REACTIONS OF SUGAR CHLOROSULFATES

PART VI. THE STRUCTURE OF UNSATURATED CHLORODEOXY SUGARS

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ABSTRACT

Methyl α- and β-L-arabinopyranosides when treated with sulfuryl chloride yielded methyl 4-chloro-4-deoxy-α-D-xylopyranoside 2,3-dichlorosulfate and methyl 3,4-dichloro-3,4-dideoxy-β-D-ribopyranoside 2-chlorosulfate respectively. L-Arabinose gave, in addition to 4-chloro-4-deoxy-D-xylosyl chloride 2,3-dichlorosulfate, an unsaturated tetrachloro–tetradeoxy dimer. The structure and mode of formation of these compounds is discussed.

DISCUSSION

L-Arabinose when treated with sulfuryl chloride gave a syrupy mixture of chloroform-soluble products, one of which was shown to be 4-chloro-4-deoxy-D-xylosyl chloride 2,3-dichlorosulfate.* Methanolysis of the syrupy mixture yielded crystalline methyl 4-chloro-4-deoxy-α-D-xylopyranoside 2,3-dichlorosulfate (I) the structure of which was proved by the following series of reactions. An identical crystalline compound was obtained by the reaction of methyl β-L-arabinopyranoside with sulfuryl chloride thus establishing the configuration of the methyl glycosidic group and the pyranose ring structure of I. When treated with pyridine I gave a crystalline cyclic sulfate ester derivative, thus indicating the presence of vicinal chlorosulfate ester groups in I (1), and dechlorosulfation of I with sodium iodide (1)† gave a crystalline methyl chlorodeoxypentopyranoside. Hydrolysis of the methyl chlorodeoxypentopyranoside required drastic conditions (25% sulfuric acid) and gave a crystalline chlorodeoxypentose the periodate oxidation of which (2 moles periodate uptake, 1 mole formic acid liberated) was consistent with presence of the chlorodeoxy group on position C-4. The chlorodeoxypentose was proved to be of the D-*xylo*-configuration because the less likely alternative structure (the result of 4-chloro-substitution with retention of configuration) 4-chloro-4-deoxy-L-arabinose had been synthesised previously and was shown to have different physical constants (2).‡

The reaction of L-arabinose with sulfuryl chloride gave in addition to the chloroform-soluble products another highly crystalline compound (II) which separated from the acid wash of the reaction mixture. Compound II originated from the carbohydrate component of the reactants because the corresponding reaction with D-arabinose yielded the crystalline L-enantiomer of II. In comparison with similar reactions of other reducing sugars with sulfuryl chloride (2, 3) this appears to be a unique property of arabinose. A tentative structure (II) was proposed (2) based on elemental analysis, infrared spectroscopy (unconjugated ethylenic bond, 1 655 cm^{-1}) and approximate molecular weight determination (ca. 300). It was a trehalo-type dimer because it was non-reducing and the presence of vinylic chlorine was inferred because II was stable when subjected to ozonolysis (4)

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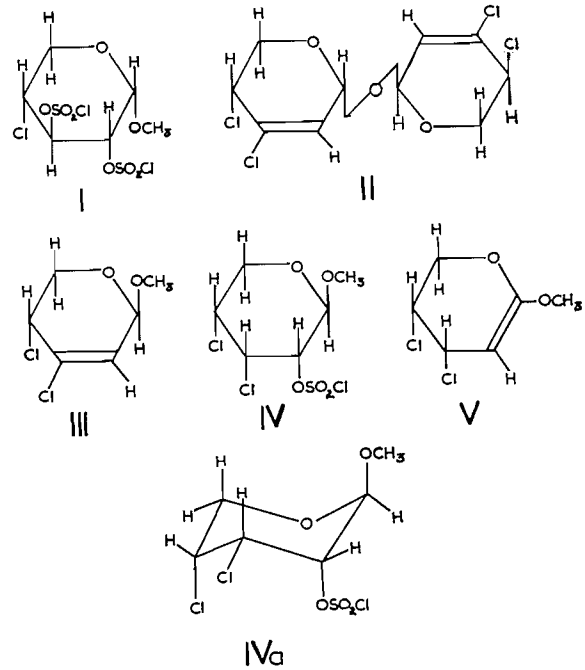
**In one reaction a crystalline compound was obtained the elemental analysis of which was consistent with this structure. However, the structure could not be proved as the crystals decomposed and could not be isolated from subsequent reactions.*

