306. *Some New Covalent- and Ionic-halogen Derivatives of Cellobiose.*

By W. M. Corbett and J. Kidd.

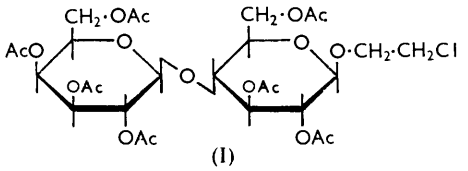
Covalent- and ionic-halogen derivatives of cellobiose have been prepared by reaction of acetobromocellobiose with 2-halogenoethanols and trimethylamine, respectively. The latter reaction has been studied in detail. The general replacement of halide by other anions in the ionic derivatives has been demonstrated.

Though determination of crystal structure by *X*-ray diffraction is often aided by presence of a heavy atom, the group containing this atom should not distort the remainder of the molecule; also, the ratio of the square of the atomic number of the heavy atom to the sum of the squares of the atomic numbers of the remaining atoms should be about unity.[1] Dr. J. Mann and his collaborators of this Association are studying the crystal structure of cellulose. As a preliminary we here report the preparation and properties of heavy-atom derivatives of cellobiose.

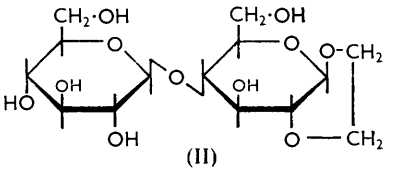
2-Chloroethyl hepta-*O*-acetyl-β-lactoside (I) was previously prepared by reaction of acetobromolactose with 2-chloroethanol.[2] Treatment of the lactoside with hot aqueous sodium hydroxide caused, not only deacetylation, but also elimination of hydrogen chloride to give an anhydride.[3] Helferich and Thiemann[4] similarly prepared 1 : 2-*O*-ethylene-β-cellobiose (II). The acetylated chloro-, bromo-, and iodo-ethyl cellobiosides and lactosides have now been prepared in a highly crystalline form, and have been catalytically deacetylated without appreciable anhydride formation. The unsubstituted glycosides were obtained crystalline, some with solvent of crystallisation. 2-Bromoethyl β-cellobioside, which otherwise would have been the most suitable derivative for study, was hygroscopic. The acetate was therefore treated with trimethylamine and deacetylated,

[1] Lipson and Cochran, "The Crystalline State. Vol. III. The Determination of Crystal Structure," Bell and Son Ltd., London, 1953, p. 207.
[2] Coles, Dodds, and Bergeim, *J. Amer. Chem. Soc.*, 1938, **60**, 1020.
[3] Helferich and Werner, *Ber.*, 1943, **76**, 595.
[4] Helferich and Thiemann, *Z. physiol. Chem.*, 1944, **281**, 126.

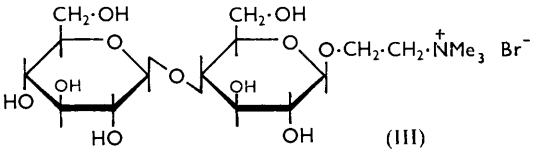
to give the quaternary ammonium salt (III). This compound was also hygroscopic and crystallised very poorly although ionic. Reacetylation with acetic anhydride in the presence of perchloric acid yielded the acetate perchlorate.



(I)

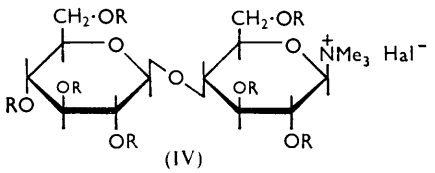


(II)

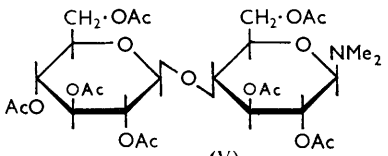


(III)

