1,2:5,6-Di-*O*-isopropylidene Derivatives of D-*Gluco*-hexodialdose and D-*Ribo*-hexos-3-ulose

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The 1,2:5,6-di-*O*-isopropylidene derivatives of D-*gluco*-hexodialdose and D-*ribo*-hexos-3-ulose (1,2:5,6-di-*O*-isopropylidene-α-D-*gluco*-hexodialdo-1,4-furanose-β-D-6,3-furanose (II) and 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (IV), respectively) have been prepared by acetonation of 1,2-*O*-isopropylidene-α-D-*gluco*-hexodialdo-1,4-furanose (I) and chromium trioxide oxidation of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (III), respectively. Borohydride reduction of IV gave exclusively 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (VI). This route offers a new method for the preparation of D-allose. The D-allose derivative VI, having an *endo*-hydroxyl at C-3 was oxidised considerably more readily with chromium trioxide than the D-glucose isomer, and the former but not the latter compound could also be oxidised catalytically.

In a previous investigation [1] 1,2-*O*-isopropylidene-α-D-glucofuranose was oxidised with chromium trioxide in water-butanone and the 3-keto, 5-keto, and 6-aldehydo derivatives were isolated in 0.6, 1.6, and 8.9 % yields, respectively. The 3-keto and 6-aldehydo compounds, 1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (V) and 1,2-*O*-isopropylidene-α-D-*gluco*-hexodialdo 1,4-furanose (I), respectively, were obtained crystalline. The absence of carbonyl absorption in their IR- and UV-spectra indicated that they existed as tricyclic structures in the crystalline state (Vb and Ib, respectively). Elemental analysis excluded the possibility of a hydrate. In solution, however, they exist partly in the open form, as is shown by a rather rapid mutarotation, carbonyl group reactions and migration in hydrogen sulphite buffer during electrophoresis.

The hemiacetal form (Ib) of the aldehydo compound has been confirmed chemically by isolation of the tetracyclic di-isopropylidene compound (II), which was the only significant reaction product resulting from the acetonation of I. The structure of this substance, 1,2:5,6-di-*O*-isopropylidene-α-D-*gluco* hexodialdo-1,4-furanose-β-D-6,3-furanose, which was obtained in the crystalline state, m.p. 75—77° and $[\alpha]_D$ + 13.5°, is obvious from its mode of formation,

elemental analysis and the absence of hydroxyl (excluding a tricyclic di-iso-propylidene compound) and carbonyl absorption in the IR. The configuration at C-6 in Ib is fixed as the hydroxyl has to be *endo*, projected into the "V" formed by the furanose and 3,6-hemiacetal rings in order to form a tetracyclic di-isopropylidene compound. The compound can be distilled almost quantitatively and has a higher mobility than di-isopropylidene-glucose when subjected to thin layer chromatography under the same conditions.
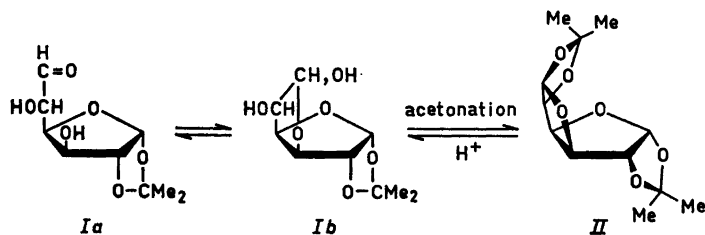

The 5,6-*O*-isopropylidene group in II was removed somewhat more slowly than that in di-isopropylidene-glucose, but considerably faster than the 1,2-*O*-isopropylidene group. Thus an almost quantitative yield of 1,2-*O*-isopropylidene α-D-*gluco*-hexodialdo-1,4-furanose (I) was isolated after partial hydrolysis in dilute sulphuric acid.

As found in the previous investigation [1] the oxidation of the hydroxyl group in 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (III) to the 3-keto derivative was almost impossible with various oxidising reagents, some of which have been previously used in the carbohydrate field, *e.g.* the chromium trioxide-pyridine system, even when used under more forcing conditions. Stensiö and Wachtmeister [2] recently introduced oxidation with the chromium trioxide-pyridine complex in acetic acid at room temperature as a rapid method (1—2 min) of oxidising many primary and secondary alcohols. When these conditions were applied to di-isopropylidene-glucose for some hours the amount of the required oxidised product was only slightly more than with chromium trioxide in water-butanone.[1] In contrast to the latter reagent, modification of the conditions gave a higher degree of oxidation before too much hydrolysis and subsequent side-reactions occurred.

