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Trichloroethylidene Derivates of D-Glucose

STURE FORSÉN

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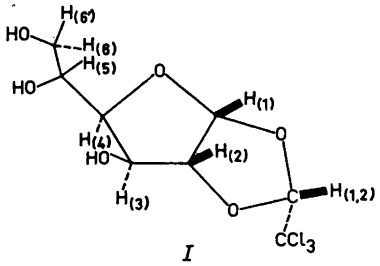
The structures and absolute configurations of two monoacetals, "α"- and "β"-glucochloralose, and four diacetals, dichloralglucose A, C, D, and E, obtained by treatment of D-glucose with chloral and an acid catalyst, have been determined by chemical methods and PMR studies. The latter also yielded information concerning the shape of the five-membered rings in these substances. In connection with this work, a recent publication dealing with the reaction between D-glucose and benzaldehyde is discussed.

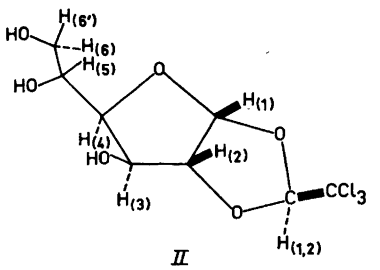
Reaction of D-glucose with chloral in the presence of an acid catalyst, gives a number of cyclic acetals, the earlier work on these substances being summarised in Ref. 1. Two of these, "α"- and "β"-glucochloralose, are monoacetals, and four, dichloralglucose A, C, D, and E, are diacetals. A fifth diacetal, dichloralglucose B, was obtained by Pictet and Reichel [2] on treatment of 1,6-anhydro-D-glucose with chloral and sulphuric acid. It seems questionable, however, whether this product represents a pure substance.

The two monoacetals, "α" and "β", both have the structure of 1,2-*O*-trichloroethylidene-D-glucofuranose, according to the following evidence. The tri-*O*-methyl ether of the "β" compound could also be prepared from 3,5,6-tri-*O*-methyl-D-glucose.[3] On oxidation with lead tetraacetate [3] or periodate [4] they both consume one mole of oxidant with the liberation of formaldehyde. On treatment with strong oxidants they give acids with one carbon atom less, that from the "β"-derivative being identical with the oxidation product of "β"-xylochloralose. On oxidation with nitrogen dioxide [5] they give glucuronic acid derivatives, which both give γ-lactones. The possibility that the two acetals have different structures at C-1 in the glucose residue, as indicated by the prefixes "α" and "β" has been suggested,[5] but is most unlikely for steric reasons. They are certainly both α-D-glucofuranose derivatives (I and II) differing on configuration at the acetal carbon atom. This type



I

"α"-glucochloralose



II

"β"-glucochloralose

of isomerism is not always observed, probably because acetals are generally prepared under conditions when the reaction is thermodynamically controlled, and one of the forms may be energetically favoured. Thus the related 1,2-*O*-benzylidene-α-D-glucofuranose is known only in one form, considered to be the *exo*-phenyl derivative.[6] The acetals of chloral are exceptionally stable to acid hydrolysis, and it seems possible that the reaction between chloral and glycols is kinetically controlled, leading to comparable amounts of the different isomers.

Of the four diacetals (A, C, D, and E) the three former have been isolated from the reaction product obtained when D-glucose is treated with chloral and an acid catalyst. Two (A and C) were also obtained on similar treatment of "β"-glucochloralose, and one (E), in a low yield, on similar treatment of "α"-glucochloralose. One of the diacetals, A, has a 1,2:5,6-di-*O*-trichloroethylidene-α-D-glucofuranose structure (III), as its monomethyl ether was also obtained from 3-*O*-methyl-D-glucose and chloral.[7] The structures of the others were not known.

In the present investigation D-glucose was reacted with chloral hydrate and sulphuric acid as described by Coles *et al.*[9] and worked up essentially as described by these authors. The two monoacetals "α" and "β" and the four diacetals, A, C, D, and E, were isolated from the reaction mixture. They were

Table 1. Physical constants of the mono- and dichloralglucoses and their fully methylated or acetylated derivatives.

