UDC 547.918

FLAVONOIDS OF CRATAEGUS. THE STRUCTURE OF CRATENACIN

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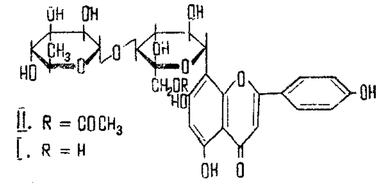
Khimiya Prirodnykh Soedinenii, Vol. 5, No. 4, pp. 234–236, 1969

We have previously reported a chemical study of cratenacin I—a new C-glycoside from the leaves of Crataegus curvisepala (Lindm.) [1, 2]. The saponification of cratenacin led to the formation of desacetylcratenacin (vitexin rhamnoside) (II) and acetic acid. A chemical and spectral study showed that substance (II) is 5, 7, 4'-trihydroxyflavone 8-C-β-[D-glucopyranosyl(4 → 1)-α-L-rhamnopyranoside].

Independently of us, Fisel [3] isolated an acetylated vitexin rhamnoside from Crataegus monogina L. and showed the presence of an acetyl group in this compound. In 1955, Kranen-Fiedler [4] isolated vitexin rhamnoside from Crataegus oxyancantha L. On the basis of spectrophotometric results, this author suggested that the rhamnose is attached at position 4' [5]. Thus, desacetylcratenacin differs from vitexin rhamnoside by the position of the rhamnose.

This paper gives the results of a determination of the position of the acetyl group in cratenacin.



II. R = $COCH_3$
I. R = H

The UV spectra of cratenacin, desactylcratenacin, and vitexin, with the addition of sodium ethoxide, showed that the hydroxyl groups in positions 7 and 4' of these compounds are obviously free; this is shown by the bathochromic shifts of bands I and II (table).

The intensity of the absorption of band I of cratenacin is 72% greater than the intensity of the same band of the initial solution and that of band II is 31% greater, which confirms the absence of substituents in positions 7 and 4' [6]. Similar results were obtained for desacetylcratenacin and vitexin.

The results of the spectroscopic investigation permit the assumption that the acetyl group in cratenacin is attached to one of the sugar components.

When cratenacin was oxidized with sodium metaperiodate, 3 moles of sodium metaperiodate were consumed. This showed that positions, 2, 3, and 4 of the rhamnose and positions 2 and 3 of the glucose are free. The acetyl group is obviously attached to position 6 of the glucose.

Experimental

Quantitative periodate oxidation of cratenacin and desacetylcratenacin. A solution of 7 mg of the substance under investigation in 15 ml of distilled water was treated with 10 ml of an aqueous solution of sodium metaperiodate, after

Results of a Spectral Study of Cratenacin, Desacetylcratenacin, and Vitexin

Substance	Concentration of the initial solutions of the substances in ethnol (M)	Absorption bands	Initial solutions		The same + 0.002 M solution of sodium ethoxide	
			λ, mn	d*	λ, mn	d*
Cratenacin	4.844×10^{-4}	I	335	100	399	172
			—	—	335**	80
		II	270	105	280	136
Desacetylcratenacin	4.316×10^{-4}	I	334	100	396	171
			—	—	335**	77
		II	270	106	281	133
Vitexin	4.374×10^{-4}	I	336	100	395	202
			—	—	335**	68
		II	272	99	280	152

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*Calculated as a percentage with respect to d of band I (d = 100%)

**Low-intensity absorption band

which 0.5 ml of the reaction mixture was diluted with 5 ml of water and 0.1 g of potassium iodide was dissolved in it. To the resulting solution was added three drops of starch. The iodine liberated was titrated with 0.01 N sodium thiosulfate solution. From the amount of iodine liberated after appropriate calculation the number of moles of sodium metaperiodate consumed was determined.

Cratenacin, and also desacetylcratenacin, absorbed 2 moles of metaperiodate in 2 hr and another 1 mole in 4 hr.

Conclusions

The complete structure of the new C-glycoside, cratenacin, isolated from the leaves of Crataegus curvisepala (Lindm.) has been determined by chemical and spectral methods; it is 5,7,4'-trihydroxyflavone 8-C-[6-O-acetyl-β-D-glucopyranosyl(4 → 1)-α-L-rhamnopyranoside].

REFERENCES

1. V. S. Batyuk, N. V. Chernobrovaya, and A. P. Prokopenko, KhPS [Chemistry of Natural Compounds], **2**, 90, 1966.
2. V. S. Batyuk, KhPS [Chemistry of Natural Compounds], **2**, 288, 1966.
3. J. Fisel, Arzneimittel-Forschung, 15, 1417, 1965.
4. U. Kranen Fiedler, Arzneimittel-Forschung, 5, 609, 1955.
5. T. A. Geissman and U. Kranen-Fiedler. Naturwissenschaften, 431, no. 10, 1956.
6. G. H. Mansfield, T. Swain, and C. G. Nordström, Nature, no. 4366, 23, 1953.

4 March 1968

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