The 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (IV) was isolated without chromatographic fractionation in 6 % yield, *via* extraction with aqueous hydrogen sulphite. In order to avoid hydrolysis, the carbonyl compound was recovered from the sulphite phase after adjusting the pH to 8, and not to a low pH-value as is usual. The reaction mixture also contained unchanged di-isopropylidene-glucose (8 % was recovered), a product which is probably its 3-acetyl derivative, acidic products and various mono-isopropylidene compounds. From the latter 1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (V) was isolated (in 2 % yield) after separation on silicic acid columns.

The 3-keto-di-isopropylidene compound crystallised as a hydrate (IVb), m.p. 108—110° and $[α]_D + 40.2°$, as shown by the elemental analysis and by a
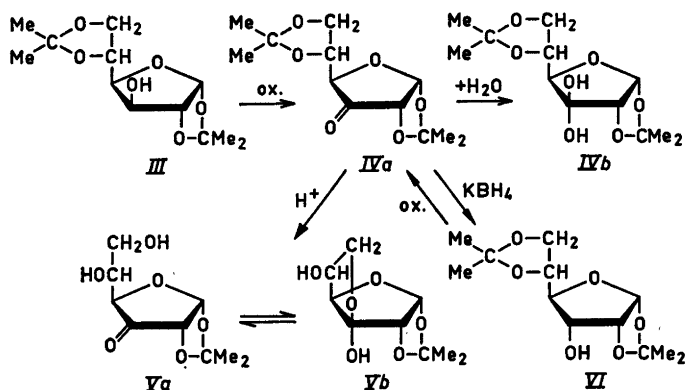
strong hydroxyl absorption but absence of carbonyl absorption in the IR (KBr). In carbon tetrachloride, however, a strong carbonyl absorption was evident. Attempts to obtain a crystalline, non-hydrated form by repeated evaporation of a benzene solution, were not successful. That the substance reacted as a carbonyl compound in aqueous solution is shown by its isolation as a hydrogen sulphite adduct and a rather high migration (M_V-value 0.52) on paper electrophoresis in this buffer. It could also be readily reduced. There were only traces left after 2 min treatment with potassium borohydride in 70 % aqueous ethanol at room temperature. The structure of IV, being evident from its mode of formation, was further confirmed by the results from the reductions. A crystalline substance, m.p. 76—77° and $[\alpha]_D + 37.7°$, shown to be 1,2:5,6-di-O-isopropylidene-α-D-allofuranose (VI), was obtained in almost theoretical yield by extraction with ethyl acetate after completion of the borohydride reduction.

The structure of this allose derivative, not previously reported, follows from its mode of formation and by the isolation in good yields of 1,2-O-isopropylidene-α-D-allofuranose and D-allose after partial and complete acid hydrolysis, respectively. No trace of the isomeric di-isopropylidene-glucose, which is readily separable from VI by thin-layer chromatography, could be detected. Similar stereospecific reduction was previously found on borohydride reduction of 1,2-O-isopropylidene-α-D-$ribo$-hexofuranos-3-ulose (V)[1] and is obviously caused by the 1,2-isopropylidene group, which makes approach by the reducing agent from beneath more difficult. With Raney nickel catalyst the reduction was not as specific; the ratio of the D-allose to D-glucose isomers being 3:1. As a comparison the mono-isopropylidene derivative V was also reduced with Raney nickel and a similar ratio of the D-allose to D-glucose isomers obtained.

In spite of the rather low yield of the 3-keto-di-isopropylidene derivative, the present procedure gives a new and rather convenient route for the preparation of the rare D-allose; the di-isopropylidene glucose is readily available, the oxidation is fairly simple, separation of the keto compound is possible without chromatographic fractionations, and specific and quantitative reduction to

the allose derivative and subsequent hydrolysis can be carried out in good yield.

