CARDIAC GLYCOSIDES OF THE Cheiranthus allioni. XII*

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The seeds of Cheiranthus allioni hort. have yielded three new cardenolides the structures of which have been established and which have been named as 4-dehydrodiosarmentogenin (II), 4-dehydrodiosarmentogenin rhamnose (I), and 4-dehydrodiosarmentogenin rhamnogluco side (IV). (II) — C_{23}H_{32}O_{6}, m.p. 296–302 °, \([\alpha]_{D}^{20} +26.2 \pm 3 °\) (in pyridine) is 3β,11α,14-trihydroxy-14β-card-4,20(22)-dienolide. (I) C_{25}-H_{42}O_{15}, m.p. 268–275 °, \([\alpha]_{D}^{20} =-38.2 \pm 3 °\) (chloroform-ethanol) is 11α,14-dihydroxy-3β-L-rhamnopyranosyloxy-14β-card-4,20(22)-dienolide. (IV) C_{35}H_{32}O_{14}, \([\alpha]_{D}^{20} =-44.1 \pm 3 °\) (methanol), is 3β-(4′-0-β-D-glucopyranosyl-α-L-rhamnopyranosyloxy)-14β-card-4,20(22)-dienolide. An independent synthesis of 4-dehydrodiosarmentogenin (II) has been carried out, starting from 3β,5,11α,14-tetrahydroxy-5β,14β-card-20(22)-enolide, which has confirmed its structure.

Cheiranthus allioni hort. (Erysimum asperum; plains erysimum) (family Cruciferae) is a unique plant with respect to the diversity of the set of cardiac glycosides and aglycons that it contains. In preceding communications published in this journal in 1969–1975, the isolation from the seeds of this plant and the structural determination of 29 glycosides composed of 9 aglycons and 6 monosaccharides have been described. These include cardenolides of both the A/B-cis and the A/B-trans series.

Continuing a study of plains erysimum, we have isolated another two new cardenolide glycosides and have provisionally called them Ch-(30) (I) and Ch-31 (IV).

Ch-30 (I) is a monoglycoside with the composition C_{25}H_{32}O_{6}, as shown by the results of elementary analysis and an investigation of hydrolysis products. After acid hydrolysis, performed by the Mannich–Siewert method [2], the new aglycon (II) and L-rhamnose were obtained. The elementary analysis and mass spectrum of the aglycon (II) showed that it had the composition C_{23}H_{32}O_{6}. The mass spectrum was characterized by a relatively intense peak of the molecular ion with m/z 388 and by fragments with m/z 370 (M – H2O)⁺, 352 (M – 2H2O)⁺, 334 (M – 3H2O)⁺, 319 (M – 3H2O – CH2)⁺, 217, 201, 199, 179, 173, 145, 91, 67, 55.

The composition C_{23}H_{32}O_{6} shows the "unsaturated" structure of the aglycon, i.e., that its molecule contains either a double C=C bond in the steroid nucleus or a carbonyl group. The presence of a carbonyl group was excluded by the characteristics of the optical rotatory dispersion spectrum and the IR spectrum. At the same time, they showed the presence of a double C=C bond. In addition to a band at 1620 cm⁻¹ due to the C=C bond of a butenolide ring there was a well resolved band at 1630 cm⁻¹ due to the stretching vibrations of an additional C=C bond present in the steroid part of the molecule. There was also a band at 810 cm⁻¹ which is apparently due to the deformation vibrations of hydrogen atoms at a double bond.

The presence of alcoholic groups at C-3 and C-14, of a butenolide ring at C-17, and of their β-configuration in the aglycon is essential for cardenolides with a high biological activity. The β-configuration of the lactone ring was also confirmed by isomerization results: when the aglycon or the glycoside Ch-30 (I) was heated in absolute dimethylformamide in the presence of anhydrous sodium tosylate and sodium acetate, more highly polar cardenolides were formed, which was due to the transformation of the initial substances into 17α-cardenolides. As was to be expected, the reaction products were revealed on chromatograms by the Jensen reagent in the form of spots with a blue fluorescence in UV light, while the initial glycosides and the aglycon had a yellow fluorescence.

*For Communication XI, see [1].

On oxidation with chromium trioxide, the aglycon formed a neutral reaction product, which excludes the presence of a primary OH group and of an aldehyde group in the initial compound.

When the aglycon was acetylated with acetic anhydride in pyridine and the course of the reaction was analyzed by a published method [3], it was found that it formed a diacetate, and the rates of acetylation of both OH groups were characteristic for secondary equatorial hydroxy groups, with a half-reaction time of less than 30 min (at 20°C).

The aglycon gave a positive reaction for a Δ⁴ or a Δ⁵ bond [4, 5]. On the basis of the following facts, the most probable position of the double bond in this case is 4:5. The optical rotatory dispersion spectrum of the aglycon consists of a smooth positive curve, which excludes a double bond in the 5:6 position and does not exclude but, on the contrary, confirms its presence in the 4:5 position [9]. Furthermore, the increased reactivity of the 38-OH group observed on the acetylation of aglycon is obviously due to the influence of a closely adjacent double bond, i.e., it is characterized by the presence of a vinyl alcohol fragment.

The choice of the position of the second equatorial OH group amounted to deciding between the 11α, 12β, and 16β positions as those most frequently found. The 12β and 16β positions were excluded, since such cardenolides, after treatment with the Jensen reagent, fluoresce blue in UV light, while, as already mentioned the aglycons under investigation fluoresced yellow.

On the basis of the results obtained, we assumed that the new aglycon was 4-dehydrosarmentogenin (II). In the light of such a structure, it could be expected that in a reaction with concentrated sulfuric acid this aglycon and bipindogenin (V) should give similar colora-