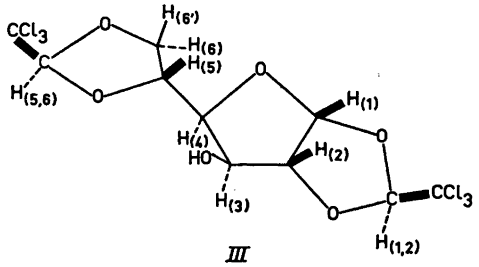
Substance			Methyl ether		Acetate	
	m.p.	$[\alpha]_{578}^{20}$ in pyridine	m.p.	$[\alpha]_{578}^{20}$ in chloroform	m.p.	$[\alpha]_{578}^{20}$ in chloroform
"α"-Glucochloralose	186–188°	+12°	syrup	− 2°	syrup	+42°
"β" »	234–238°	−14°	114–115°	−30°	106–108°	+22°
Dichloralglucose A	275–278°	− 9°	203–204°	−24°	202–203°	−13°
» C	237–241°	+ 1°	130–132°	−31°	132–137°	−25°
» E	199–205°	+26°	120–123°	− 2°	96–98°	+11°
» D	140–145	+18°	syrup	− 7°	96–98°	− 5°

further characterised as their acetates and methyl ethers, several of which have been prepared before. The physical constants of the different substances are given in Table 1.

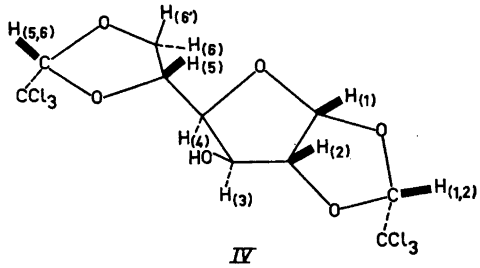
Thin layer chromatography on silica gel was used for following the fractionations. The four diacetals were well separated, their R_F-values increasing in the same order as their melting points (A > C > E > D). The same order was observed for their monoacetates and monomethyl ethers. The monoacetals were not separated as such, but readily separated as their acetates or methyl ethers, the derivatives of the higher melting "β"-isomer having the higher R_F-values.

In addition to these substances, the chromatograms revealed the presence of a substance with a R_F-value between those of the monoacetals and the diacetals and a group of substances with higher R_F-values than the diacetal A. The first and one of the latter were obtained chromatographically pure after fractionation on a silica gel column. The former, which did not crystallise could be distilled under reduced pressure and showed $[\alpha]_D^{20}$ + 24° in chloroform. It was not pure but analysis indicated that it was a monoacetal. The second substance was crystalline, m.p. 210—214°, $[\alpha]_D^{20}$—3° in chloroform. Elemental analysis showed that it was impure but indicated that it was a condensation product from one mole of glucose and three moles of chloral. These products, which were formed in small amounts, were not further investigated.

The diacetals were unchanged after treatment with 80 % sulphuric acid at room temperature overnight. The conversion of the "β"-monoacetal, on treatment with chloral hydrate and sulphuric acid,into a mixture of the diacetals A and C was confirmed. Similar treatment of the "α"-monoacetal yielded a mixture of all four diacetals, in which D and E were predominant.



III
Dichloralglucose A



IV
Dichloralglucose D

The mono-*O*-methyl ethers of the diacetals, after catalytic reduction and acid hydrolysis, all yielded 3-*O*-methyl-D-glucose. This observation, together with their formation from "α"- and "β"-1,2-*O*-trichloroethylidene-α-D-glucofuranose (I and II), respectively, shows that they are the four isomeric 1,2:5,6-di-*O*-trichloroethylidene-α-D-glucofuranoses, (*e.g.* III and IV) differing only in the configurations at the two acetal carbon atoms. From the above results it follows that the "β"-monoacetal and the diacetals A and C have the same, and the "α"-monoacetal and the diacetals D and E the opposite configuration at the acetal carbon atom of the 1,2-*O*-trichloroethylidene group. A comparison

Table 2. Proton chemical shifts (δ-values) and spin coupling constants (c/s) in derivatives of the two isomeric monochloralglucoses ("α"- and "β"-) and of the four isomeric dichloralglucoses (A, C, D, and E).