As 1,2:5,6-di-*O*-isopropylidene-*α*-D-allofuranose (VI) was available it was of interest to study how readily the hydroxyl group at C-3, which is *endo* (projecting inside the V formed by the fused bicyclic system) was oxidised compared with the *exo*-hydroxyl group in the corresponding glucose derivative. It was found to be completely oxidised by catalytic oxidation over platinum catalyst (50°, 4 h) and chromium trioxide-pyridine/acetic acid (45°, 1 h). The yields of the keto compound, whith properties identical with those of the one obtained from di-isopropylidene-glucose, were *ca.* 80 % and 50 %, respectively. When di-isopropylidene-glucose was treated under these conditions, the yields as determined by thin-layer chromatography were 0 and < 5 %, respectively.

These results show how the configurations of the hydroxyl groups at C-3 cause remarkable differences in the reactivity of the two compounds. In 1,2:5,6-di-*O*-isopropylidene-*α*-D-glucofuranose (VII) containing an *exo*-hydroxyl the catalytic oxidation, according to Wieland's dehydrogenation theory,[3] requires the approach of the catalyst from the rear to react with the *endo*-hydrogen, which is obviously extremely hindered by the 1,2-*O*-isopropylidene ring. This is in agreement with the recent results of Heyns and coworkers,[4]

VII
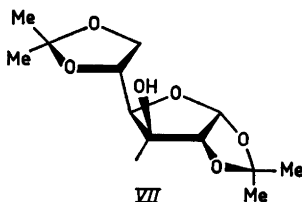
who catalytically oxidised *endo*-hydroxyls in 1,4:3,6-dianhydro-hexitols, but obtained no oxidation of the *exo*-hydroxyls. Displacement reactions of tosyl groups in bicyclic compounds, containing fused five-membered ring systems, has been studied by many workers [5,6] (and references in these papers), and the differences in reactivity have been interpreted in terms of the configurations of the tosyl groups. An *endo*-tosyl is more readily displaced than an *exo*-tosyl due to the less hindered approach from the rear.

Without discussing the various mechanisms for chromic acid oxidation, the difference between the ease of oxidation of the *exo*-hydroxyl in VII and the *endo*-hydroxyl is the isomeric D-allose derivative is notable.

EXPERIMENTAL

Concentrations were carried out under reduced pressure below 45°. All melting points are corrected. The optical rotations were measured in a Perkin-Elmer polarimeter 141.

Butan-1-ol-ethanol-water, 10:3:5 (solvent A), ethyl acetate-acetic acid-water, 3:1:1 (solvent B) and ethyl acetate-pyridine-water, 8:2:1 (solvent C) were used for paper chromatography, and 0.1 M hydrogen sulphite, pH 4.7 (used at 50°) for electrophoresis

(Whatman No. 1 paper). Thin-layer chromatography was carried out with ethyl acetate-light petroleum (b.p. 40—60°), 3:1, as solvent and "Kieselgel G nach Stahl" as adsorbent. The technique of using p-anisidine hydrogen chloride combined with methanolic hydrochloric acid for differentiating between carbonyl and non-carbonyl compounds on thin-layer and paper chromatograms, was as previously described.[1]

Acetonation of 1,2-O-isopropylidene-α-D-*gluco*-hexodialdo-1,4-furanose

Crystalline 1,2-O-isopropylidene-α-D-*gluco*-hexodialdo-1,4-furanose (I) (400 mg) was added to freshly distilled acetone (10 ml) containing conc. sulphuric acid (0.05 ml) and freshly prepared anhydrous cupric sulphate (800 mg) and shaken in a stoppered flask at 22°. The reaction was followed by thin-layer chromatography, and it was shown that a compound giving a brick-red colour with the anisidine-spray, and having a faster rate of migration than 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose was increasing with time, and that I was decreasing. After 45 h, when the yield of the predominant compound was about a maximum and the solution becoming brownish, the reaction was stopped. Apart from the predominating reaction product and *ca.* 25 % starting material there were only small amounts of other components present. The solution was cooled in ice-water, and excess of barium carbonate and water (10 ml) added to the stirred mixture. After filtration, the solution was extracted with benzene (3 × 10 ml) and the latter phase dried and evaporated to yield a crystalline product (269 mg), which as estimated by thin-layer chromatography contained *ca.* 90 % of the unknown compound, later shown to be II (corresponding to *ca.* 50 % yield). The aqueous phase contained mostly unreacted I. After extraction of the crystalline product with light petroleum, evaporation of the extract and recrystallisation from light petroleum and some benzene, pure crystalline II (156 mg) was obtained:

