THE REACTION OF SULPHURYL CHLORIDE WITH REDUCING SUGARS

PART I

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ABSTRACT

The reaction of sulphuryl chloride with D-glucose, with D-xylose, and with maltose is described. The products were fully substituted compounds containing both chlorodeoxy and chlorosulphate groups. Formation of the methyl glycosides and subsequent removal of the chlorosulphate groups enabled structural investigations to be carried out on the resultant chlorodeoxy methyl glycosides.

INTRODUCTION

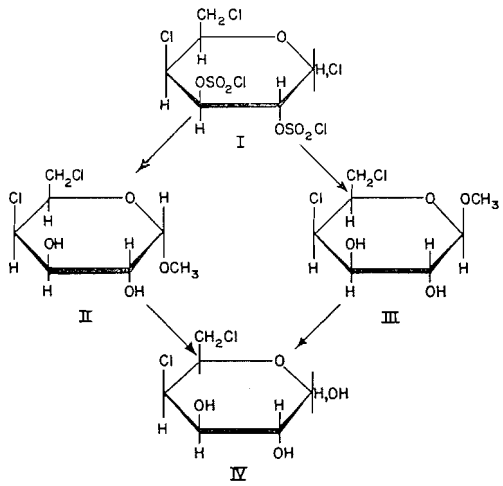
Previous communications (1, 2) on the reaction of sulphuryl chloride with methyl glycosides have described the isolation of fully substituted glycosides containing chlorodeoxy and cyclic sulphate groups. In the case of methyl α-D-glucopyranoside the 2,3-cyclic sulphate derivative was desulphated to yield substances characterized as methyl 4,6-dichloro-4,6-dideoxy-α-D-galactoside and 4,6-dichloro-4,6-dideoxy-D-galactose (2). When conditions similar to those described by Bragg *et al.* (1) were employed the reaction of sulphuryl chloride with reducing sugars produced considerable degradation of the carbohydrate, and a crystalline product, tentatively identified as a dichloro pyridine derivative, was isolated. When the reaction was carried out at a much lower temperature degradation of the sugar was reduced and good yields of carbohydrate derivatives were obtained. Changes in reaction conditions also produced a new range of carbohydrate derivatives which contained the chlorosulphate group.

DISCUSSION

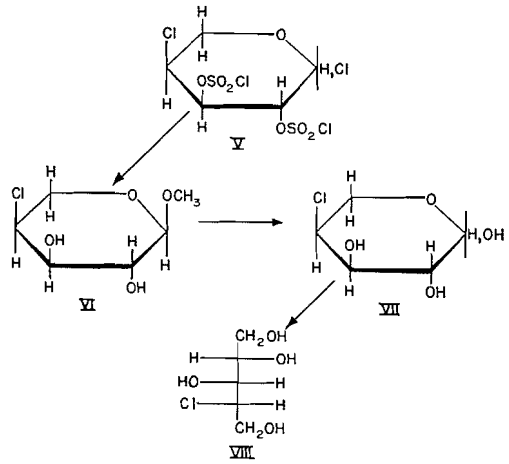
In view of the work of Bragg *et al.* (1, 2) it was considered likely that sulphuryl chloride would react with reducing sugars in pyridine solution to yield cyclic sulphate derivatives with the possible replacement of the hydroxyl group of C_1 by a chloro group. Analysis of the crystalline derivative from maltose indicated that such a reaction had in fact occurred but that the cyclic sulphate grouping was absent. Further examination of the crystalline derivative from maltose and of the syrupy products from D-glucose and D-xylose showed that chlorosulphate residues as well as chlorodeoxy groupings were present in the products. The infrared spectra of the compounds had two characteristic strong absorption frequencies, at 1431–1435 cm^{-1} and 1195–1200 cm^{-1}, the values of which compared well with the frequencies of absorption of the O—SO_2—Cl group reported by Robinson (3). The spectra also showed the absence of hydroxyl absorption. The presence of the chlorosulphate group was further substantiated by the reaction of the compounds with aniline and pyridine (4) to give a characteristic red dye. This dye was previously reported by König and Bayer (5) and was prepared by them from a wide range of inorganic acid chlorides.

