 (method described previously [2]); calculated for $C_{35}H_{54}O_{10}$ 714.8. The elementary analysis also corresponded to the molecular formula given.

Enzymatic Hydrolysis of Glucobipindogulomethyloside. The diglycoside was hydrolyzed with an enzyme preparation from the grape snail and the hydrolysis products were separated as described previously [7]. The monosaccharide was crystallized from ethanol–ether. Its melting point was 144-146°C; a mixture with a sample of D-glucose also had mp 144-146°C. Paper chromatography showed the same R_f values as D-glucose. The monoglycoside had mp 150-153/167-169°C, $[\alpha]_D^{23} - 16.6 \pm 2°$ (c 0.82; methanol). On paper chromatography, $R_{bipindogulomethyloside} = 1.00$. A mixture with dipindogulomethyloside gave no depression of the melting point (150-153/167-170°C).

The monoglycoside (30 mg) was hydrolyzed by the Mannich–Siewert method [6] for 70 h. The aglycone fraction of the hydrolyzate, according to paper chromatography, consisted of bipindogenin and its anhydro derivatives. The carbohydrate component and the phenylosazone obtained from it showed R_f values corresponding to D-gulomethylose and gulomethylose phenylosazone.

Erycordinobiose from Glucobipindogulomethyloside. Glucobipindogulomethyloside (0.15 g) was dissolved in 7 ml of 0.22 N sulfuric acid and the solution was heated in a sealed tube at 100°C for 2. Then it was neutralized with barium carbonate, filtered through a layer of kieselguhr, and evaporated. It was chromatographed on seven sheets of paper (18 × 60 cm) in the butan-1-ol–acetic acid (4 : 1)/water system. The chromatographic paper was previously washed carefully with distilled water. The chromatograms were dried and the zones of the most polar carbohydrate component – the presumed disaccharide – were cut out. The dissacharide was transferred into aqueous solution and the solution was evaporated. The product was crystallized from methanol–butan-1-ol, using erycordinobiose as seed. The crystals obtained had mp 133-136/159-163°C. A mixture with a sample of erycordinobiose gave no depression of the melting point (133-136/160-163°C). On chromatography on paper, the sugar showed $R_{erycordinobiose} = 1.00$.

SUMMARY

Another two cardiac glycosides have been isolated from the seeds of Cheiranthus allioni hort. One of them has been identified as bipinogulomethyloside. The second, which we have called glucobipindogulomethyloside is new and is bipindogenin 3β-O-[O-β-D-glucopyranosyl-(1→4)-β-D-gulomethylopyranoside].

The glycoside M-64 isolated previously from this plant, which is uzarigenen 3β-O-[O-β-D-glucopyranosyl-(1→4)-β-D-glucopyranoside] is also new and has been called neouzarin.

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