1,2:5,6-Di-O-isopropylidene-α-D-gluco-hexodialdo-1,4-furanose-β-D-6,3-furanose (II), m.p. 75—77°; $[\alpha]_D^{22}$ + 13.5° (c 0.3, water). (Found: C 55.8; H 7.22; O 37.1. $C_{12}H_{18}O_6$ requires C 55.7; H 7.04; O 37.2). IR-spectrum (KBr) revealed neither hydroxyl nor carbonyl peaks. The rate of migration in thin-layer chromatography was 1.21 relative to compound III.

A sample could be distilled almost quantitatively (*ca.* 90° bath temperature at *ca.* 0.05 mm) and the distillate crystallised spontaneously. Another sample was boiled under reflux with an excess of potassium borohydride in 70 % aqueous ethanol for 2 h without any effect; the product could be recovered almost quantitatively.

The hydrolysis of II in 0.025 M sulphuric acid at 45° was compared with that of di-O-isopropylidene-glucose (III); the reactions being followed by thin-layer chromatography of neutralised samples taken at certain time intervals. The 5,6-O-isopropylidene group in *III* was completely removed after 10 min, but in II after *ca.* 30 min. A sample of II (30 mg) hydrolysed with 0.025 M sulphuric acid (2 ml) at 45° for 40 min gave after neutralisation with barium carbonate, evaporation, and extraction with ethyl acetate, almost pure 1,2-O-isopropylidene-α-D-*gluco*-hexodialdo-1,4-furanose (I) (22 mg), which after recrystallisation from ethyl acetate had m.p. 124—125°, and was identical with an authentic sample (m.p. and mixed m.p.).

Oxidation of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (III)

The 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (III) used had m.p. 110—111° and was chromatographically pure. Treatment of III with the chromium trioxide-pyridine complex in acetic acid at room temperature [2] gave negligible oxidation even after many hours. A series of preliminary oxidations were carried out in order to determine the best conditions for the oxidation and isolation of the 3-keto derivative that would not also cause too much hydrolysis. Before describing the final conditions in a typical experiment, it should be pointed out that the temperature control is very important. Efficient stirring and the addition of III in portions is necessary to avoid a sudden uncontrolled

increase in temperature which leads to a decreased yield of the desired product and a more complex reaction mixture.

Chromium trioxide (60.0 g) was added in portions to a well-stirred solution of pyridine *p.a.* (100 ml) in acetic acid *p.a.* (600 ml) in a three-necked flask (2 l), keeping the temperature <45°. The flask was then transferred to a 60°-bath, and provided with a thermometer. Di-*O*-isopropylidene-glucose (40.0 g) was added in portions to the stirred solution over a period of 45 min (the solution rapidly turned brown and precipitate was formed); the average temperature was 65° and the highest temperature never exceeded 70°. After the final addition the stirred mixture was left for another 15 min in the bath, and then ethyl acetate (300 ml) added. After a few minutes the flask was cooled under tap-water, the brown inorganic precipitate filtered off and washed with ethyl acetate (300 ml). The solution was then evaporated under reduced pressure (45°-bath) for 3 h, by which time most of the acetic acid had been removed. The product was cooled to *ca.* −20°, ice-water (300 ml) added to the semi-solid mass, and the pH of the resulting mixture adjusted to *ca.* 6 by the addition of solid sodium carbonate. After the addition of Celite, the precipitated chromium salts were filtered off and the precipitate washed with water (200 ml). The violet aqueous solution was extracted with ether (4 × 300 ml) and ethyl acetate (2 × 300 ml), and the solvent removed from the combined extracts to yield a thin syrup (15.5 g). The product was taken up in boiling ether (800 ml) and after keeping the solution at 0° overnight it could be decanted almost colourless from a sticky precipitate of chromium salts which also contained some carbonyl compounds. The ether solution was then shaken with saturated aqueous hydrogen sulphite (6 × 100 ml) for periods of 10 min on a shaking machine. The dried ether phase was evaporated (7.58 g) and some starting material, III, (3.10 g) could be recovered after crystallisation from benzene. In the mother liquors were some oxidation products which in some experiments were isolated (see below), and also a compound which was probably the 3-*O*-acetyl derivative of III, as a component with the chromatographic properties of 3-*O*-acetyl-glucose was present after complete acid hydrolysis. The combined hydrogen sulphite fractions were extracted with ether (6 × 300 ml) after adjusting the pH to 8 by the addition of sodium carbonate. The dried ether extracts on evaporation gave a product (2.77 g) which was the almost pure 3-keto derivative of III (represents a yield of *ca.* 6 %). This was considered to be pure enough for further reactions. There were small amounts of some more lipophilic compounds present, but no mono-*O*-isopropylidene compounds. After crystallisation from benzene-light petroleum pure III (1.83 g) was obtained (for characterisation see below).