†*Part IV in this series.*

‡*Part III in this series.*

and lead tetraacetate oxidation (5). The structure of II, 4-deoxy-3,4-dichloro-α-D-*glycero*-pent-2-enopyranosyl 4′-deoxy-3′,4′-dichloro-α-D-*glycero*-pent-2′-enopyranoside, was finally confirmed by methanolysis of the dimer (II) to give III, methyl 4-deoxy-3,4-dichloro-β-D-*glycero*-pent-2-enopyranoside, which was also obtained from methyl α-L-arabinopyranoside by an independent synthesis.



Methyl α-L-arabinopyranoside was treated with sulfuryl chloride to give a syrupy product, which was further heated with pyridine hydrochloride in chloroform solution to ensure chlorodeoxy-substitution and replacement of as many chlorosulfate groups as possible. A crystalline compound (IV) was isolated from the reaction mixture which was shown to be methyl 3,4-dichloro-3,4-dideoxy-β-D-ribopyranoside 2-chlorosulfate in the following way. Dechlorosulfation of IV with sodium iodide (1) gave a syrupy methyl dichlorodideoxypentopyranoside which was shown to be homogeneous by thin layer chromatography (t.l.c.) and which gave an elemental analysis consistent with this formulation. Prolonged hydrolysis of the syrupy methyl glycoside afforded a crystalline dichlorodideoxypentose in small yield. The presence of hydroxyl groups on adjacent carbon atoms and thus of chlorodeoxy groups on C-3 and C-4 of the dichlorodideoxypentose was proved by its considerable electrophoretic mobility in borate buffer (M_g = 0.68). This precludes the possibility of C-5 chlorodeoxy-substitution (3). Also a crystalline dichlorodideoxy-1,2-*O*-isopropylidene derivative was obtained from the mother liquors of the above hydrolysis products which were shown to contain only the 3,4-dichlorodideoxypentose and the unhydrolyzed methyl 3,4-dichlorodideoxypentopyranoside (t.l.c.). It was argued that 3,4-dichloro-3,4-dideoxy groups were both formed with inversion of configuration to give the D-*ribo* derivative on the following evidence. Inversion of configuration at C-4 would be expected as both methyl β-L-arabinopyranoside and L-arabinose gave 4-chloro-4-deoxy-D-*xylo* derivatives when treated with sulfuryl chloride. Methyl β-L-arabinopyranoside on treatment with sulfuryl chloride gave only a 4-chloro-4-deoxy-*xylo* derivative

(I) (axial anomeric methoxyl groups in the *CI* conformation) resistant to further chloro-substitution whereas methyl α-L-arabinopyranoside (equatorial anomeric methoxyl group in the *CI* conformation) gave a 3,4-dichloro-substituted derivative (IV). This observation is consistent with a mechanism of chloro-substitution with inversion of configuration at C-3 in the latter case. This has been demonstrated previously, when it was found that only the β-D-anomer (equatorial anomeric methoxyl group in the *CI* conformation) of the analogous methyl α- and β-D-galactopyranosides gave a 3,4,6-trichloro-D-*allo* derivative using similar reaction conditions. Chloro-substitution at C-3 in this case was shown to be dependent on the removal of the 1:3-diaxial interaction to the approach of chloride ion (3). A further example of a similar effect has also been reported (6).

