the whole group of reflections we found the missing basis atoms. The structure was refined first by successive electron-density approximations (R = 0.232) and by the method of least squares (MLS) in the isotropic approximation (R = 0.208). Subsequently, in the full-matrix MLS with allowance for the anisotropy of the thermal vibrations of the non-hydrogen atoms it was refined to R = 0.105.

Attempts to determine the positions of the H atoms from the electron-density difference synthesis were unsuccessful. The coordinates of the atoms are given in Table 3.

SUMMARY

The stereochemistry of the new carotane ester ferticin has been established unambiguously as 8β-angeloyloxy-5β-hydroxy-9-oxo-cis-carotane.

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CARDIAC GLYCOSIDES OF Cheiranthus allioni.

XIII. GLUCOERYCORDIN

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UDC 547.92/93+615.224:547.918

From plains erysimum (Cheiranthus allioni) Hort., (Erysimum asperum) a new cardiac glycoside has been isolated which has been called glucoerycordin. Its chemical structure has been established mainly by stepwise hydrolysis and the identification of the hydrolysis products. Glucoerycordin $C_{41}H_{64}O_{19}$, mp 131-135°C, $[\alpha]_D^{20}$ −22.2 ± 3° (c 0.65; methanol) is 3β-[O-β-D-glucopyranosyl-(1 → 4)-O-β-D-glycopyranosyl-(1 → 4)-gulomethylopyranosyloxy]-14,19-dihydroxy-5β,14β-card-20(22)-enolide.

Continuing a study of plains erysimum Cheiranthus allioni Hort. (Erysimum asperum) (family Cruciferae), we have isolated from the highly polar fraction a new cardiac glycoside and, after determining its structure, have called it glucoerycordin. The substances were separated with the aid of absorption chromatography in silica gel columns.

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0009-3130/89/2501-0063 $12.50

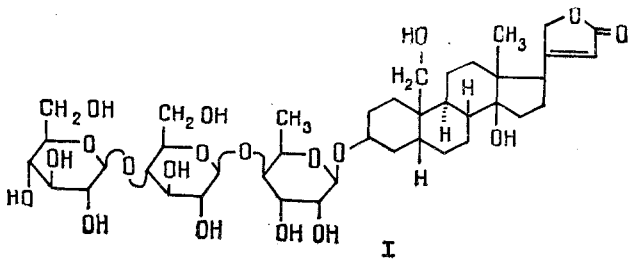
Glucoerycordin (I) has the composition $C_{41}H_{64}O_{19}$. On enzymatic hydrolysis it formed D-glucose and deglucoerycordin. The latter, as is known [2] is 3β-(β-D-glucomethylopyranosyloxy)-14,19-dihydroxy-5β-card-20(22)-enolide. These facts, and also the high polarity of the glycoside under study gave grounds for assuming the molecule could contain two D-glucose units linked to deglucoerycordin. This hypothesis was confirmed by the results of partial enzymatic and acid hydrolysis.

Thus, on controlled (partial) enzymatic hydrolysis we identified chromatographically as a reaction product – in addition to glucoerycordin and D-glucose – erycordin, which is 3β[O-β-D-glucopyranosyl-(1 → 4)-β-D-glucomethylopyranosyloxy]-14,19-dihydroxy-5β,14β-card-20(22)-enolide [2].

Partial acid hydrolysis of the glycoside obtained led to the formation of the aglycon cannogenol and the sugars D-glucose, D-gulomethylose, erycordinobiose (for structure, see [3]) and cellobiose, which were identified by paper chromatography in various solvents systems, and a presumed trisaccharide corresponding in structure to the carbohydrate moiety of glycoside (I).

In view of the known structure of erycordin [2] and the presence of cellobiose (4-O-β-D-glucopyranosyl-D-glucose) in the hydrolysate, it is possible to conclude that in the glycoside the carbohydrate moiety consists of an unbranched chain in which all the monosaccharide units are present in the pyranose form and are linked with one another in the 1 → 4 positions by β-glycosidic bonds. The β-configuration of the terminal D-glucose unit was also shown by the contribution of this carbohydrate component to the molecular rotation: $[M]_D$ term. D-Glc = −14 ± 40°.

Thus, glucoerycordin is 3β-[O-β-D-glucopyranosyl-(1 → 4)-O-β-D-glucopyranosyl-(1 → 4)-β-D-gulomethylopyranosyloxy]-14,19-dihydroxy-5β,14β-card-20(22)-enolide (I).