Isomer	Derivative	$H_{(1)}$	$H_{(2)}$	$H_{(3)}$	$H_{(4)}$	$H_{(5)}$	$H_{(6)}$	$H_{(6')}$	1,2-*O*-trichloro ethylidene	5,6-*O*-trichloro ethylidene	Spin couplings (c/s)
"α"	trimethyl	6.07	4.69	3.95	(4.56)[a]				5.29	—	$J_{12} = 4.0$; $J_{23} \leq 0.5$ $J_{34} = 3.4$
"β"	trimethyl	6.17	4.88	3.85	(4.07)[a]				5.58	—	$J_{1} = 3.9$; $J_{23} \leq 0.5$ $J_{34} = 3.2$
"α"	triacethyl	6.12	4.69	5.54	4.87	5.18	4.52	4.09	5.34	—	$J_{12} = 3.8$; $J_{23} \leq 0.5$ $J_{34} = 3.0$; $J_{45} = 8.5$ $J_{56} = 2.1$; $J_{56'} = 4.5$ $J_{66'} = 12.5$
"β"	triacethyl	6.24	4.85	5.45	4.30	5.15	4.55	4.03	5.63	—	$J_{12} = 3.7$; $J_{23} \leq 0.5$ $J_{34} = 3.0$; $J_{45} = 8.4$ $J_{56} = 2.6$; $J_{56'} = 5.5$ $J_{66'} = 12.4$
A[c]	monomethyl	6.19	4.89	(3.87)[a]					5.58	5.40	$J_{12} = 4.0$; $J_{23} \leq 0.5$ $J_{34} \approx 2.9$
C	»	6.19	4.92	(3.92)[a]					5.60	5.32	$J_{12} = 3.9$; $J_{23} \leq 0.5$ $J_{34} \approx 2.5$
D	»	6.03	4.70	3.99					5.29[b]	5.27[b]	$J_{12} = 4.0$; $J_{23} \leq 0.5$ $J_{34} = 3.0$

E	»	6.05	4.68	3.98	5.27	5.38	$J_{12} = 4.0; J_{23} \leq 0.5$
A[c]	monoacetyl	6.20	4.86	5.45	5.62	5.38	$J_{12} = 3.7; J_{23} \leq 0.5$ $J_{34} = 3.2$
C	»	6.18	4.86	5.41	5.63	5.27	$J_{12} = 3.8; J_{23} \leq 0.5$
D	»	6.06	4.68	5.52	5.30[b]	5.28[b]	$J_{12} = 4.0; J_{23} \leq 0.5$ $J_{34} = 3.2$
E	»	6.07	4.67	5.54	5.29	5.37	$J_{12} = 4.0; J_{23} \leq 0.5$ $J_{34} \approx 3.0$

[a] The assignment of these signals is not completely unambigous.
[b] The assignment of these closely spaced signal pairs could possibly be the reverse — this will, however, not affect the conclusions drawn in the text.
[c] The spectra of these compounds were obtained at *ca.* 50°C due to solubility difficulties. The temperature of the samples was in all other cases *ca.* 35°C.

of the optical rotations of the diacetal acetates and methyl ethers (Table 1) indicates that A and E have the same and C and D the opposite configuration at the acetal carbon atom of the 5,6-*O*-trichloroethylidene group. PMR studies confirmed these conclusions and also made it possible to assign absolute configurations to all the substances.