Treatment of IV with pyridine gave compound III previously obtained by the methanolysis of the unsaturated dimer (II), and the structure of III was ascertained as follows. The elemental analysis and infrared spectrum (unconjugated ethylenic bond 1 657 cm^{-1}) of III indicated that it (III) was a product of elimination from IV and that it still contained two chlorodeoxy groups. Although structure III is the preferred elimination product as it involves a 2,3-*trans* elimination from IV, structure V is the alternative possibility the formation of which would involve a 1,2-*cis* elimination from IV. The n.m.r. spectrum of the elimination product (in carbon tetrachloride) contained two doublets (1 proton each) at 5.88 and 4.87 p.p.m. which could be assigned unambiguously to the vinylic and the anomeric proton of III respectively. Although the alternative structure V also has a vinylic proton it is unlikely that the C-3 proton of V would give a simple doublet. The remaining signals in the spectrum were a singlet assigned to the anomeric methoxyl group (3 protons, 3.34 p.p.m.) and a complex group of signals (3 protons) which were assigned to the remaining protons on C-4 and C-5 of III. A comparison of the n.m.r. spectra of II with III (in hot pyridine solution because of the insolubility of II in most solvents) was made and the spectra are shown in Fig. 1. Except for the anomeric methoxyl protons (3 protons, 2.59 p.p.m.) of III the remaining three groups of peaks in the spectra of II and III were similar in appearance and had the same proton ratios. The principal difference in the remaining groups of peaks was the difference in chemical shift of the signal assigned to the anomeric protons of II (two protons, 4.88 p.p.m.) and III (one proton, 4.33 p.p.m.). This could be attributed to the difference of configuration of the anomeric protons of II and III (α and β respectively) and provides tentative evidence that II is a symmetrical α,α′-linked dimer. Some support for this is also found in the high positive rotation of II.

In the formation of III from IV it is likely that 2,3-*trans*-diaxial elimination from the *1C* conformation of IV (IV*a*) had taken place, as this has previously been demonstrated to be the preferred mode of elimination of chlorosulfate groups under these conditions (1). This supports the fact that chloro-substitution had taken place on C-3 of IV with inversion of configuration as the alternative product (C-3-chlorodeoxy-substitution with retention of configuration) would require a 2,3-*cis* elimination to give III. Also this *trans*-diaxial elimination process provides a possible explanation of the formation of the monomeric unit of the dimer (II). It might be expected that 4-chloro-4-deoxy-D-xylosyl chloride, previously obtained in the reaction of sulfuryl chloride with L-arabinose, would be further substituted at C-3 to give 3,4-dichloro-3,4-dideoxy-D-ribosyl chloride 2-chlorosulfate (VI) which could undergo an analogous elimination to give compound VIII. Thus VI and VIII would be the precursors of the dimer II although it is difficult to see how either of these highly substituted compounds is extracted from chloroform solution by aqueous sulfuric acid to become the water-soluble precursor. Perhaps this is achieved