Attention was then directed to the preparation of ionic derivatives of the type (IV). Micheel and Micheel [5] observed that acetobromo-sugars in which the 2-acetyl group is *cis* to the bromine atom with trimethylamine readily give the *N*-(*O*-acetyl-β-glycosyl)trimethylammonium bromides (*e.g.*, IV; R = Ac, Hal = Br). Acetobromocellobiose appeared to react anomalously,[6] to give a product which was shown by Zemplén and Bruckner [7] to be *N*-hepta-*O*-acetyl-β-cellobiosyldimethylamine (V). The present



(IV)



(V)

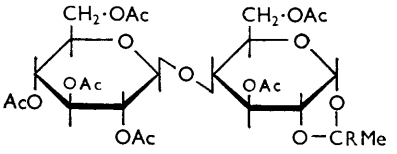
reinvestigation of the reaction has shown that under certain conditions the ammonium salt is formed normally, in high yield, but readily loses methyl halide.

Trimethylamine and acetobromocellobiose at −180° gave an unstable compound with the same elemental analysis as the starting material, but with a lower melting point and optical rotation. Because of the sharpness of the melting point and its reproducibility, it is believed that the material consists of one component only. The melting point of the material was slowly raised by repeated recrystallisation from chloroform–light petroleum and eventually acetobromocellobiose was obtained. Thus the compound is closely related to the latter. It is well known that β-acetohalogeno-sugars are unstable and readily revert to the α-form [8] but the possibility that this new compound is β-acetobromocellobiose must be dismissed because of the high positive optical rotation. The presence of an ortho-acetate group (VI; R = Br) (cf. the similar maltose derivative obtained by Freudenberg and Ivers [9]) would explain the observed physical properties. Such a derivative would, however, be expected to give the corresponding acetate (VI; R = OAc) and ethyl derivative (VI; R = OEt) on treatment with silver acetate, and with ethanol in the presence of silver carbonate, respectively. Instead, these reactions led to β-cellobiose octa-acetate and ethyl hepta-*O*-acetyl-β-cellobioside. Finally, the possibility that the isolated compound is a crystalline modification of acetobromocellobiose is not accepted because of the difference in optical rotation. It is therefore tentatively suggested that the

[5] Micheel and Micheel, *Ber.*, 1930, **63**, 386.
[6] Zemplén, Csuros, and Bruckner, *Ber.*, 1928, **61**, 927.
[7] Zemplén and Bruckner, *ibid.*, p. 2481.
[8] Cf. Schlubach, Stadler, and Wolf, *ibid.*, p. 287; Lemieux, *Adv. Carbohydrate Chem.*, 1954, **9**, 1.
[9] Freudenberg and Ivers, *Ber.*, 1922, **55**, 929; Freudenberg, Hochstetter, and Engels, *Ber.*, 1925, **58**, 666.

compound is acetobromocellobiose of an unstable conformation. Such a change would be expected to decrease the rotation [10] and change the melting point.

The reaction of trimethylamine with a solution of acetobromocellobiose at room temperature (the conditions used by Micheel [11] for acetobromogalactose) produced *N*-hepta-*O*-acetyl-β-cellobiosyltrimethylammonium bromide (IV; R = Ac, Hal = Br) in high yield,



(VI)

together with small amounts of tetramethylammonium bromide. This product was more conveniently prepared by heterogeneous reaction of acetobromocellobiose with trimethylamine and chloroform. The quaternary bromide appeared to form a complex compound with chloroform (cf. Steinkopf *et al.*[12]). When heated, the complex melted and then resolidified, the weight loss corresponding approximately to one mol. of chloroform. The loss of chloroform was indicated by a positive test for *gem.*-polyhalides [13] before heating, and a negative test after heating. The presence of a trimethylammonium bromide group was proved by the solubility in water (despite the presence of seven acetyl groups), quantitative reaction of the bromine with silver nitrate solution, production of trimethylamine by hot alcoholic alkali, and conversion into the tertiary β-cellobiosylamine acetate (V) which with methyl bromide regenerated the ammonium salt.