In connection with other studies we required 1,2:4,6-di-*O*-benzylidene-D-glucose and prepared it in 11 % yield, from D-glucose, benzaldehyde and zinc chloride, by the method of Wood, Diehl and Fletcher.[9] In a recent paper by Dorcheus and Williams,[10] kinetic studies on this reaction are reported and the authors claim that the formation of 1,2:4,6-di-*O*-benzylidene-D-glucose goes to completion when the reaction time is extended. When we tried to improve our yields by using considerably larger reaction times than recommended by Wood *et al.*,[9] however, we did not obtain any 1,2:4,6-diacetal at all but a non-crystalline product, which on thin layer chromatography gave a complicated picture, similar to that obtained from the reaction product of D-glucose and chloral. Dorcheus and Williams [10] did not isolate their reaction product but followed the reaction by paper chromatography in a system in which di-*O*-benzylidene glucoses may be expected to have R_F-values close to unity. It therefore seems probable that they have studied not the formation of a specific substance but of a complex mixture of isomers, in which 1,2:4,6-di-*O*-benzylidene-D-glucose is a minor component.

PMR STUDIES

The proton magnetic resonance (PMR) spectra were recorded at 60 Mc/s on a Varian A 60 spectrometer. All spectra were run on *ca.* 10 % solutions in deuterochloroform with a small amount of tetramethylsilane added as internal reference. The shifts are reported as δ-values.

The results of the PMR measurements on the acetates and methyl ethers of the isomeric glucochloraloses and dichloralglucoses are summarised in Table 2. The spectra of the two tri-*O*-acetyl-glucochloraloses are well resolved with few overlapping lines and are depicted in Figs. 1a and 1b. For the other compounds more complex PMR spectra were obtained but assignment of the signals due to the trichloroethylidene proton and the hydrogens on the ring carbon atoms C-1, C-2, and C-3 was possible in most cases. The three latter signals generally appeared as doublets since the spin coupling constant between $H_{(2)}$ and $H_{(3)}$ is nearly zero and $H_{(4)}$ was in most compounds not very strongly coupled to $H_{(5)}$.

It may be noted from Table 2 that the α- and β-isomers have significantly different shifts not only for the trichloroethylidene proton but also for the protons $H_{(1)}$, $H_{(2)}$, $H_{(3)}$ and $H_{(4)}$. This fact greatly aided the assignment of the PMR signals from the derivatives of the four isomeric dichloralglucoses (A, C, D, and E).

It has recently been shown by Bagget *et al.*[11] that the chemical shift for the benzyl proton in 2-phenyl-1,3-dioxolans varies with the number of *cis*-protons in the 4- and 5-positions. With two *cis*-protons, the δ-value falls in the range 5.33—5.38, with one *cis*-proton in the range 5.48—5.54 and with no *cis*-proton

at even higher δ-values, 5.64 or higher. The same effects were observed for 2-phenyl-1,3-dioxans. The shifts observed for the two isomeric 2,4,6-trichloromethyl-trioxans[12] also vary in this manner. Similar differences are observed for the shifts of the signal from the trichloroethylidene proton in the trichloroethylidene derivatives of glucose. In the derivatives of "β"-glucochloralose and the dichloralglucoses A and C, the signal from the 1,2-*O*-trichloroethylidene proton appears at $\delta = 5.58-5.63$, in the derivatives of "α"-glucochloralose and the dichloralglucoses D and E at $\delta = 5.27-5.34$. The shifts of the protons $H_{(1)}$, $H_{(2)}$, and $H_{(3)}$ are also similar within each group. By analogy with the results of Bagget *et al.* we can therefore conclude that in the former group of substances the 1,2-trichloroethylidene proton occupies the *endo*-position and in the latter group the *exo*-position.

The shift for the 5,6-*O*-trichloroethylidene proton in the dichloralglucoses appears either at $\delta = 5.37-5.40$ (A and E) or at $\delta = 5.27-5.32$ (C and D). This proton must therefore be *trans* to the proton at C-5 in A and E and *cis* in C and D.

The PMR results also reveal some information regarding the shape of the glucose rings in solution. The shifts and spin coupling constants obtained from the completely analysable spectra of the triacetyl derivatives of the α- and β-isomers (*cf.* Fig. 1a and b) are particularly valuable in this respect.