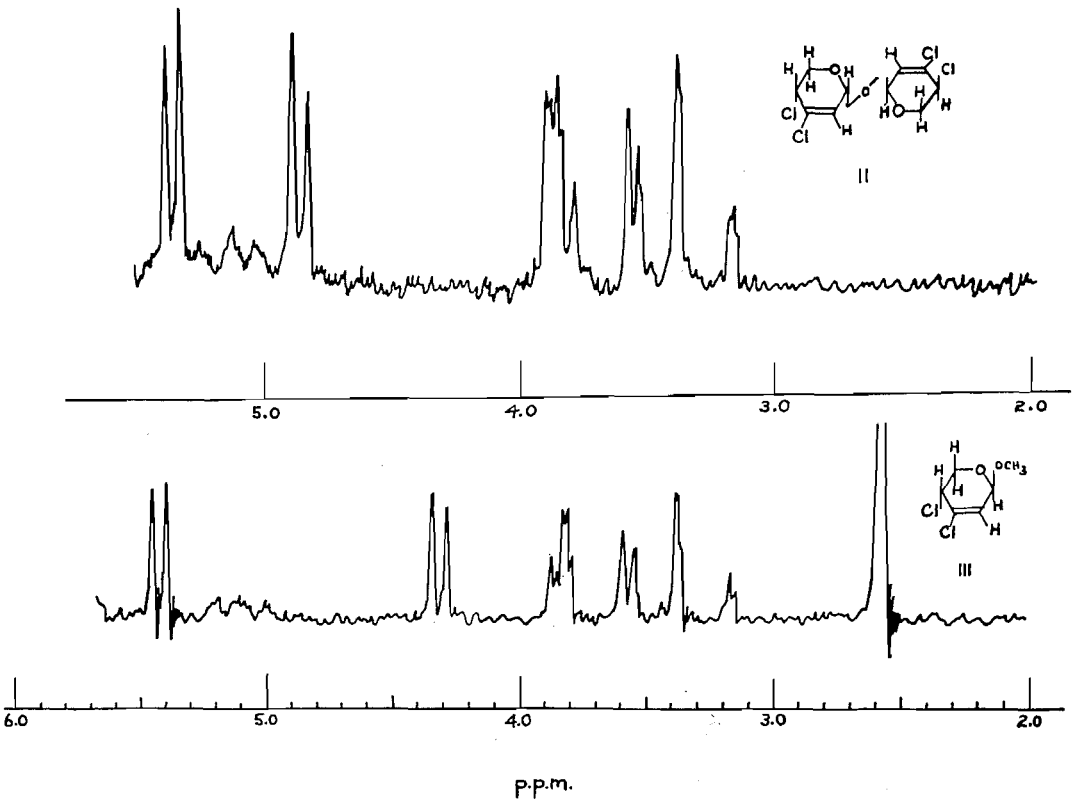
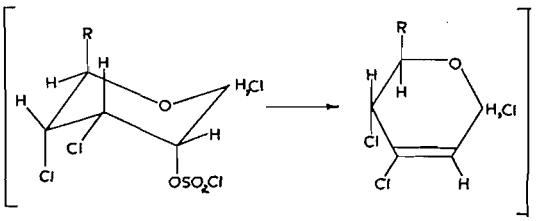


FIG. 1. Spectra of II and III both run in pyridine.



VI R=H
VII R=CH_2Cl

VIII R=H
IX R=CH_2Cl

through the agency of C-1 quaternary pyridinium salts which are known to form from acetohalo sugars (7). This still leaves the basic problem of the mechanism of the aqueous dimerization process which at present is not understood.

It is interesting to note that although reaction of sulfuryl chloride with D-galactose gave a fairly good yield of 3,4,6-trichloro-3,4,6-trideoxy-D-allosyl chloride 2-chlorosulfate (configurational analogue of VI) it does not appear to yield any analogous aqueous insoluble dimeric product from the acid wash of the reaction mixture (3). This might be explained by the inability of the allosyl chloride derivative to attain its *1C* conformation (VII) under these conditions, thus preventing the attainment of the favored *trans*-diaxial arrangement of the groups on C-2 and C-3 for elimination to give intermediate IX. This

could be attributed to the higher energy state of the *1C* conformation of the allosyl chloride derivative (VII) in comparison with VI due to the larger —CH_2Cl group at C-5 of VII. Some corroborating evidence for this is that methyl 3,4,6-trichloro-3,4,6-trideoxy-α-D-allopyranoside 2-chlorosulfate when treated with pyridine gave only the product of hydrolysis of the 2-chlorosulfate ester whereas the analogous compound IV (minus the large —CH_2Cl group at C-5) gave the 2,3-*trans* elimination product III. 3,4,6-Trichloro-3,4,6-trideoxy-D-allose gave a syrupy 1,2-*O*-isopropylidene derivative after a prolonged reaction time using the same vigorous conditions as applied in the formation of the corresponding 3,4-dichloro-3,4-dideoxy-D-ribose derivative. A previous attempt to make this 1,2-*O*-isopropylidene derivative had been unsuccessful (3).

