NEW FLAVONE C-BIOSIDES FROM *Crataegus monogyna* AND *Cr. pentagyna*

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In addition to the flavone C-monoglycosides vitexin, saponaretin, orientin, and homoorientin [1-3], vitexin rhamnoside and monoacetylvitexin rhamnoside have been isolated previously from *Cr. monogyna* [4], and vitexin rhamnoside from *Cr. pentagyna* [2]. By preparative chromatography on paper in systems 1) butan-1-ol–acetic acid–water (4 : 1 : 5), and 2) 15% acetic acid, from the fraction containing the vitexin rhamnoside from both species of hawthorn we have isolated another three substances of glycoflavonoid nature. From their qualitative reactions, chromatographic behavior, UV spectra, and product of acid hydrolysis, these substances belong to the flavone C-biosides.

Substance (I), composition $C_{27}H_{30}O_{14}$, mp 216-218°C, R_f 0.62 (1) and 0.85 (2). UV spectrum (in methanol): λ_{max} 274, 310 (shoulder), 336 nm.

Substance (II), composition $C_{27}H_{30}O_{15}$, mp 223-225°C, R_f 0.47 (1) and 0.60 (2). UV spectrum (in methanol): λ_{max} 259, 272, 312 (shoulder), 349 nm.

Substance (III), composition $C_{27}H_{30}O_{15}$, mp 218-220°C, R_f 0.49 (1) and 0.70 (2). UV spectrum (in methanol): λ_{max} 260, 272, 350 nm.

When they were boiled with 5% sulfuric acid for 4 h, all the substances investigated split out L-rhamnose, and in each case the acid solution was found to contain two aglycones present in a ratio of approximately 2 : 1 (measured spectrophotometrically). The aglycones were isolated by preparative paper chromatography (in systems 1 and 2), (I) giving the compounds $C_{21}H_{20}O_{10}$ (mp 262-264°C, $[\alpha]^{20}_{D}$ – 14°) and $C_{21}H_{20}O_{10}$ (mp 240-242°C, $[\alpha]^{20}_{D}$ + 45°), and (II) and (III) giving $C_{21}H_{20}O_{11}$ (mp 260-261°C, $[\alpha]^{20}_{D}$ + 22) and $C_{21}H_{20}O_{11}$ (mp 229-230°C, $[\alpha]^{20}_{D}$ + 28°). On the basis of qualitative color reactions, their main physicochemical properties, and the results of chemical and spectral (in the UV and IR regions) investigations and by a direct comparison with authentic samples, the aglycones isolated from substance (I) were identified as vitexin and saponaretin, respectively, and those from substances (II) and (III) as orientin and homoorientin.

To answer the question of the nature of the glycosides studied, they were cleaved by an enzyme preparation from the pancreatic juice of the grape snail *Helix pomatia*, each substance giving only one aglycone – saponaretin from (I), orientin from (II), and homoorientin from (III). Similar results were obtained on acid hydrolysis under mild conditions – heating (50-60°C) with 0.1% HCl for 30 min or boiling with 10% acetic acid for 5 h. On investigation of their UV spectra with the aid of ionizing and complex-forming additives [5, 6], free hydroxy groups were found in positions 4', 5, and 7 in substance (II) and (III).

On the basis of the results obtained in the investigation, substance (I) was identified provisionally as a saponaretin rhamnoside, substance (II) as an orientin rhamnoside, and substance (III) as a homoorientin rhamnoside. A saponaretin rhamnoside has recently been isolated from *Sophora microphylla* [7] and homoorientin 2"-O-rhamnoside from *Coronilla varia* [8]. The orientin rhamnoside that we have isolated is a new compound, and the other two substances (I and II) will be compared with known compounds of the same type after the complete elucidation of their structure. This is the first time that any of these three substances has been isolated from hawthorns.

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