Valence bond calculations by Karplus on the proton coupling constants in H—C—C—H fragments have disclosed that the coupling constant $J_{H,H'}$ between the two protons will be dependent on the dihedral angle φ between the C—H bonds approximately according to eqn. (1).[13,14]

$$J_{H,H'} = A + B \cos \varphi + C \cos 2 \varphi \qquad (1)$$

The theoretical values of the constants obtained assuming a C—Ċ bond length of 1.353 Å and sp^3 hybridised carbon atoms have been given by Karplus as $A = 4.22$, $B = 0.5$ and $C = 4.5$ c/s. It has been stressed by Karplus[14] that significant deviations from the results for the unpertubed fragment are to be expected if a substituent is introduced whose electronegativity is different from that of hydrogen, if the angles H—C—C or C—C—H′ deviate from the tetrahedral angle and if the C—C bond length deviates from that of ethane (1.353 Å). Estimates of the relative importance of these three effects have recently been given.[14] Considerable care must thus be exercised when conclusions regarding dihedral angles are drawn from vicinal coupling constants with the aid of eqn. (1). There seems, however, to be little doubt that eqn. (1) gives a qualitatively correct picture of the angular dependence of vicinal proton spin couplings in most compounds.

As can be seen from Table 2 the coupling constant between $H_{(1)}$ and $H_{(2)}$ is about 3.7—3.8 c/s, that between $H_{(2)}$ and $H_{(3)}$ nearly zero, and that between $H_{(3)}$ and $H_{(4)}$ about 3.0 — 3.4 c/s. This pattern of coupling constants is very similar to that observed by Abraham *et al.* for a number of 1,2-*O*-isopropylidene derivatives of hexofuranoses[15] (*cf.* also Ref. 16).

From eqn. (1) one would conclude that the hydrogens $H_{(1)}$ and $H_{(2)}$ are not eclipsed but that the carbon atoms C-2 and C-3 are displaced in opposite directions from the plane defined by the glucose ring oxygen and the atoms

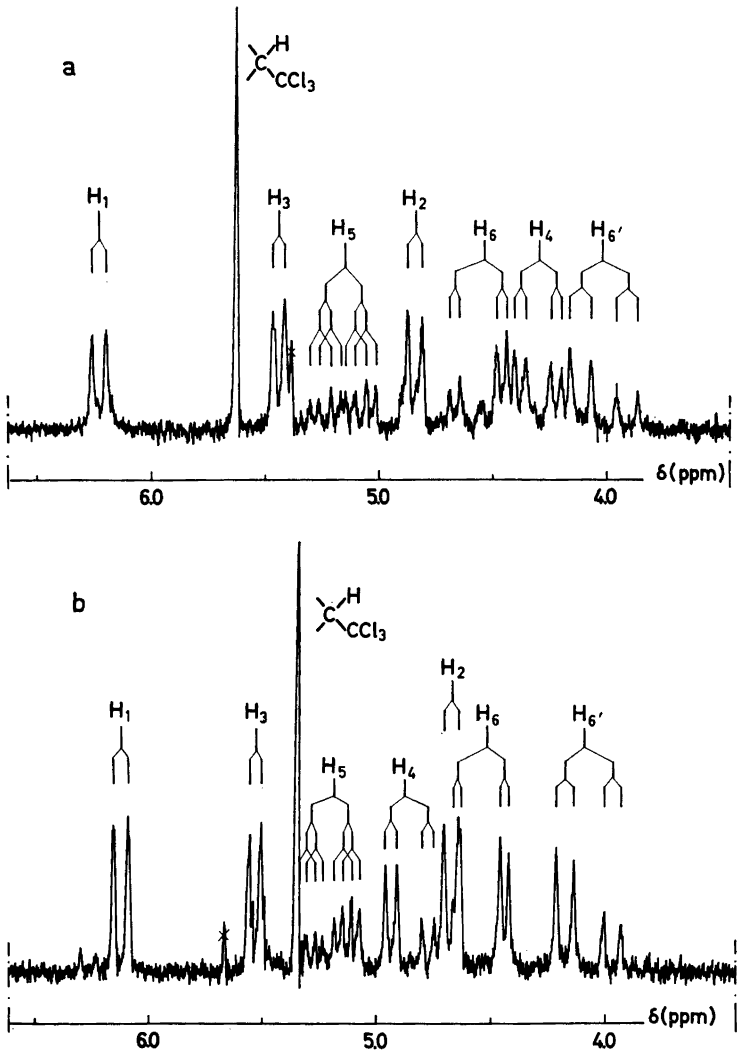
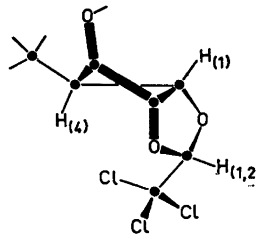