EXPERIMENTAL

Optical rotations were measured at 21 ± 3°. Melting points were determined on a Kofler hot stage and are uncorrected. All solutions were concentrated under reduced pressure below 50°. Thin layer chromatographic analysis was carried out on prepared silica gel G plates. Infrared spectra were determined using a Perkin-Elmer model 21 instrument on samples dissolved in chloroform (6% w/v) unless otherwise stated. The n.m.r. spectra were determined at 60 Mc/s using a Varian M.60 n.m.r. spectrometer and trimethyl silane was used as an internal indicator.

4-Chloro-4-deoxy-D-xylosyl Chloride 2,3-Dichlorosulfate

L-Arabinose (10 g) was treated with sulfuryl chloride (21 ml) and pyridine (40 ml) in chloroform solution (2), and the reaction mixture was allowed to stand at room temperature for 4 h. The chloroform solution was then filtered and washed with 10% sulfuric acid, saturated sodium bicarbonate solution, and distilled water. Concentration of the chloroform extract afforded a syrup (7 g) which was shown to be a mixture containing at least 2 components (t.l.c.). The syrup partially crystallized on standing and the crystals (1 g) were removed from the syrup by washing them with chloroform–petrol (b.p. 40–60°). They had m.p. 84° and $[\alpha]_D$ +80° (*c*, 0.6 in chloroform).

Anal. Calcd. for $C_5H_6Cl_4O_7S_2$: C, 15.7; H, 1.6; Cl, 37.0; S, 16.7. Found: C, 16.0; H, 1.7; Cl, 36.4; S, 16.0.

This crystalline product could not be isolated again in subsequent reactions, and as it decomposed on standing, further reactions were carried out on the syrupy mixture of products.

Methyl 4-Chloro-4-deoxy-α-D-xylopyranoside 2,3-Dichlorosulfate

The syrupy mixture of products from above (7 g) was refluxed with anhydrous methanol for 8 h. Concentration of the methanol solution to a small volume produced a crystalline compound which was removed from the solution by filtration. Successive recrystallizations from methanol–water and chloroform–petrol (b.p. 40–60°) gave colorless needles (1 g) of $[\alpha]_D$ +49° (*c*, 1.0 in chloroform) and m.p. 89° undepressed on admixture with an authentic sample synthesised by another route (see below).

4-Deoxy-3,4-dichloro-α-D-glycero-pent-2-enopyranosyl 4′-Deoxy-3,4-dichloro-α-D-glycero-pent-2′-enopyranoside (II)

The 10% sulfuric acid wash from the above described reaction was left to stand in a beaker open to the atmosphere, and after 24 h fine colorless needles began to appear, the yield of which increased on further standing. The acid wash was allowed to stand for a further 48 h before the crystals were removed by filtration. Recrystallization from acetone–water gave colorless needles (0.8 g) of m.p. 223° and $[\alpha]_D$ +190° (*c*, 1.1 in doxane).

Anal. Calcd. for $C_{10}H_{10}Cl_4O_3$: C, 37.4; H, 3.1; Cl, 44.3. Found: C, 37.3; H, 3.5; Cl, 43.3.

The infrared spectrum of the crystals (0.8% in KBr) indicated no hydroxyl absorption and the presence of an unconjugated ethylenic bond (1 655 cm^{-1}). The crystals did not reduce Fehlings' solution and had an approximate molecular weight of 300 as determined by the Rast method (8). It was found that the yield of this crystalline product could be improved considerably (1.5 g) by allowing the L-arabinose–sulfuryl chloride reaction mixture to stand for 24 h before working up the products. The yield of chloroform-soluble product decreased correspondingly. The crystals were unaffected by ozonolysis (4) and by lead tetraacetate oxidation (5) of the chloroform solution.

The acid wash from the reaction between D-arabinose and sulfuryl chloride also gave a similar non-reducing crystalline product which when recrystallized from acetone–water gave needles of m.p. 223° and $[\alpha]_D$ −186° (*c*, 0.7 in dioxane).