A metathetical reaction in acetone between the quaternary ammonium salt and sodium iodide produced the iodide which has previously been prepared, but not isolated, by treatment of *N*-hepta-*O*-acetyl-β-cellobiosyldimethylamine with methyl iodide.[14] The chloride was obtained by chloroform extraction of an aqueous solution of the bromide containing a large excess of chloride ions. Use of a saturated solution of ammonium nitrate led to the isolation of the nitrate. The chloride, bromide, iodide, and nitrate have been catalytically deacetylated to give the respective *N*-β-cellobiosyltrimethylammonium salts in highly crystalline form.

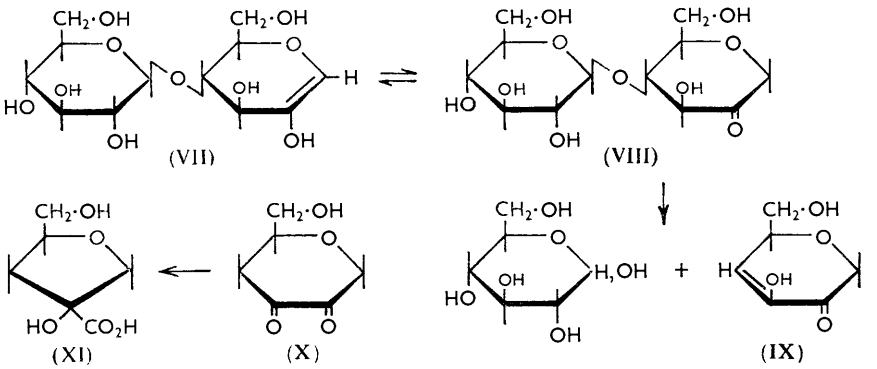
A repetition of Zemplen and Bruckner's reaction [7] at room temperature confirmed the production of *N*-hepta-*O*-acetyl-β-cellobiosyldimethylamine. Hepta-*O*-acetyl-2-hydroxycellobial was also isolated, but in low yield.

Reaction at 90° involved considerable decomposition and the major product was *N*-hepta-*O*-acetyl-β-cellobiosyldimethylamine together with tetramethylammonium bromide. A crystalline modification of the cellobiosylamine derivative was obtained in low yield. It was converted into the higher-melting, more stable form by recrystallisation and seeding. Small amounts of hepta-*O*-acetyl-2-hydroxycellobial and trimethylammonium bromide were isolated, as well as a very small quantity of an unknown compound, m. p. 214—215°, whose analysis suggested its formulation as a hexa-*O*-acetylcellobiose anhydride.

The structure of the hepta-*O*-acetyl-2-hydroxycellobial was proved by a mixed melting point with an authentic sample. However, alkaline saponification indicated the presence of eight acetyl groups. A similar phenomenon has previously been observed for tetra-*O*-acetyl-2-hydroxyglucal.[15] The titration solutions were chromatographed in basic and acidic solvents, giving indications respectively of glucose (but no other reducing component), and a non-lactonisable acid which reacted only very slowly with periodate. Thus, 2-hydroxycellobial had undergone scission at the glycosidic link to yield glucose and an

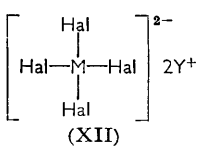
[10] Reeves and Blouin, *J. Amer. Chem. Soc.*, 1957, **79**, 2261.
[11] Micheel, *Ber.*, 1929, **62**, 687.
[12] Steinkopf and Teichmann, *J. prakt. Chem.*, 1930, **127**, 337, and previous papers.
[13] Feigl, "Spot Tests in Organic Analysis," Elsevier, Amsterdam, 1956, p. 313.
[14] Karrer and Harloff, *Helv. Chim. Acta*, 1933, **16**, 962.
[15] Maurer, *Ber.*, 1929, **62**, 332.