In one experiment the hydrogen sulphite solution was further extracted with ethyl acetate (3 × 200 ml) giving only a small fraction (0.17 g). This was combined with the sticky, violet precipitate from the ether phase, described above, and also with the mother liquors obtained after recovery of some of the starting material. The mixture, which amoung other components contained both mono- and di-*O*-isopropylidene derivatives of D-*ribo*-hexos-3-ulose, was hydrolysed (0.05 M sulphuric acid for 30 min at 45°) and the product worked up and fractionated on silicic acid columns as previously [1] described. The mixture, however, was simpler to fractionate this time; after two column fractionations and recrystallisations, 1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose, V (0.67 g, yield 2 %) was obtained. However, for preparative purposes this rather complicated procedure to obtain more hexos-3-ulose derivative is not considered worthwhile. A small amount of an unidentified, crystalline carbonyl compound (0.15 g, m. p. 155−157°), was also isolated from the hydrolysis product.

*1,2:5,6-Di-O-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (IV)* crystallised as a hydrate (IVb) recrystallised either from benzene-light petroleum or from water), m.p. 108−110° $[\alpha]_D^{22}$ + 40.2° (c 0.5, water, no mutarotation observed at −5° or +22°). (Found: C 52.1; H 7.51; O 40.8. $C_{12}H_{20}O_7$ requires C 52.2; H 7.31; O 40.6). There was no loss in weight when a sample was dried in vacuum (*ca.* 10 mm) over phosphorus pentoxide at 40° for 2 days. IR $\lambda_{max}^{CCl_4}$ 5.63 μ (carbonyl, strong; also in CCl_4 saturated with water). The rate of migration on thin-layer chromatography was 1.04 relative to compound III, one sharp khaki-coloured spot being given on spraying with anisidine. The $M_{vanillin}$-value on hydrogen sulphite electrophoresis was 0.52. Attempts to isolate the non-hydrated form (IVa) in a crystalline state after repeated evaporations of a benzene solution of IVb failed.

A sample of IV (50 mg) was hydrolysed in 0.05 M sulphuric acid (5 ml) at 45° for 15 min and gave after neutralisation with barium carbonate, filtration, evaporation, and extraction with ethyl acetate, a product (39 mg), which crystallised spontaneously. It was chromatographically and electrophoretically indistinguishable from 1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (V) and contained *ca*. 10 % of impurities. After recrystallisation from benzene the m.p. was 79–80° (m.p. and mixed m.p. identical with an authentic sample) and $[\alpha]_D^{23}$, + 36.0° (equil. *c* 0.5, water), previous value[1] + 36.7°.

A sample of IV (200 mg) was reduced with an excess of potassium borohydride (200 mg) in 70 % aqueous ethanol at room temperature for 2 h (in a later series in which the reaction was followed by thinlayer chromatography, it was shown that only traces of IV remained after 2 min). After the addition of water (30 ml), the solution was extracted with ethyl acetate (8 × 30 ml). The product obtained by evaporation (197 mg, 98 % yield) crystallised spontaneously, was completely pure as revealed by thin-layer chromatography and was shown to be 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose, VI (for characterisation see below).