Methyl 4-Deoxy-3,4-dichloro-β-D-glycero-pent-2-enopyranoside (III)

The crystals of the D-enantiomer above (0.6 g) were refluxed with 100 ml of anhydrous methanol and 0.6 ml of concentrated sulfuric acid for 24 h. The solution was concentrated to a small volume and partitioned between chloroform and water. The chloroform solution was washed with saturated sodium bicarbonate

solution, dried (anhydrous sodium sulfate), and concentrated to a syrup which crystallized. Recrystallization from methanol–water gave colorless plates (0.4 g, 58%) of $[\alpha]_D$ +53° (*c*, 0.8 in methanol) and m.p. 72–73° undepressed on admixture with the authentic compound synthesised by another route (see below). The crystals also gave an infrared spectrum indistinguishable from that of the authentic compound.

Methyl 4-Chloro-4-deoxy-α-D-xylopyranoside 2,3-Dichlorosulfate

Methyl β-L-arabinopyranoside (5 g) was treated with sulfuryl chloride (11 ml) and pyridine (20 ml) in chloroform solution (2). The washed chloroform extracts gave on concentration a syrup which crystallized. Recrystallization from methanol–water gave colorless needles (4 g, 29%) of m.p. 88–90° and $[\alpha]_D$ +49° (*c*, 1.0 in chloroform).

Anal. Calcd. for $C_6H_9Cl_3O_8S_2$: C, 19.0; H, 2.4; Cl, 28.1; S, 16.9. Found: C, 19.0; H, 2.3; Cl, 28.3; S, 16.6.

No further chloro-substitution was obtained when the crystals were heated with pyridine hydrochloride in chloroform solution (3) and the original crystalline compound was obtained in good yield (80%).

Methyl 4-Chloro-4-deoxy-α-D-xylopyranoside 2,3-Cyclic Sulfate

The above crystals (2 g) were dissolved in anhydrous pyridine and the solution was left at room temperature for 16 h. The solution was poured into ice water and the aqueous solution was extracted with chloroform. The chloroform solution was washed with 5% sulfuric acid, saturated sodium bicarbonate solution, and distilled water. The chloroform solution was dried (anhydrous sodium sulfate), filtered, and concentrated to a syrup which rapidly crystallized (0.6 g, 56%). Recrystallization from ether–petrol (b.p. 40–60°) gave colorless crystals of m.p. 106–107° and $[\alpha]_D$ +100° (*c*, 1.0 in methanol).

Anal. Calcd. for $C_6H_9ClO_6S$: C, 29.5; H, 3.7; Cl, 14.5; S, 13.1. Found: C, 29.7; H, 3.6; Cl, 14.2; S, 12.8.

Methyl 4-Chloro-4-deoxy-α-D-xylopyranoside

The crystals of the dichlorosulfate ester derivative described above (5 g) were dechlorosulfated in methanol solution by sodium iodide in the presence of barium carbonate (1). The solution was filtered and the filtrate was concentrated to a small volume. Water was added and the aqueous solution was continuously extracted with chloroform. Concentration of the chloroform solution gave a syrup which crystallized, and recrystallization of the product from ethyl acetate gave colorless needles (0.8 g, 37%) of m.p. 102–103° and $[\alpha]_D$ +135° (*c*, 0.9 in methanol).

Anal. Calcd. for $C_6H_{10}ClO_4$: C, 39.4; H, 6.1; Cl, 19.5. Found: C, 39.8; H, 6.1; Cl, 19.2.

4-Chloro-4-deoxy-D-xylopyranose

The crystals of the methyl glycoside above were unaffected by boiling *N* sulfuric acid; therefore, more drastic conditions were tried.

The methyl glycoside (0.6 g) was dissolved in 25% sulfuric acid and the solution was heated at 100° for 5 h. The solution was diluted with water, neutralized with barium carbonate, filtered, deionized by passage through Amberlite IR120 (H form) and Duolite A4 (OH form) ion exchange resins, and concentrated to a syrup which crystallized. Recrystallizations from acetone–ether gave colorless crystals (0.3 g, 55%) of m.p. 145° and $[\alpha]_D$ −45.5° (5 min) → +9° (equilibrium, 24 h) (*c*, 1.1 in methanol).

