

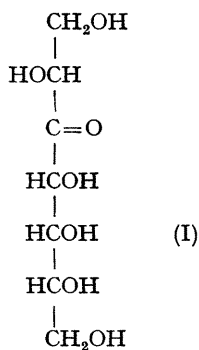
## $\alpha$ -Coriofuranose: Conformationally Unfavoured Structure in the Crystalline State and Rapid Mutarotation of Coriose

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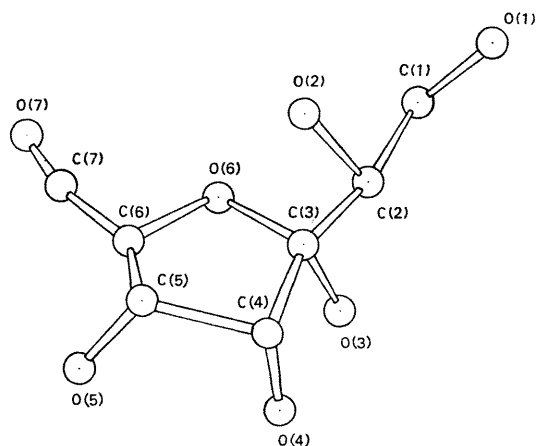
**Summary** Coriose was found to undergo rapid mutarotation which was attributed to the furanose structure of this sugar in the crystalline state revealed by X-ray analysis.

CORIOSE (I) is the 3-heptulose isolated from *Coriaria japonica* A. Gray.<sup>1</sup> It is obtained from either methanol,



aqueous ethanol, or water, as solvent-free crystals which show identical melting point and i.r. spectra. The same crystals are obtained on evaporation of an aqueous solution to dryness at a higher temperature, or on lyophilization of

the equilibrated aqueous solution, followed by exposure to the air.



FIGURE

Rapid downward mutarotation was observed when crystalline coriose was dissolved in water. The specific rotation reached the equilibrium,  $+21^\circ$ , within 3 min. at

28°, and within 20 min. at 13°. Although it has been reported that mutarotation of carbohydrates in dimethylsulphoxide is slow,<sup>2</sup> a fast change was observed in the case of coriose, attaining  $[\alpha]_D^{25} + 10^\circ$  within 30 min. This fast mutarotation was followed by another very slow one, which was observed for a week.

In order to solve an apparent contradiction between the stability of crystalline coriose and the instability of its molecular conformation in solution, an X-ray structure analysis was carried out on the coriose crystals obtained from ethanol-water. They are monoclinic, space group  $P2_1$ ,  $a = 11.33$ ,  $b = 7.460$ ,  $c = 5.205$  Å,  $\beta = 90.75^\circ$ ,  $Z = 2$ . The crystal structure was derived by symbolic addition method using three-dimensional intensity data from Weissenberg photographs, and was refined by the least-squares procedure to  $R = 0.08$ .

The coriose molecule was found to have the  $\alpha$ -furanose

structure shown in the Figure, and is therefore  $\alpha$ -D-*altro*-3-heptulofuranose. This is the first instance of establishing a furanose form of monosaccharide in the crystalline state. Such a structure, having hydroxy-groups at C(3), C(4), and C(5) *cis* to one another, is generally regarded as unfavourable from the point of conformational stability and a molecule with such a conformation would be expected to be quickly transformed into a more stable structure in solution, with fast mutarotation.

The downward mutarotation is in agreement with the generally approved correlation between the configuration at the anomeric carbon and the convention concerning the prefixes  $\alpha$  and  $\beta$  based on the optical rotation,<sup>3</sup> if this mutarotation is attributable to the anomerisation, although transformation into the pyranose form could also be involved.

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<sup>1</sup> T. Okuda and K. Konishi, *Chem. Comm.*, 1968, 553; *J. Pharm. Soc. Japan*, 1968, **88**, 1329; *Tetrahedron*, 1968, **24**, 6907.

<sup>2</sup> B. Casu and M. Reggiani, *Tetrahedron Letters*, 1964, 2839; 1965, 2253; A. S. Perlin, *Canad. J. Chem.*, 1966, **44**, 539.

<sup>3</sup> C. S. Hudson, *J. Amer. Chem. Soc.*, 1909, **31**, 66.