The reactions of sulphuryl chloride with D-glucose (experiments i and ii) gave syrupy products which were probably mixtures of the α- and β-chlorodeoxy compounds (I). The formation of the methyl glycosides and the simultaneous dechlorosulphation with methanol alone produced, as the main product, methyl 4,6-dichloro-4,6-dideoxy-α-D-

galactopyranoside (II). The corresponding β-anomer (III) was obtained when methanol and silver oxide were employed. This was evident because both II and III gave on hydrolysis 4,6-dichloro-4,6-dideoxy-D-galactose (2) (IV). The reason for the isolation of both the α and β methyl glycosides is not clear and could be attributed to either a preponderance of the α- or β-1-chloro compound in the original product (I) due to different reaction conditions, or to the different methods used for the formation of the methyl glycosides from I. If it is assumed that in all these reactions the chlorosulphate group is substituted and removed without inversion, discounting the less likely process of double inversion; then compound I was 4,6-dichloro-4,6-dideoxy-D-galactopyranosyl chloride 2,3-dichlorosulphate.



The reaction of sulphuryl chloride with D-xylose gave a syrup (V) which was dechlorosulphated with great difficulty using silver oxide and aqueous methanol. Analysis indicated the presence of one chlorodeoxy group in the dechlorosulphated methyl glycoside (VI) and periodate oxidation of VI gave results (1 mole/mole uptake) consistent with the presence of adjacent hydroxyl groups. Hydrolysis of VI yielded a monochloropentose (VII) which formed a phenylosazone which still contained chlorine. D-Xylose may have reacted in the pyranose or furanose form and the chlorodeoxy group could be assigned to positions C_4 or C_5 depending whether V was a pyranose or furanose derivation. Periodate oxidation of the monochloropentitol (VIII) (produced by reduction of VII) liberated 0.9 mole of formic acid and proved that the chlorodeoxy group was on position C_4 of the molecule, thus establishing that the original sugar had reacted in the pyranose form. The high positive rotation of VI (+237°) suggested that inversion of configuration had taken place at C_4, forming an L-arabinose derivative, and this was supported by the fact that VI remained unchanged when treated with sodium hydroxide solution. If inversion had not occurred the compound would have remained in the D-xylose configuration, and it is known that under alkaline conditions chlorine is eliminated from methyl 4-chloro-4-deoxy-α-L-xyloside to give the 3,4-anhydro compound (2). Compound VI was found to have a specific rotation similar to that of methyl β-L-arabinopyranoside (+245.5°) (6) and therefore it was characterized as methyl 4-chloro-4-deoxy-β-L-arabinopyranoside. On this evidence V was probably 4-chloro-4-deoxy-L-arabinopyranosyl chloride 2,3-dichlorosulphate.