Fig. 1. The PMR spectra of (a) the α-isomer and (b) the β-isomer of triacetylmonochloralglucose. The signals near $\delta = 5.5$ (marked with a cross) are due to impurities — presumably the other isomer.

C-1 and C-4. The mode of puckering would be that which makes the dihedral angle between $H_{(2)}$ and $H_{(3)}$ smaller than the value (120°) expected for a planar conformation. This conclusion is in full agreement with that of Abraham *et al.* for the hexofuranose derivatives.[15] It does not seem possible at present to make a reliable calculation of the angles of deformation. The atom C-1 is for example bonded to one more oxygen atom than C-2 and C-3 and this

alone is predicted to lower the dihedral coupling constant $J_{1,2}$. The magnitude of this effect is not yet well known.



V

The skewing of the furanose ring and accordingly also of the 1,2-*O*-trichloroethylidene ring (V), is further demonstrated by the fact that the chemical shift of $H_{(2)}$ changes considerably more than that of $H_{(1)}$ when going from the α- to the β-isomer of monochloralglucose. This indicates that $H_{(2)}$ is closer to the C—Cl_3 group than $H_{(1)}$. Even more striking is the difference in chemical shift for $H_{(4)}$ in the α- and β-isomers — the difference is as large as 0.57 ppm. This clearly indicates that the C—Cl_3 group and the hydrogen $H_{(4)}$ come very close in the α-isomer. An approach of these groups is only possible for the mode of puckering discussed above in connection with the spin coupling constants. For the type of puckering where the dihedral angle between $H_{(2)}$ and $H_{(3)}$ would become larger than 120° the hydrogen $H_{(3)}$ would be expected to come close to the C—Cl_3 group in the "α"-isomer. The difference in the shift of $H_{(3)}$ between the "α"- and "β"-isomers is, however, found to be only 0.09 ppm.

EXPERIMENTAL

Concentrations were carried out under reduced pressure at 40°. All melting points are corrected.

Synthesis of the mono- and diacetals

D-Glucose (200 g) was treated with chloral hydrate and sulphuric acid and the mixture worked up essentially as described by Coles *et al.*[8], to give two monoacetals and four diacetals. The yield of "α"-glucochloralose was much lower than reported by these authors.

Dichloralglucose. A. The diacetal mixture was partially dissolved in hot ethanol-acetone (500 ml, 1:1). The undissolved material (4.0 g) and that crystallising on cooling the solution (9.2 g) both consisted of dichloralglucose A, melting at about 260°. By recrystallisation from glacial acetic acid the m.p. was raised to 275—278°.

Dichloralglucose C. The combined mother liquors were concentrated to about 300 ml and allowed to cool, when crystals (19 g), m.p. 218°, separated. Recrystallisation from ethanol yielded pure dichloralglucose C, m.p. 237—241°.

Dichloralglucose E. The mother liquors from the above fraction were evaporated to dryness and treated with hot carbon tetrachloride (150 ml). Undissolved material (essentially dichloralglucose C) was removed by filtration, and on cooling dichloralglucose E (15 g), m.p. 175°, precipitated out. Recrystallisation from 50 % aqueous ethanol raised the melting point to 199—205°. (Found: C 27.6; H 2.31; O 21.9; Cl 48.3. Calc. for $C_{10}H_{10}O_6Cl_6$: C 27.4; H 2.30; O 21.9; Cl 48.5).

Dichloralglucose D. The mother liquors from dichloralglucose E were concentrated to 100 ml and cooled, when dichloralglucose D (35 g), m.p. 125°, precipitated out. Recrystallisation from the same solvent, raised the melting point to 140—145°.