Another sample of IV (100 mg) was treated with Raney nickel according to the procedure of Karabinos and Ballun[7] by boiling under reflux in 70 % aqueous ethanol for 4 h. After this treatment a thin-layer chromatogram showed that there was no IV present, and apart from small amounts of mono-*O*-isopropylidene compounds, the mixture consisted of di-*O*-isopropylidene-glucose (III) and -allose (VI,) with the latter predominating. After filtration and evaporation (90 mg), VI was obtained pure (21 mg) by crystallisation from benzene-light petroleum and shown to be identical with 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (VI) obtained by borohydride reduction of IV. The mother liquors were hydrolysed in 0.025 M sulphuric acid at 45° for 40 min. After neutralisation with barium carbonate, filtration, evaporation, and extraction with ethyl acetate, 1,2-*O*-isopropylidene-α-D-allofuranose (18 mg; m.p. 132–133°) was obtained crystalline from ethyl acetate and 1,2-*O*-isopropylidene-α-D-glucofuranose (13 mg; m.p. 159–160°) from the mother liquors. The chromatographic properties on thin-layer and paper chromatography as well as m.p. and mixed m.p. were identical with those of authentic samples. In a separate experiment on 50 mg, the product after the Raney nickel treatment was hydrolysed (0.25 M sulphuric acid; 96°, 0.5 h) and the ratio of D-allose to D-glucose estimated to be 3.0:1.0 after separation on Whatman 3 MM papers (pre-washed with water) using solvent C. As a comparison 1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (V) was reduced in the same way, giving a D-allose to D-glucose ratio of 3.3:1.0. Corrections were made for the formation of 1,6-anhydro-D-allose.

1,2:5,6-Di-O-isopropylidene-α-D-allofuranose (*VI*), m.p. 76–77° (recrystallised from benzene-light petroleum); $[\alpha]_D^{22}$ + 37.7° (*c* 0.5, water). (Found: C 55.2; H 7.65; O 36.8. $C_{12}H_{20}O_6$ requires C 55.4; H 7.77; O 36.8). The rate of migration on thin-layer chromatography was 0.88 relative to compound III.

A sample of VI (100 mg) was hydrolysed in 0.025 M sulphuric acid at 45° for 40 min. After neutralisation with barium carbonate, filtration, and extraction with ethyl acetate, a product (82 mg) was obtained, which crystallised spontaneously on evaporation, and was pure 1,2-*O*-isopropylidene-α-D-allofuranose as revealed by paper- and thin-layer chromatography. On recrystallisation from ethyl acetate it had m.p. and mixed m.p. 132–133° and $[\alpha]_D^{22}$ + 43.7° (*c* 0.5, water), previous value:[1] +44.0. Part of the mono-*O*-isopropylidene derivative was hydrolysed (0.25 M sulphuric acid; 96°, 0.5 h) and D-allose obtained crystalline from ethanol, m.p. 127–128° (the chromatographic properties, m.p. and mixed m.p. were identical with those of an authentic sample).

Oxidation of 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (VI)

A rapid stream of oxygen was bubbled through a solution of VI (100 mg) in water (10 ml) at 50° containing platinum catalyst[8] (*ca*. 100 mg). After 4 h (after which time all of VI had reacted according to a preliminary study) the solution was filtered and evaporated (97 mg) giving a product which crystallised after some hours, and which as estimated from thin-layer chromatography contained *ca*. 80 % 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose, IV, (a semi-quantitative determination was made by comparing the areas of a series of known quantities of IV with that of the reaction

product). Pure IV (32 mg), m.p. 107 — 109° (m.p., mixed m.p. and IR-spectrum identical with those of the substance IV obtained by oxidation of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose) was obtained by extraction of the product with light petroleum, evaporation, and recrystallisation from benzene-light petroleum. When 1,2:5,6-di-O-isopropylidene α-D-glucofuranose was treated in a similar way, no oxidation products could be detected on thin-layer chromatography.

Another sample (100 mg) was treated with chromium trioxide-pyridine/acetic acid (150 mg CrO_3) in the same manner as the corresponding glucose derivative (III) but at 45°. The treatment was stopped after 1 h (after which time all VI had reacted according to a preliminary study), and the product worked up as that from III except for the hydrogen sulphite extraction of the ether soluble products (60 mg). They amounted to *ca.* 90 % of the product, indistinguishable by thin-layer chromatography and paper electrophoresis from IV, and a crystalline sample was obtained (as described above from the catalytic oxidation) m.p. 107 — 109° (m.p. and mixed m.p. identical with IV). A sample of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose was treated in a similar way and the amount of IV estimated by thin-layer chromatography directly on the reaction mixture after 1 h, was less than 5 %.

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