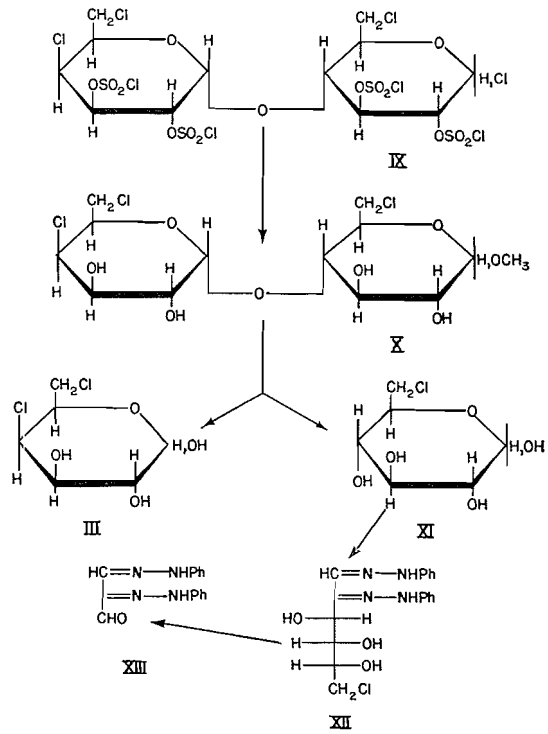


The reaction of sulphuryl chloride with maltose gave a crystalline product (IX) ($C_{12}H_{14}O_{15}Cl_8S_4$). Formation of the methyl glycoside and dechlorosulphation using sodium iodide gave two crystalline products, one of which was shown by analysis to be a trichlorotrideoxy methyl glycoside (X). Sodium iodide was employed because of the difficulty encountered in dechlorosulphating this product by the previous methods. Hydrolysis of X produced a syrup from which two main products were separated and identified as chlorodeoxy hexoses (III and XI). The crystalline dichlorodideoxy hexose (III) was characterized as 4,6-dichloro-4,6-dideoxy-D-galactopyranose (2). The other chlorohexose (XI), which could not be obtained crystalline, was identified as 6-chloro-6-deoxy-D-glucopyranose on the following evidence. It was found to have a specific rotation similar to that of the equilibrium value obtained for crystalline 6-chloro-6-deoxy-D-glucopyranose (7) and gave a phenylosazone (XII) identical with the phenylosazone of 6-chloro-6-deoxy-D-glucopyranose obtained by a synthetic route (8). The phenylosazone (XII) was oxidized with periodate by the method of Hough, Powell, and Woods (9) and initially consumed 1.93 moles of periodate, releasing 0.64 mole of formic acid and no formaldehyde, with an immediate precipitation of the 1,2-bisphenylhydrazone of mesoxaldehyde (XIII). The low yield of formic acid agreed with the findings of Hough, Powell, and Woods, who obtained similar results from the periodate oxidation of phenylosazones (9), but the gradual loss of formic acid with time cannot be satisfactorily explained. The initial results, however, are consistent with the presence of a chlorodeoxy group on position C_6 of the molecule. Accordingly compound X was characterized as methyl 4-*O*-α-4′,6′-dichloro-4′,6′-dideoxy-D-galactopyranosyl 6-chloro-6-deoxy-D-glucopyranoside, and the fully substituted compound (IX) from which it was obtained would be 4-*O*-α-4′,6′-dichloro-4′,6′-dideoxy-D-galactopyranosyl-6-chloro-6-deoxy-D-glucopyranosyl chloride 2,3,2′,3′-tetrachlorosulphate.

The other crystalline compound obtained from IX gave, on hydrolysis, products similar in properties to those observed when X was hydrolyzed. Failure to obtain a sharp melting point and a consistent analysis of the crystalline product from IX indicates that it is probably a mixture containing the α- and β-anomers of compound X.

EXPERIMENTAL

Melting points were determined on a Kofler hot stage and were uncorrected. Optical rotations were measured at 21±3° C. Solutions were concentrated under reduced pressure below 50° C. Paper chromatography was carried out by the descending method on Whatman No. 1 filter paper using the following



solvent systems (v/v): (*a*) ethyl acetate, acetic acid, formic acid, water (18:3:1:4) and (*b*) butan-1-ol, ethanol, water (3:1:1). Sugars were located on chromatograms by *p*-anisidine hydrochloride (10) or alkaline silver nitrate (11) sprays and the rates of movement are quoted relative to that of D-xylose (R_x). Sugars containing the chlorosulphate group were located specifically with a spray made of a butan-1-ol solution of aniline and pyridine (4). Infrared absorptions were measured as solutions in chloroform or as a powder suspended in a potassium bromide pellet on a Perkin–Elmer Model 21 spectrophotometer. All solutions were deionized by passage through Amberlite IR120 (H form) and Duolite A4 (OH form) unless otherwise stated.

General Method

The reducing sugar (10 g), previously dried over phosphoric oxide, was partially dissolved in dry pyridine (40 ml). Chloroform (100 ml), dried over anhydrous sodium sulphate, was added to the pyridine solution, and precipitation of some of the reducing sugar occurred. The heterogeneous reaction mixture was cooled in a solid carbon dioxide – acetone bath, and an excess of redistilled sulphuryl chloride was added drop by drop over a period of half an hour with vigorous stirring (21 ml of sulphuryl chloride for a pentose and 26 ml for a hexose or disaccharide). Cooling was continued for a further 2 hours and the reaction mixture was then allowed to come to room temperature. During this rise in temperature the viscosity of the solution decreased rapidly and a white precipitate, possibly of pyridine salts, was formed. The precipitate was filtered from the chloroform solution, and the chloroform solution was washed successively with 10% sulphuric acid, saturated sodium bicarbonate solution, and distilled water. The final chloroform solution was dried over anhydrous sodium sulphate, filtered, and the filtrate was concentrated to a syrup which crystallized on standing, in the case of maltose.