acid. Such a scission is readily explained by a β-alkoxycarbonyl elimination [16] as follows. Under alkaline conditions 2-hydroxycellobial (VII) is in equilibrium with 1-deoxy-2-dehydrocellobiose (VIII) in which the glucosyl group is in a position β to the carbonyl group. Elimination of the glucosyl group would leave the carbonyl-enol (IX) which would then be converted through the dicarbonyl compound (X) into the acid (XI). Since the acid contains a tetrahydrofuran ring, a second ring produced by lactonisation at the



primary hydroxyl group would impose excessive strain. The absence of a glycol group readily explains the slow oxidation by periodate.

N-Hepta-*O*-acetyl-β-cellobiosyltrimethylammonium bromide, like simple quaternary ammonium salts, forms complexes with inorganic halides,[17] *e.g.* with 0·5 mol. of calcium chloride, mercuric bromide, or mercuric iodide. These are probably co-ordination compounds. Co-ordination cannot occur through the nitrogen atoms since they bear a positive charge; moreover, the optical rotation of the organic halide is little affected by the dissolution of inorganic salt, so that it is more likely to occur by virtue of the halogen ions to give a complex of the type (XII) where Y is the cation of (IV; R = Ac). Several metal halides dissolved in a chloroform solution of *N*-hepta-*O*-acetyl-β-cellobiosyltrimethylammonium bromide, as shown in the annexed Table.



(XII)

Salt	Colour of solution	M. p. of complex	Salt	Colour of solution	M. p. of complex
$CaCl_2$	Colourless	177° (decomp.)	$FeCl_3$	Red-brown	
$CoBr_2$	Blue	140—142°	Hg_2I_2	Colourless (Hg formed)	
$CrCl_3$	Green		$HgBr_2$	Colourless	160—162°
Cu_2Cl_2	Brown		HgI_2	Olive-green	
$CuBr_2$	Purple ($CHCl_3$)		MgF_2	Milky	
	Yellow (MeOH)	85°	$NiCl_2$	Blue-green	

X-Ray structural analysis of the unacetylated compounds described above is being made by Dr. W. Ferrier at the University of St. Andrews, Queen's College, Dundee.

Experimental

2-Halogenoethyl β-Cellobiosides.—(a) *2-Chloroethyl β-cellobioside.* Freshly prepared silver carbonate (2·6 g.) was added to a solution of acetobromocellobiose (3·6 g.) in 2-chloroethanol (8·8 ml.), and the mixture kept for 2½ hr. at room temperature in the dark, then for 1 hr. at 100°. The silver salts were filtered off and washed with hot ethanol; the combined filtrate and washings afforded needles (1·93 g.), m. p. 199—201°. A further crop (1·30 g.; total yield 89%) isolated from the mother-liquors had m. p. 186—198°. Several recrystallisations from ethanol gave pure 2-chloroethyl hepta-*O*-acetyl-β-cellobioside, m. p. 205—206°, $[\alpha]_D^{28}$ −8·0° (*c* 35 in

[16] Corbett and Kenner, *J.*, 1953, 2245.

[17] Amiel, *Compt. rend.*, 1935, **200**, 138; Remy and Laves, *Ber.*, 1933, **66**, 401; Remy and Meyer, *Ber.*, 1944, **77**, 679; Mellor and Quodling, *J. Proc. Roy. Soc., N.S. Wales*, 1936, **70**, 205; Mellor, *Z. Krist.*, 1939, **101**, 160.

