Preliminary communication

Rearrangement of some D-ribose and D-lyxose derivatives under acetolysis conditions[*]

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Acetolysis has been widely used in structural studies and as a general method for preparing peracetylated monosaccharides[1]. The conditions used are often very similar to those needed to cause anomerisation of sugar peracetates[2—6].

Attempted acetolysis of 2,3:5,6-di-*O*-isopropylidene-D-mannose, followed by de-acetylation of the crude product, has been shown[7] to yield D-glucose and D-mannose in the ratio 8:2. Other mannofuranose compounds gave a similar result, whereas furanoid derivatives of D-galactose, D-xylose, and L-arabinose did not undergo rearrangement. It was suggested that the reaction was similar in type to the epimerisation of sugar peracetates in liquid hydrogen fluoride[8], in which a *cis–trans* arrangement of three, contiguous acetoxyl groups is changed to a *trans–cis* arrangement. Other analogies were the rearrangements of D-quinic acid in acetic acid–sulphuric acid[9], and of 6-deoxy-6-iodo-*aldehydo* sugars in acetic anhydride–zinc chloride[10].

It was predicted[7] that rearrangement would also occur during the acetolysis of furanoid derivatives of ribose, lyxose, and talose. However, no such epimerisations have been reported so far. Acetolysis of methyl 2,3-di-*O*-acetyl-4-*S*-benzoyl-4-thio-β-D-ribopyranoside yields[11] a furanoid product retaining the D-*ribo* configuration.

Acetolysis of some D-ribofuranose and D-lyxofuranose derivatives has now shown that rearrangement can occur, as predicted, and the results are reported here.

Methyl β-D-ribofuranoside[12] (1), methyl β-D-ribofuranoside 2,3,5-triacetate[13] (2), 1,2-*O*-isopropylidene-D-ribofuranose[14] (3), 1,2-*O*-isopropylidene-D-ribofuranose 3,5-diacetate (4) {syrup, $[\alpha]_D^{22}$ +120.5° (*c* 2.8, chloroform)[**]}, and 2,3-*O*-isopropylidene-D-ribofuranose[15] (5) were treated with acetic acid–acetic anhydride–conc. sulphuric acid mixtures by the methods of Guthrie and Smith[16] (*A*) and Jerkeman[7] (*B*). The crude products were deacetylated with aqueous, methanolic trimethylamine[7] and then separated

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[*] During the course of this work, similar results have been described: W. Sowa, *Can. J. Chem.*, 49 (1971) 3292.

[**] New compound: satisfactory elemental analysis obtained.

by paper chromatography on Whatman No. 1 or 3MM paper with propan-1-ol–ethyl acetate–water[17] (7:1:2). Reducing sugars were located with aniline hydrogen phthalate[18] and their relative proportions estimated spectrophotometrically[19]. By method *A*, compounds **1**–**5** yielded mixtures of D-ribose and D-arabinose in the ratio ~ 4:1; by method *B*, the ratio was 3:1. The arabinose produced in these reactions was also identified by isolation and conversion into the known *N*-(4-nitrophenyl)-D-arabinopyranosylamine, m.p. 204–205°; lit.[20] m.p. 206°. Although it has been reported[16] that acetolysis of methyl D-ribofuranosides does not yield any pyranoid derivatives, an unidentified compound was found in the product. It is now thought, from consideration of the above results, that this may have been the corresponding arabinofuranose. Treatment of β-D-ribofuranose 1,2,3,5-tetra-acetate[16] (**6**) by methods *A* and *B* yielded mixtures of D-ribose and D-arabinose in the ratios 6:1 and 4:1, respectively.

On a larger scale, **4** was acetolysed (method *A*) to give **6** (57%), m.p. 79–82°, $[\alpha]_D^{22}$ $-12.5°$ (*c* 2.46, chloroform) (lit.[21] m.p. 81–82°, $[\alpha]_D^{24.5}$ $-12.9°$), thus providing an economical route to **6** from D-glucose.

Acetolysis of methyl 2,3-*O*-isopropylidene-α-D-lyxofuranoside[22] (**7**) yielded mixtures of D-lyxose and D-xylose in the ratio ~ 5:2, by both methods *A* and *B*.

It has been reported that anomerisation of sugar peracetates in acetic acid–acetic anhydride–sulphuric acid mixtures does not involve inversion at any carbon atom other than C-1 in the aldopyranose ring. This appears to be an assumption based on results with D-glucose derivatives[3]. The products of anomerisation of other sugars, under the same conditions, have not been thoroughly investigated[5]. Treatment of β-D-ribopyranose 1,2,3,4-tetra-acetate[23] (**8**) by methods *A* and *B*, followed by deacetylation of the products, has now yielded mixtures of D-ribose and D-arabinose in the ratios 10:1 and 6:1, respectively. The equilibration constant and rate constants for the anomerisation of **8** under acidic conditions have been calculated[5] previously from specific rotation values. It may be noted that the specific rotation (–43.6°) of α-D-arabinopyranose 1,2,3,4-tetra-acetate[24] (**9**) does not differ greatly from that (–52°) recorded[23] for **8**. The formation of noticeable amounts of **9** during the anomerisation of **8** would not, therefore, have a large effect upon the specific rotation at equilibrium[5] (–31.9°).

All the compounds used in the above studies were subjected to appropriate acidic and alkaline hydrolyses prior to reaction, and were found to be homogeneous with respect to the parent pentose.

The rearrangements reported herein are being further investigated.

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