D-*Glucose (i)*

The general method was applied and the reaction mixture was allowed to stand for 24 hours at room temperature. D-Glucose gave a pale yellow syrup (8.8 g) which could not be obtained crystalline. It had $[\alpha]_D$ +66° (*c*, 2.8 in chloroform) and paper chromatography in solvent (*a*) gave one spot that moved with the solvent front (aniline/pyridine spray).

*Methyl 4,6-Dichloro-4,6-deoxy-α-*D*-galactopyranoside*

The above syrup (8.2 g) was refluxed in anhydrous methanol (200 ml) solution for 12 hours. The methanolic solution was passed through Duolite A4 (OH form) ion exchange resin and concentrated to a pale yellow syrup (4.5 g) which crystallized on standing. The crude crystals were dissolved in water, the solution was continuously extracted with chloroform, and the chloroform solution on concentration gave a crystalline

mass. Recrystallization from chloroform – light petroleum (b.p. 40–60° C) gave long colorless needles (2.5 g) of m.p. 157° C and $[\alpha]_D$ +179° (*c*, 2.1 in water). The mixed melting point with an authentic sample of methyl 4,6-dichloro-4,6-dideoxy-α-D-galactopyranoside (1, 2) was 157° C. The crystals gave an infrared spectrum identical with that of the authentic specimen of the galactoside derivative.

D-*Glucose (ii)*

The same method was applied as in the previous case (i) except that the reaction product was isolated immediately after the reaction mixture had attained room temperature. D-Glucose gave a pale yellow syrup (8 g) which could not be obtained crystalline and paper chromatography in solvent (*a*) gave one spot that moved with the solvent front (aniline/pyridine spray).

Methyl 4,6-Dichloro-4,6-dideoxy-β-D-galactopyranoside

The above syrup (6 g) was dissolved in anhydrous methanol (150 ml) and the solution was shaken in an aluminum foil covered flask with silver oxide (10 g), 'drierite' (5 g), and glass beads for 24 hours. Distilled water (10 ml) was then added to the reaction mixture, which was shaken for a further 24 hours. The heterogeneous mixture was filtered and the filtrate was deionized and concentrated to a syrup (2.5 g) which crystallized immediately. Two recrystallizations from chloroform – light petroleum (b.p. 40–60° C) gave colorless needles (0.5 g) of m.p. 154° C and $[\alpha]_D$ −8° (*c*, 0.8 in water). Analysis: Calc. $C_7H_{12}Cl_2O_3$: C, 36.4%; H, 5.2%; Cl, 30.7%. Found: C, 36.3%; H, 5.5%; Cl, 30.4%.

The crystals were hydrolyzed with *N* sulphuric acid and the solution was neutralized with barium carbonate, filtered, and the filtrate was deionized to give a syrup which crystallized on standing. Recrystallization from methanol gave colorless crystals of m.p. 184° C (decomp.), $[\alpha]_D$ +130° (30 minutes) → +97° (equilibrium, 24 hours) (*c*, 0.98 in methanol), and mixed melting point with authentic 4,6-dichloro-4,6-dideoxy-D-galactose (2) 184° C (decomp.).

D-*Xylose*

The reaction was carried out by the general method and the reaction product was isolated after the reaction mixture had been allowed to stand at room temperature for 4 hours. D-Xylose gave a yellow syrup (9.5 g) which had $[\alpha]_D$ −41° (*c*, 5.8 in chloroform) and did not crystallize. Paper chromatography in solvent (*a*) gave one spot that moved with the solvent front (aniline/pyridine spray).

Methyl 4-Chloro-4-deoxy-β-L-arabinopyranoside

The above syrup (5.5 g) was treated in the same way as the syrup from D-glucose (ii). Dechlorosulphation of the syrup using silver oxide, methanol, and distilled water was found to be incomplete even after 96 hours. Therefore, the sulphur-containing syrup (3.75 g) was dissolved in chloroform and the chloroform solution was extracted with distilled water. The distilled-water fraction was concentrated to a syrup (0.75 g) which partially crystallized and which was found to be free of sulphur. The semicrystalline mass was then dissolved in water and continuously extracted with ether. The ether extract on concentration produced a crystalline product (0.7 g). Recrystallization from ethyl acetate gave needle-shaped crystals of m.p. 152° C and $[\alpha]_D$ +237° (*c*, 0.96 in methanol). Analysis: Calc. $C_6H_{11}ClO_4$: C, 39.4%; H, 6.0%; Cl, 19.5%. Found: C, 39.4%; H, 6.3%; Cl, 19.1%.