Anal. Calcd. for $C_5H_9ClO_4$: C, 35.6; H, 5.4; Cl, 21.1. Found: C, 36.1; H, 5.3; Cl, 21.3.

Periodate Oxidation of 4-Chloro-4-deoxy-D-xylopyranose

The oxidation was carried out in the dark at 25° using a small sample (10 mg) of the compound in distilled water (25 ml) containing 0.3 *M* sodium metaperiodate (1 ml). Aliquots (2 ml) were removed at intervals and the consumption of periodate (9) and the production of formic acid (10) were measured and were respectively as follows: 1.66, 0.77 (1.30 h); 1.88, 0.89 (6.30 h); 2.00, 1.02 (24 h); 2.14, 1.18 (48 h).

Methyl 3,4-Dichloro-3,4-dideoxy-β-D-ribopyranoside 2-Chlorosulfate

Methyl α-L-arabinopyranoside (5 g) was treated with sulfuryl chloride (11 ml) and pyridine (20 ml) in chloroform solution (2). The chloroform-soluble product was isolated as in previous reactions and was a syrup (6 g). To ensure maximum chloro-substitution the syrup was further heated with pyridine hydrochloride in chloroform at 50° for 10 h (3). The chloroform solution was washed with water and saturated sodium bicarbonate solution, dried (anhydrous sodium sulfate), filtered, and concentrated to a syrup which crystallized. Recrystallization from chloroform–*n*-hexane gave large colorless crystals (2.5 g, 30%) of m.p. 74° and $[\alpha]_D$ −102° (*c*, 1.3 in chloroform).

Anal. Calcd. for $C_6H_9Cl_3O_5S$: C, 24.0; H, 3.0; Cl, 35.6; S, 10.7. Found: C, 23.6; H, 2.9; Cl, 35.3; S, 10.6.

Methyl 3,4-Dichloro-3,4-dideoxy-β-D-ribopyranoside

The crystals above (2.5 g) were dechlorosulfated in methanol solution using sodium iodide in the presence of barium carbonate (1). The filtered solution was concentrated to small volume and partitioned between chloroform and water. The chloroform extract was dried (anhydrous sodium sulfate), filtered, and concentrated to a syrup (1.7 g, 100%) which did not crystallize but which was shown to be homogeneous by thin layer chromatography. A small quantity of the syrup was distilled under reduced pressure and had $[\alpha]_D$ −55° (*c*, 0.8 in methanol).

Anal. Calcd. for $C_6H_{10}Cl_2O_3$: C, 35.8; H, 5.0. Found: C, 35.7; H, 5.0.

3,4-Dichloro-3,4-dideoxy-β-D-ribopyranose

The syrup above (1.5 g) was refluxed in a *N* sulfuric acid solution of dioxane–water and the hydrolysis was followed by thin layer chromatography. The hydrolysis was extremely slow and was stopped after 3 days, when not completely hydrolyzed, because substantial decomposition had taken place. The solution was neutralized with barium carbonate, filtered, and the filtrate was deionized by passage through Amberlite 1R120 (H form) and Duolite A4 (OH form) ion exchange resins. The solution was then concentrated to a syrup (1 g) which slowly crystallized. Recrystallization from chloroform–petrol (b.p. 40–60°) gave needles (0.1 g, 7%) of m.p. 107–108° and $[\alpha]_D$ −9.5° (15 min) → −3.2° (24 h equilibrium) (*c*, 0.6 in methanol).

Anal. Calcd. for $C_5H_{10}Cl_2O_3$: C, 31.8; H, 5.3; Cl, 37.6. Found, C, 31.9; H, 5.3; Cl, 37.9.

Paper electrophoretograms of the crystals run in 0.05 *M* borate solution (3) and sprayed with alkaline silver nitrate (11) indicated one component at $M_g = 0.68$.

