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Note

Synthesis of D-arabinose from D-*glycero*-D-*gulo*-heptono-1,4-lactone*

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In the course of our studies involving the synthesis of some rare sugars, use was made of the selective cleavage of certain bonds by periodic acid in unsubstituted carbohydrates. It was reported in the synthesis of 4-*C*-(hydroxymethyl)-L-xylurono-5,2-lactone from 2-*C*-(hydroxymethyl)-D-glucono-1,4-lactone that the side chain of an aldonolactone could be selectively cleaved by periodic acid, while maintaining the lactone ring intact[1]. Another example of this reaction was the production of L-lyxurono-5,2-lactone from D-galactono-1,4-lactone[2].

Oxidation of D-*glycero*-D-*gulo*-heptono-1,4-lactone with one mole of periodic acid, however, yielded not the expected shorter-chained lactone, but D-arabinose in 70% yield, evidently through selective cleavage of the C-2–C-3 bond.

Examination of the structures of the three starting materials indicates that the course of the reaction is dependent upon the configuration of the hydroxyl groups in the lactone ring. In the first two examples, the only vicinal pair of hydroxyl groups in the ring is oriented trans, and is thus unfavorably situated for cleavage by periodic acid. Furthermore, in the case of 2-*C*-(hydroxymethyl)-D-glucono-1,4-lactone, one of the vicinal hydroxyl groups of the ring is tertiary. Apparently, cleavage on the side chain occurs faster than ring cleavage or ring opening (hydrolysis), and the product having an intact lactone ring is obtained.

In the case of D-*glycero*-D-*gulo*-heptono-1,4-lactone, however, there is a vicinal *cis*-diol in the ring, at C-2 and C-3. In this situation, cleavage in the ring is more favorable than side-chain cleavage, and D-arabinose is produced in good yield. The arabinose was identified by physical constants and by preparation of the tetraacetate and arabinitol as derivatives.

EXPERIMENTAL

General. — All evaporations and concentrations were done in a rotary evaporator under diminished pressure at 40° (bath). Melting points are uncorrected.

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*Dedicated to the memory of Professor M. L. Wolfrom.

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D-*Arabinose*. — A solution of D-*glycero*-D-*gulo*-heptono-1,4-lactone (50 g) in water (400 ml), in a low-actinic Erlenmeyer flask, was cooled to 0° in an ice–salt bath and a solution of periodic acid (50 g) in water (200 ml) was added dropwise with stirring over 30 min. The reaction mixture was kept overnight at 4°, and was passed over a column of Amberlite IR-4B(OH^-) (200 ml of wet resin) at 4°. Concentration to a syrup and crystallization from 95% ethanol gave D-arabinose (25 g, 70%) having m.p. and mixture m.p. 163–165°, $[\alpha]_D^{28} - 104°$ (24 h) (*c* 2.06, water) (lit[3] m.p. 160° and $[\alpha]_D^{20} - 104.5°$).

Acetylation of the product gave 1,2,3,5-tetra-*O*-acetyl-D-arabinofuranose having m.p. 97–99° (lit.[4] m.p. 97°), and borohydride reduction gave D-arabinitol having m.p. 103–104° (lit.[5] m.p. 102°).

REFERENCES

1 R. J. Woods and A. C. Neish, *Can. J. Chem.*, 32 (1954) 404.
2 R. K. Hulyalkar and M. B. Perry, *Can. J. Chem.*, 43 (1965) 3241.
3 E. M. Montgomery and C. S. Hudson, *J. Amer. Chem. Soc.*, 56 (1934) 2074.
4 C. S. Hudson and J. K. Dale, *J. Amer. Chem. Soc.*, 40 (1918) 995.
5 B. Lindberg, A. Misiorny, and C. A. Wachmeister, *Acta. Chem. Scand.*, 7 (1953) 591.