4-Chloro-4-deoxy-L-arabinose

The above crystals (0.36 g) were refluxed in *N* sulphuric acid solution (50 ml) for 10 hours. The solution was neutralized with barium carbonate, filtered, and the filtrate was deionized and concentrated to a syrup (0.33 g) which crystallized on standing. Recrystallization from ethanol gave colorless crystals of m.p. 150° C and $[\alpha]_D$ +155° (10 minutes) → +119° (equilibrium, 36 hours) (*c*, 0.4 in water). Analysis: Calc. $C_5H_9ClO_4$: C, 35.6%; H, 5.4%; Cl, 21.0%. Found: C, 35.6%; H, 5.6%; Cl, 20.4%.

The phenylosazone of the above compound was made and purified by three successive precipitations from methanol solution using distilled water to give fine yellow crystals of m.p. 123° C (decomp.). Analysis: Calc. $C_{17}H_{19}ClN_4O_2$: Cl, 10.3%; N, 16.2%. Found: Cl, 10.0%; N, 15.8%.

4-Chloro-4-deoxy-L-arabitol

The crystalline monochloropentose (0.15 g) was dissolved in distilled water (50 ml) and an excess of sodium borohydride (0.15 g) was added. When the solution became non-reducing acetone was added to decompose the excess sodium borohydride. The solution was deionized and concentrated to a syrup which was codistilled (×10) with methanol. The resultant colorless syrup (0.14 g) did not crystallize and had $[\alpha]_D$ +10° (*c*, 0.9 in water). The syrup contained chlorine and gave one spot with alkaline silver nitrate (11) at R_x 1.0 on paper chromatograms when developed in solvents (*a*) and (*b*).

Periodate Oxidations

The oxidations were carried out in the dark at 25° C, using a small sample (20 mg) of the compounds in distilled water (25 ml) containing 0.3 *M* sodium metaperiodate (1 ml). Aliquots (1 ml) were removed at intervals and the consumption of periodate (12) and the production of formic acid (13) were measured.

Oxidation of Methyl 4-Chloro-4-deoxy-β-L-arabinopyranoside

The moles of periodate consumed were as follows: 0.37 (3.25 hours); 0.37 (5 hours); 1.01 (23 hours); 1.13 (68 hours). No formic acid was produced.

Oxidation of 4-Chloro-4-deoxy-L-arabitol

The moles of periodate consumed and moles of formic acid produced were respectively as follows: 2.04, 0.89 (0.5 hour); 2.08, 0.9 (9.5 hours).

Reaction of Methyl 4-Chloro-4-deoxy-β-L-arabinopyranoside with Sodium Hydroxide

The crystals (18 mg) were dissolved in 0.1 *N* sodium hydroxide solution (2 ml) and the solution was left to stand for 8 hours. Titration of the solution with 0.1 *N* sulphuric acid, using phenolphthalein as the indicator, indicated that only a negligible quantity of the sodium hydroxide solution had been spent in the reaction (0.02 ml). The solution was deionized and concentrated to a crystalline mass (18 mg) which was recrystallized from ethyl acetate to give a product with m.p. 151° C and mixed melting point with the starting material 150–151° C.

Maltose

The general method was applied except that the reaction product was isolated immediately after the reaction mixture had attained room temperature. Maltose gave a pale yellow syrup (11.6 g) which crystallized on standing. Recrystallization was carried out by cooling a saturated solution of the crude crystalline product in chloroform in an acetone – solid carbon dioxide bath. The crystals (6.8 g) were isolated by filtration and washed with chloroform – light petroleum (b.p. 40–60° C) (1:1, v/v). The crystals had m.p. 203° (decomp.) and $[\alpha]_D$ +143° (*c*, 1.28 in chloroform). Analysis: Calc. $C_{12}H_{14}Cl_8O_{15}S_4$: C, 18.2%; H, 1.8%; Cl, 35.8%; S, 16.1%. Found: C, 18.0%; H, 2.0%; Cl, 35.4%; S, 15.7%. Paper chromatography in solvent (*a*) gave one spot that moved with the solvent front (aniline/pyridine spray).