chloroform) (Found: C, 48·2; H, 5·5. Calc. for $C_{28}H_{39}O_{18}Cl$: C, 48·1; H, 5·6%). Helferich and Thiemann [4] give m. p. 202°, $[\alpha]_D$ −17·1°. A suspension of the acetate (2 g.) in anhydrous methanol (10 ml.) and methanolic sodium methoxide (0·6 ml.; *ca.* 0·5M) was left with occasional shaking at room temperature until dissolution was complete (3 hr.). Neutralisation with solid carbon dioxide followed by evaporation *in vacuo* yielded a yellow amorphous powder. Crystallisation from aqueous acetone yielded 2-*chloroethyl* β-*cellobioside hemihydrate*, m. p. 213—214° (decomp.), $[\alpha]_D^{21}$ −9·5° (*c* 9·8 in water) (Found: C, 40·5; H, 6·3. $C_{14}H_{25}O_{11}Cl,\frac{1}{2}H_2O$ requires C, 40·7; H, 6·3%).

(b) 2-*Bromoethyl* β-*cellobioside*. Acetobromocellobiose (4·4 g.) was similarly treated with 2-bromoethanol (15 ml.) and silver carbonate (3·2 g.) to yield 2-*bromoethyl hepta*-O-*acetyl*-β-*cellobioside* (2·66 g., 57%), m. p. 208—211°. After recrystallisation from ethanol–acetone (1 : 1), it had m. p. 214—215·5°, $[\alpha]_D^{24}$ −11·0° (*c* 21·6 in chloroform) (Found: C, 45·1; H, 5·2; Br, 10·7. $C_{28}H_{39}O_{18}Br$ requires C, 45·2; H, 5·3; Br, 10·8%). A suspension of the acetate (1·06 g.) in methanol (5 ml.) and methanolic sodium methoxide (0·3 ml.; *ca.* 0·5M) was kept for 5 days at room temperature until dissolution was complete. A compound which separated from the neutralised solution (carbon dioxide) separated from aqueous acetone as halogen-free crystals (0·07 g.), m. p. 235—238°, depressed on admixture with cellobiose. Helferich and Thiemann [4] give m. p. 236° for 1 : 2-*O*-ethylene-β-cellobiose. Addition of ethyl acetate to the methanolic reaction solution caused the separation of hygroscopic 2-*bromoethyl* β-*cellobioside*, m. p. 134—135° (decomp.), $[\alpha]_D^{20}$ −8·1° (*c* 4·8 in water) (Found: C, 37·4; H, 5·6. $C_{14}H_{25}O_{11}Br$ requires C, 37·4; H, 5·6%).

(c) 2-*Iodoethyl* β-*cellobioside*. 2-Chloroethyl hepta-*O*-acetyl-β-cellobioside (2 g.), sodium iodide (2·15 g.), and acetone (15 ml.) were heated together at 85° for 6½ hr. in a sealed tube. The crystals which separated were washed with a little acetone, water (to remove sodium chloride), and finally further acetone, to give 2-*iodoethyl hepta*-O-*acetyl*-β-*cellobioside* (1·22 g.), m. p. 223—224°, $[\alpha]_D^{22}$ −18·2° (*c* 21·1 in chloroform) (Found: C, 42·5; H, 4·9; I, 16·0. $C_{28}H_{39}O_{18}I$ requires C, 42·5; H, 5·0; I, 16·1%). Addition of water (150 ml.) containing a little sodium thiosulphate to the reaction solution caused further product to separate (0·41 g.; total 77%) which was recrystallised from acetone–ethanol (1 : 1).

A suspension of the acetate (1·05 g.) in methanol, deacetylated as previously described, gave in 77% yield 2-*iodoethyl* β-*cellobioside*, m. p. 147—148°. This recrystallised with a mol. of ethyl acetate of crystallisation from methanol–ethyl acetate, then having m. p. 149—150°, $[\alpha]_D^{19}$ −12·0° (*c* 6·7 in water) (Found: C, 36·4; H, 5·5. $C_{14}H_{25}O_{11}I,C_4H_8O_2$ requires C, 37·0; H, 5·7%).