The four dichloralglucoses were well separated by thin-layer chromatography on silica gel, using ethyl acetate-light petroleum (b.p. 40—60°) 1:1 as the developing solvent. The spots were detected by spraying with 10 % sulphuric acid and subsequent heating.

Reaction between "β"-glucochloralose and chloral. "β"-Glucochloralose (2 g) was treated with chloral hydrate (2 g) and concentrated sulphuric acid (10 ml) as described by Coles *et al.*[8] The reaction mixture was poured into water and the precipitated diacetals collected. This mixture was shown by thin layer chromatography to consist essentially of the dichloralglucoses A and C. A (0.6 g), m.p. 277—278° and C (0.5 g), m.p. 235—238° were isolated by methods analogous to those described above.

Reaction between "α"-glucochloralose and chloral. An experiment analogous to that described above, was performed with "α"-glucochloralose. Thin layer chromatography revealed that the reaction mixture contained all four dichloralglucoses, the main components being D and E. Pure fractions of A, C, D, and E were obtained as described above, but in small amounts, not representative of the composition of the product.

Acetates and *O*-methyl ethers

The acetates of the mono- and di-acetals were prepared by acetylation with acetic anhydride in pyridine, and the *O*-methyl ethers by methylation with dimethyl sulphate-barium hydroxide-barium oxide in a mixture of dimethyl sulphoxide and dimethyl formamide, by the method of Kuhn and Trischmann.[17]

Dichloralglucose E monoacetate melted at 96—98° after recrystallisation from aqueous ethanol. (Found: C 30.0; H 2.65; O 23.5; Cl 43.9. $C_{12}H_{12}O_7Cl_6$ requires: C 30.0; H 2.52; O 23.3; Cl 44.3).

"α"-Glucochloralose triacetate did not crystallise, but was purified by distillation under reduced pressure. (Found: C 38.7; H 4.06; O 33.2; Cl 24.2. $C_{14}H_{17}O_9Cl_3$ requires: C 38.6; H 3.90; O 33.1; Cl 24.4).

Dichloralglucose E mono-O-methyl ether melted at 120—123° after recrystallisation from light petroleum. (Found C 29.3; H 2.38; O 21.4; Cl 47.1; OCH_3 6.6. $C_{11}H_{12}O_6Cl_6$ requires: (C 29.2; H 2.67; O 21.2; Cl 47.0; OCH_3 6.9).

Reduction and acid hydrolysis of the mono-*O*-methyl ethers of the dichloralglucoses

The mono-*O*-methyl ether of dichloralglucose E (0.4 g) was dissolved in ethanol (20 ml), 50 % sodium hydroxide (0.6 ml) and Raney-nickel (1.2 g) added, and the mixture shaken in an atmosphere of hydrogen. After 15 min when the uptake of hydrogen had ceased (total uptake 50 ml), the catalyst was removed by filtration, and the solution neutralised with M sulphuric acid and concentrated. Thin layer chromatography revealed the presence of several compounds, none of which corresponded to the starting material. The mixture was partitioned between chloroform and water, the chloroform phase was concentrated and the residue (0.2 g) dissolved in ethanol (20 ml). 0.1 M aqueous sulphuric acid (20 ml) was added and the solution kept at 100° overnight, neutralised (Dowex 3, free base), and concentrated. The remaining product, on paper chromatography in several solvent systems and on electrophoresis in borate, germanate and sulphonated phenyl boronic acid buffer gave a spot, indistinguishable from that of authentic 3-*O*-methyl-D-glucose and no other spot corresponding to a reducing sugar. Probably due to some impurity, however, it crystallised with great difficulty, and only a small amount of crystalline 3-*O*-methyl-D-glucose (2 mg), which did not melt sharply, m.p. 147—150°, could be isolated. That the product was 3-*O*-methyl-D-glucose was however firmly established by the paper chromatographic and electrophoretic studies, by which all the mono-*O*-methyl-D-glucoses are readily separated.

This procedure was repeated with the mono-*O*-methyl ethers of the other dichloralglucoses (A, C, and D) and they all yielded 3-*O*-methyl-D-glucose, which again was difficult to obtain crystalline.

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