Methyl 4-O-α-4′,6′-dichloro-4′,6′-dideoxy-D-galactopyranosyl 6-chloro-6-deoxy-D-glucopyranoside

The above crystals (10 g) were dissolved in anhydrous methanol and refluxed for 8 hours to form the methyl glycoside. Sodium iodide (10 g) was added to the solution and an immediate evolution of iodine and sulphur dioxide was noticed. The reaction mixture was left to stand for 8 hours. Iodine was removed from the solution by passing hydrogen sulphide through it and the excess hydrogen sulphide was removed by aeration. The solution was neutralized with barium carbonate and filtered. Silver nitrate was added to remove the iodides from solution and after filtration of the silver iodide, potassium chloride was added to the solution to remove the excess silver nitrate. Finally the silver chloride was filtered from the solution and the solution was concentrated to a semicrystalline mass, which was extracted with cold acetone (×3). Evaporation of the acetone solution gave a colorless syrup (5 g). The syrup was dissolved in water and extracted continuously with chloroform for 4 hours and then for a further 4 hours, giving two fractions, A and B.

Fraction A

Concentration of the chloroform solution gave a colorless syrup (2 g) which did not crystallize. Crystallization occurred from ethyl acetate – chloroform and recrystallization from *n*-propanol gave colorless needles (0.25 g) of m.p. 184–186° C and $[\alpha]_D$ +174° (*c*, 0.58 in methanol). Analysis: Calc. for the monohydrate $C_{13}H_{24}O_9Cl_3$: C, 36.2%; H, 5.6%; Cl, 24.7%. Found: C, 36.0%; H, 5.0%; Cl, 24.6%. The sample above was dried to constant weight at 60° C *in vacuo* over phosphoric oxide. Analysis: Calc. for $C_{13}H_{22}O_8Cl_3$: C, 37.8%; H, 5.3%; Cl, 25.8%. Found: C, 37.8%; H, 5.1%; Cl, 26.1%.

6-Chloro-6-deoxy-D-glucose and 4,6-Dichloro-4,6-dideoxy-D-galactose

The crystals of the monohydrate above (0.25 g) were dissolved in *N* sulphuric acid (50 ml) and the solution was refluxed for 16 hours. The reaction mixture was neutralized and deionized as described for previous hydrolyzates. Concentration of the resultant solution gave a syrup (0.2 g) which was shown by paper chromatography in solvents (*a*) and (*b*) to contain two major reducing components at R_x 1.7 and R_x 2.5. A minor reducing component at R_x 0.63 cochromatographed with D-glucose in solvents (*a*) and (*b*). The syrup was fractionated on Whatman 3MM paper using solvent (*b*). End strips of the chromatogram were sprayed with alkaline silver nitrate and the areas of paper corresponding to the two components at R_x 1.7 and R_x 2.5 were eluted with water to give solutions of the two components.

Component at R_x 2.5

The solution was filtered and concentrated to give a crystalline mass (120 mg) which was recrystallized from ethanol. The crystals had m.p. 183–184° C (decomp.) and mixed melting point with an authentic sample of 4,6-dichloro-4,6-dideoxy-D-galactose (2) 184° C (decomp.). The crystals also cochromatographed with the authentic specimen in solvents (*a*) and (*b*).

Component at R_x 1.7

The solution was filtered and concentrated to give a syrup (100 mg) which could not be obtained crystalline. It had $[\alpha]_D$ +34° (*c*, 0.98 in water), and formed a phenylosazone which was recrystallized from methanol–

water to give yellow needles of m.p. 167–168° C (decomp.). Analysis: Calc. $C_{18}H_{21}ClN_2O_3$: C, 57.2%; H, 5.6%; Cl, 9.4%; N, 14.9%. Found: C, 57.6%; H, 5.7%; Cl, 9.1%; N, 15.0%.