2-*Halogenoethyl* β-*Lactosides*.—2-Chloroethyl hepta-*O*-acetyl-β-lactoside was prepared in 54% yield by reaction of acetobromolactose with 2-chloroethanol as above. It had m. p. 70—75°, $[\alpha]_D^{18}$ −2·3° (*c* 1·6 in chloroform) (Found: C, 48·1; H, 5·5; Cl, 4·5. Calc. for $C_{28}H_{39}O_{18}Cl$: C, 48·1; H, 5·6; Cl, 5·1%). Coles, Dodds, and Bergeim [2] give m. p. 78—80°. Deacetylation of the acetate gave in 55% yield 2-*chloroethyl* β-*lactoside*, m. p. 148—149° (decomp.), $[\alpha]_D^{18}$ +0·9° (*c* 3·7 in water) (Found: C, 41·1; H, 6·5; Cl, 8·3. $C_{14}H_{25}O_{11}Cl$ requires C, 41·5; H, 6·2; Cl, 8·8%).

Treatment of 2-chloroethyl hepta-*O*-acetyl-β-lactoside with sodium iodide as described for the cellobiose derivative yielded 2-*iodoethyl hepta*-O-*acetyl*-β-*lactoside* (57%), m. p. 70—72°, $[\alpha]_D^{18}$ −9·4° (*c* 1·6 in chloroform) (Found: C, 42·5; H, 5·0; I, 15·3. $C_{28}H_{39}O_{18}I$ requires C, 42·5; H, 5·0; I, 16·1%). Deacetylation gave 2-*iodoethyl* β-*lactoside* (56%), m. p. 154—155° (decomp.), $[\alpha]_D^{17}$ −2·0° (*c* 4·9 in water) (Found: C, 34·0; H, 5·3. $C_{14}H_{25}O_{11}I$ requires C, 33·9; H, 5·1%).

N-(2-β-*Cellobiosyloxyethyl*)*trimethylammonium Bromide*.—2-Bromoethyl hepta-*O*-acetyl-β-cellobioside (3 g.) and alcoholic 40% trimethylamine (*ca.* 40 ml.) were heated together at 90—95° for 1 hr. in a sealed tube, dissolution being complete after 10 min. On cooling, the yellow solution deposited colourless needles of N-[2-(*hepta*-O-*acetyl*-β-*cellobiosyloxy*)*ethyl*]*trimethylammonium bromide* (2·1 g.), m. p. 226—227° (decomp.). On recrystallising from ethanol–ether the salt was obtained as prisms, m. p. 226—227°, $[\alpha]_D^{22}$ −21·9° (*c* 10 in water) (Found: C, 46·3; H, 6·0; N, 1·7; Br, 10·0. $C_{31}H_{48}O_{18}NBr$ requires C, 46·4; H, 6·0; N, 1·8; Br, 10·0%). The salt (0·80 g.), deacetylated in the usual manner, gave deliquescent N-(2-β-*cellobiosyloxyethyl*)*trimethylammonium bromide* (0·33 g., 65%), m. p. 102° (decomp.), $[\alpha]_D^{20}$ −14·6° (*c* 3·1 in water) (Found: C, 39·6; H, 6·9. $C_{17}H_{34}O_{11}NBr$ requires C, 40·2; H, 6·7%). Reacetylation with acetic anhydride containing perchloric acid yielded N-[2-(*hepta*-O-*acetyl*-β-*cellobiosyloxy*)*ethyl*]-*trimethylammonium perchlorate*, m. p. 180°, $[\alpha]_D^{23}$ −16·3° (*c* 0·7 in chloroform) (Found: C, 45·5; H, 5·6. $C_{31}H_{48}O_{22}NCl$ requires C, 45·3; H, 5·9%).