3,4-Dichloro-3,4-dideoxy-1,2-O-isopropylidene-α-D-ribopyranose

The mother liquors from the recrystallization from above were concentrated to a syrup (0.9 g). The syrup (0.9 g) was shaken with anhydrous acetone (40 ml), concentrated sulfuric acid (0.3 ml), and anhydrous copper sulfate (4 g) for 4 days. The solution was neutralized with concentrated ammonia solution, filtered, and concentrated to a syrup which rapidly crystallized. Recrystallization from chloroform–petrol (b.p. 40–60°) gave colorless needles (0.3 g) of m.p. 171° and $[\alpha]_D$ −52° (*c*, 0.7 in chloroform).

Anal. Calcd. for $C_8H_{12}Cl_2O_3$: C, 42.3; H, 5.3; Cl, 31.3. Found: C, 42.4; H, 5.4; Cl, 31.2.

1,2-O-Isopropylidene-3,4,6-trichloro-3,4,6-trideoxy-α-D-allopyranose

3,4,6-Trichloro-3,4,6-trideoxy-D-allose (0.5 g) (3) was shaken for 6 days with anhydrous acetone, concentrated sulfuric acid, and anhydrous copper sulfate and the product isolated as described previously. The product was a syrup which partially crystallized. Recrystallization from chloroform gave needles (0.15 g) of m.p. 170° undepressed on admixture with the starting compound. The mother liquors were washed with water (×3) and the chloroform solution was concentrated to a syrup (0.3 g, 51%) which was shown to be homogeneous except for a small quantity of the starting compound (t.l.c.). The syrup was purified by distillation under reduced pressure and had $[\alpha]_D$ −25° (*c*, 0.6 in chloroform).

Anal. Calcd. for $C_9H_{13}Cl_3O_3$: C, 39.2; H, 4.7. Found: C, 39.4; H, 4.7.

Methyl 4-Deoxy-3,4-dichloro-β-D-glycero-pent-2-enopyranoside

Crystalline methyl 3,4-dichloro-3,4-dideoxy-β-D-ribopyranoside 2-chlorosulfate (1.2 g) obtained previously was dissolved in pyridine (6 ml) and the reaction mixture was allowed to stand for 24 h. The reaction mixture was then partitioned between chloroform and water and the chloroform extract, after treatment with charcoal, was filtered and concentrated to a syrup (0.52 g, 71%) which crystallized. The crystalline product was purified by sublimation to give colorless plates of m.p. 70–71° and $[\alpha]_D$ +52° (*c*, 1.0 in methanol).

Anal. Calcd. for $C_6H_8Cl_2O_2$: C, 39.4; H, 4.4; Cl, 38.8. Found: C, 39.9; H, 4.8; Cl, 38.7.

The infrared spectrum of the crystals indicated no hydroxyl absorption and the presence of an unconjugated ethylenic bond (1 657 cm^{-1})

Methyl 3,4,6-Trichloro-3,4,6-trideoxy-α-D-allopyranoside 2-Chlorosulfate

Methyl 3,4,6-trichloro-3,4,6-trideoxy-α-D-allopyranoside (3) (2 g) was treated with sulfuryl chloride (6.5 ml) and pyridine (10 ml) in chloroform solution (2). The chloroform-soluble product was a syrup which rapidly crystallized. Recrystallization from chloroform–petrol (b.p. 40–60°) gave crystals (2.4 g, 90%) of m.p. 95° and $[\alpha]_D$ +81° (*c*, 1.1 in chloroform).

Anal. Calcd. for $C_7H_{10}Cl_4O_5S$: C, 24.2; H, 2.9; Cl, 40.8; S, 9.2. Found: C, 24.4; H, 2.8; Cl, 41.0; S, 9.2.

The crystals above (2 g) were treated with pyridine as in the previous reaction with methyl 3,4-dichloro-β-D-ribopyranoside 2-chlorosulfate and after 48 h the only isolable chloroform-soluble product was crystalline methyl 3,4,6-trichloro-3,4,6-trideoxy-α-D-allopyranoside as confirmed by a mixed melting point with the authentic compound (3).

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