Preparation of 6-Chloro-6-deoxy-D-glucose

This was carried out essentially by the method of Wiggins and Wood (8). 6-*O*-Tosyl methyl α-D-glucoside (0.5 g) was heated with anhydrous lithium chloride (0.25 g), absolute methanol (10 ml), and anhydrous acetone (10 ml) at 150° C in a sealed tube for 60 hours. The solution was concentrated to a syrup which was dissolved in water, deionized, and reconcentrated to a syrup (0.35 g) which did not crystallize and gave no spots on paper chromatograms developed in solvents (*a*) and (*b*). The syrup was refluxed with *N* sulphuric acid for 8 hours, and the solution was neutralized and deionized as in previous hydrolyses. The solution was concentrated to a syrup which was shown to consist of one major reducing component (R_x 1.9) and two minor reducing components (R_x 0.65 and R_x 1.35) by paper chromatography in solvents (*a*) and (*b*). The syrup was fractionated on Whatman 3MM paper in solvent (*b*) and the component at R_x 1.9 was isolated by the method used in the previous fractionation by chromatography on 3MM paper. Concentration of the aqueous solution gave a syrup (0.17 g) which could not be obtained crystalline. The syrup gave a phenylosazone of m.p. 165° C (decomp.) and had a mixed melting point with the phenylosazone from above of 166–167° C (decomp.). The two phenylosazones also gave identical infrared spectrums.

Periodate Oxidation of 6-Chloro-6-deoxy-D-glucose Phenylosazone

The crystalline phenylosazone (above) (14.7 mg) was oxidized with sodium metaperiodate in 50% aqueous ethanol by the method of Hough, Powell, and Woods (9). A yellow-orange precipitate was filtered from the solution after 30 minutes and the moles of periodate consumed and the formic acid produced were respectively as follows: 1.93, 0.64 (0.66 hour); 2.06, 0.62 (2.66 hours); 2.09, 0.17 (29.5 hours). No formaldehyde was produced.

1,2-Bisphenylhydrazone of Mesoxaldehyde (9)

The yellow-orange precipitate was recrystallized from 50% aqueous ethanol and gave crystals of m.p. 189° C. An authentic specimen had m.p. 193–194° C and the mixed melting point was 187–189° C. The infrared spectra of the authentic and derived specimens were identical over the range 4000–600 cm^{-1}.

Fraction B

The chloroform solution gave on concentration a syrup (2 g) which crystallized on the addition of hot chloroform. Recrystallization from chloroform – ethyl acetate gave non-reducing colorless crystals (1 g) of m.p. 98–102° C and $[\alpha]_D$ +76° (*c*, 1.0 in methanol). A consistent analysis could not be obtained for this compound even after repeated recrystallizations; therefore it was considered to be a mixture.

6-Chloro-6-deoxy-D-glucose and 4,6-Dichloro-4,6-dideoxy-D-galactose

The crystals from fraction B gave results similar to those observed when the crystalline product from fraction A was hydrolyzed under the same conditions. Paper chromatography produced reducing spots of the same intensities with similar R_x values at R_x 0.63, R_x 1.7, and R_x 2.5. The hydrolysis product was fractionated as described for the crystalline product from fraction A and both 6-chloro-6-deoxy-D-galactose and 4,6-dichloro-4,6-dideoxy-D-glucose were isolated and characterized.

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REFERENCES

1. P. D. Bragg, J. K. N. Jones, and J. C. Turner. Can. J. Chem. **37**, 1412 (1959).
2. J. K. N. Jones, M. B. Perry, and J. C. Turner. Can. J. Chem. **38**, 1122 (1960).
3. E. A. Robinson. Can. J. Chem. **39**, 247 (1961).
4. G. Crank. M.Sc. Thesis, Queen's University, Kingston, Ontario. 1960.
5. W. König and R. Bayer. J. prakt. Chem. **83** (2), 325 (1911).
6. C. S. Hudson. J. Am. Chem. Soc. **47**, 265 (1925).
7. B. Helferich and H. Bredereck. Ber. **60**, 1995 (1927).
8. L. F. Wiggins and D. J. C. Wood. J. Chem. Soc. 1180 (1951).
9. L. Hough, D. B. Powell, and B. M. Woods. J. Chem. Soc. 4799 (1956).
10. L. Hough, J. K. N. Jones, and W. H. Wadman. J. Chem. Soc. 1702 (1950).
11. W. E. Trevelyan, D. P. Proctor, and J. S. Harrison. Nature, 166, 444 (1950).
12. G. Neumüller and E. Vasseur. Arkiv. Kemi, **5**, 235 (1953).
13. D. M. W. Anderson, C. T. Greenwood, and E. L. Hirst. J. Chem. Soc. 225 (1955).