I

EXPERIMENTAL

Elementary analysis of the glycoside was performed with the use of an automatic C–H–N–S analyzer. The results correspond to those calculated for the structure (I) shown. The substances were separated with the aid of column chromatography on silica gel activated at 120°C for 2 h. Elution was performed with mixtures of chloroform and ethanol with increasing polarity. The glycoside was crystallized from isopropanol.

Glucoerycordin, $C_{41}H_{64}O_{19}$, mp 131-135°C, $[\alpha]_D^{20}$ −22.2 ± 3° (c 0.65; methanol).

Enzymatic Hydrolysis. A solution of 0.1 g of glucoerycordin in 3 ml of water was treated with 0.25 g of a dry enzyme preparation obtained from the pancreatic juice of the grape snail, and the solution was left at 40°C for 42 h. The enzymes were precipitated with hot ethanol. The cardenolide was extracted from the solution with chloroform and with chloroform–methanol (2:1) and was crystallized from acetone; mp 162-164°C, $[\alpha]_D^{20}$ −21.0 ± 2° (c 0.57; methanol). These results correspond to the monoglycoside deglucoerycordin [2]. A direct chromatographic comparison and a mixed melting point with a sample of deglucoerycordin also showed the identity of these compounds.

According to the results of paper chromatography the aqueous phase contained D-glucose.

The partial enzymatic hydrolysis of glycoside (I) was carried out similarly but with the difference that the reaction time was 3 h. Paper chromatography showed the presence in the hydrolysate of erycordin, diglucoerycordin, the initial glycoside (I), and D-glucose.

Partial Acid Hydrolysis. A solution of 30 ml of the glycoside in 0.1 N sulfuric acid was heated at 100°C for 3 h. The solution was neutralized with barium carbonate and, after the usual working up and separation into aglycon and carbohydrate moieties, these were

analyzed by paper chromatography in various solvent systems. The following were identified: cannogenol (aglycon), D-glucose, erycordinobiose, cellobiose, and, presumably, a trisaccharide.

SUMMARY

A new cardiac glycoside has been isolated from the seeds of plains erysimum Cheiranthus allioni Hort., (Erysimum asperum), and has been called glucoerycordin. Glucoerycordin is 3β-[O-β-D-glycopyranosyl-(1 → 4)-O-β-glucopyranosyl-(1 → 4)-β-D-gulomethylopyranosyloxy]-14,19,dihydroxy-5β,14β-card-20(22)-enolide.

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2-BENZOPYRYLIUM SALTS.

XXXV.* SYNTHESIS OF THE NATURAL ALKALOID DEHYDRONORCORALDINE AND OTHER SUBSTITUTED DIBENZO[a,g]QUINOLIZINIUM SALTS

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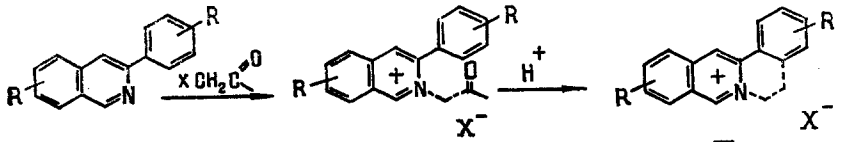
UDC 547.814.837.07

The interaction of 6,7-dimethoxy-3-(3,4-dimethoxyphenyl)-2-benzopyrylium perchlorate with α-aminocarbonyl compounds forms N-α-aminocarbonyl-substituted isoquinolinium compounds which on treatment with acids are converted into dibenzo[a,g]quinolizinium compounds, one of which is the natural alkaloid dehydronorcoraldine. The products were characterized by the results of elementary analysis and IR, PMR, and UV spectroscopy.

One of the most convenient synthetic approaches to alkaloids of the berberine and protoberberine classes is based on the use of 3-arylisoquinolines (I) as the initial structural units. Their alkylation with α-halogenocarbonyl compounds leads to the isoquinolinium salts (II) which readily cyclize in the presence of acids into dibenzo[a,g]quinolizinium structures of type (III) [2].



I II III

However, the multistage synthesis of the initial 3-arylisoquinolines that are used [2-4] and the difficulty of their alkylation [2], due, apparently, to the steric influence to the aryl substituent in position 3 are fundamental limitations of this method which do not allow its preparative use in the chemistry of natural alkaloids.

*For Communication XXXIV, see [1].

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