Reaction of Acetobromocellobiose with Trimethylamine at −180°.—Trimethylamine (*ca.* 8 g.)

cooled to −180° was added to acetobromocellobiose (5·70 g.) also cooled to −180°. The whole was allowed to attain room temperature. The residue was recrystallised from chloroform–light petroleum to give a *product* (2·82 g.), m. p. 165—180° (decomp.). Further recrystallisation from the same solvent gave long needles (1·3 g.), m. p. 157—158°, $[\alpha]_D^{21}$ +83·6° (*c* 2·0 in chloroform) (Found: C, 44·8; H, 5·2; Br, 11·7. $C_{26}H_{35}O_{17}Br$ requires C, 44·7; H, 5·1; Br, 11·5%).

The bromide (0·6 g.) was dissolved in ethanol (10 ml.) and silver carbonate added to the solution which was then kept at room temperature for 2 days. Refluxing the reaction mixture for 2 hr., and then evaporation of the solution yielded long needles of ethyl hepta-*O*-acetyl-β-cellobioside, m. p. and mixed m. p. 185—186°, $[\alpha]_D^{20}$ −21·6° (*c* 2 in chloroform).

The bromide (0·2 g.) in benzene (5 ml.) was added to silver acetate (0·12 g.), and the mixture kept at room temperature for 18 hr. with occasional shaking. It was then refluxed for 30 min., the silver salts were filtered off and washed with chloroform, and the combined filtrate and washings concentrated under reduced pressure. The residue, after recrystallisation from ethanol, had m. p. 198—199°, undepressed on admixture with an authentic sample of octa-*O*-acetyl-β-cellobiose.

Reaction of Acetobromocellobiose with Trimethylamine at Room Temperature. Isolation of N-*Hepta*-O-*acetyl*-β-*cellobiosyltrimethylammonium Bromide.*—To a solution of acetobromocellobiose (20 g.) in chloroform (40 ml.) at −90° was added trimethylamine (12 g.) also at −90°. After 20 hr. at room temperature crude N-*hepta*-O-*acetyl*-β-*cellobiosyltrimethylammonium bromide* (16·9 g.) was deposited. This was dissolved in the minimum of chloroform and extracted with a little water to remove a brown impurity. The aqueous washings were back-extracted with chloroform, and the combined chloroform solutions were dried ($CaCl_2$) and diluted with an equal volume of chloroform. Addition of light petroleum (b. p. 40—60°) caused the salt to crystallise as needles (13·3 g.), m. p. 178—179° (decomp.) (soften at 125°, effervesce at 130—145°, and resolidify), $[\alpha]_D^{21}$ −12·7° (*c* 1·5 in chloroform), −6·2° (*c* 11·8 in water). When heated at 78° *in vacuo* for 80 min., the crystals lost 15·3% of their weight (Calc. for $C_{29}H_{44}O_{17}NBr,CHCl_3$: $CHCl_3$, 13·8%). The salt before this treatment gave a strong positive test [13] for *gem.*-polyhalides, a weak test afterwards, and a negative test after being heated at 140° for 30 sec. Bromine remained detectable by the Beilstein test. The desolvated compound had m. p. 180—181° (decomp.) (Found: C, 45·2; H, 6·0; Br, 10·5. $C_{29}H_{44}O_{17}NBr$ requires C, 45·9; H, 5·9; Br, 10·5%).

Distillation of the solvated salt (1·5 g.) with alcoholic 2% sodium hydroxide (25 ml.) produced trimethylamine which was collected in N-hydrogen bromide (5 ml.). Evaporation of the distillate to dryness and recrystallisation of the residue from ethanol yielded colourless plates of trimethylammonium bromide (0·13 g., 47%), m. p. 258—260° (Found: Br, 57·6. Calc. for $C_3H_{10}NBr$: Br, 57·2%).

