DI-C-GLYCOSIDES FROM Crataegus monogyna

N. Tsv. Nikolov and R. I. Vodenicharov

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By preparative chromatography on paper in systems 1) butan-1-ol—acetic acid—water (4 : 1 : 5), and 2) 15% acetic acid we have isolated flavonoids M and N found previously in the leaves of Cr. monogyna [1].

Substance M has the composition $C_{27}H_{30}O_{15}$, mp 232-234° C, R_f 0.38 (1) and 0.46 (2). UV spectrum (in methanol): λ_{max} 275, 310 (shoulder), 336 nm.

Substance N has the composition $C_{27}H_{30}O_{15}$, mp 224-226° C, R_f 0.40 (1) and 0.52 (2). UV spectrum (in methanol): λ_{max} 274, 312 (shoulder), 335 nm. Acid hydrolysis with 10% HCl for 3-4 h did not lead to the liberation of an aglycone and reducing sugars. Among the products of hydrolysis of substance M four substances were found one of which coincided in its R_f value with the initial material and another with substance N. The same four substances were found on the hydrolysis of substance N. All these compounds were isolated by preparative chromatography on paper and were again subjected to acid hydrolysis. The same four substances were found in all the hydrolysis products.

These results characterize substances M and N as di-C-glycosides [2-5]. Furthermore, the corresponding isomers obtained on acid hydrolysis showed a great similarity in their structures. And, in actual fact, from the products of the cleavage of substances M and N with hydriodic acid in liquid phenol [6] we isolate the same aglycone — apigenin — and after acid hydrolysis according to Kiliani [7] in both cases D-glucose was found as the sugar component.

The presence of two sugar residues in the molecule of each of the substances investigated was confirmed by their chromatographic behavior, and also by a comparison of the intensity of absorption of the corresponding maxima in the spectra of the glycosides and of their aglycones ($E^{1\%}_{1cm}$) [8, 9].

In a study of the UV spectra with the aid of ionizing and complex-forming additives [10, 11], free hydroxy groups were found in flavonoids M and N in positions 4', 5, and 7, while the aglycone and the isomerization products did not show the presence of additional hydroxy groups in comparison with the initial glycosides.

On the basis of the results obtained, substances M and N can be characterized as apigenin 6,8-di-C-glucosides of the type of the vicenins-1, -2, and -3 described in the literature [4, 5].

Usually, the isomerization of di-C-glycosides is due to Wessely-Moser rearrangements [12] for cases with different sugar substituents at C_6 and C_8 (vicenins-1 and -2, lucenins-1, -3, and -4) [4, 5], while in cases with the same sugars such isomerization is completely excluded [4, 5, 13]. The isomerization of the 6,8-di-C-glucosyl derivatives of apigenin that we have isolated can be explained by the rotation theory of the isomerization of glycoflavonoids which permits the existence of four isomers for di-C-glycosides [2].

This is the first time that di-C-glycosides have been isolated from hawthorns.

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Sofia Scientific-Research Institute of Pharmaceutical Chemistry, People's Republic of Bulgaria.
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