Elimination of Methyl Bromide from N-*Hepta*-O-*acetyl*-β-*cellobiosyltrimethylammonium Bromide.*—(a) *By triethylamine.* A solution of the solvated salt (0·75 g.) in chloroform (7 ml.) was heated with triethylamine (10 ml.) in a sealed tube at 90° for 2¾ hr. From the mixture was isolated *N*-hepta-*O*-acetyl-β-cellobiosyldimethylamine (0·08 g., 14%), m. p. 185—188°. After three recrystallisations from ethanol, the product had m. p. 210—211° (decomp.) (Found: C, 50·5; H, 5·9. Calc. for $C_{28}H_{41}O_{17}N$: C, 50·8; H, 6·2%). Zemplen and Bruckner [7] give m. p. 203°. A compound (0·015 g.) having m. p. 177—178° (decomp.), undepressed on admixture with a compound of similar melting point obtained in the normal preparation of the cellobiosylamine derivative, and starting material (0·16 g.) were also isolated.

(b) *By thermal decomposition.* The solvated salt (0·053 g.) was heated at 130—150° for 15 min. The residue (0·043 g.), recrystallised four times from ethanol, had m. p. 202—205° (decomp.), undepressed on admixture with *NN*-dimethylhepta-*O*-acetyl-β-cellobiosylamine.

N-β-*Cellobiosyltrimethylammonium Bromide.*—Solvated *N*-hepta-*O*-acetyl-β-cellobiosyltrimethylammonium bromide (0·6 g.) was deacetylated in the normal way. The *cellobiosylammonium salt* crystallised from methanol–acetone as plates (0·36 g., 98%), m. p. 216—217° (decomp.). Recrystallisation from water gave cubes, m. p. 219° (decomp.), $[\alpha]_D^{19}$ +6·3° (*c* 6·6 in water) (Found: C, 38·8; H, 6·3; N, 2·9; Br, 17·0. $C_{15}H_{30}O_{10}NBr$ requires C, 38·8; H, 6·5; N, 3·0; Br, 17·2%).

N-β-*Cellobiosyltrimethylammonium Iodide.*—A solution of sodium iodide (0·80 g.) in acetone (5 ml.) was added dropwise with stirring to a solution of the desolvated acetylated *N*-β-cellobiosyltrimethylammonium bromide (4·0 g.) in chloroform (15 ml.) and acetone (70 ml.). The solution was filtered from sodium bromide, evaporated to a small volume, diluted with chloroform, and filtered from a small amount of sodium iodide, and light petroleum (b. p. 40—60°) was added. N-*Hepta*-O-*acetyl*-β-*cellobiosyltrimethylammonium iodide* crystallised from the solution

as needles containing one mol. of chloroform of crystallisation (4·06 g., 94%), m. p. 166° (decomp.) (effervesce at 130—150°, resolidify), $[\alpha]_D^{23}$ −13·1° (*c* 1·9 in chloroform) (Found: C, 38·7; H, 4·8. $C_{29}H_{44}O_{17}NI,CHCl_3$ requires C, 39·0; H, 4·9%). The acetate (2·0 g.) was deacetylated, to give N-β-*cellobiosyltrimethylammonium iodide* (0·99 g., 78%), m. p. 212—216° (decomp.). Addition of acetone to a concentrated aqueous solution yielded crystals of the *monohydrate*, m. p. 221° (decomp.), $[\alpha]_D^{20}$ +5·7° (*c* 8·7 in water) (Found: C, 34·0; H, 6·0. $C_{15}H_{30}O_{10}NI,H_2O$ requires C, 34·0; H, 6·1%). The anhydrous salt was obtained by heating the hydrate at 100° *in vacuo* over phosphoric oxide for 18 hr. and had m. p. 219° (decomp.) (Found: C, 35·2; H, 6·1. $C_{15}H_{30}O_{10}NI$ requires C, 35·3; H, 5·9%).

Elimination of Methyl Iodide from N-*Hepta*-O-*acetyl*-β-*cellobiosyltrimethylammonium Iodide.*—The solvated compound was heated at 130—150° for 10 min. The pale yellow residue was extracted with water, and crystallised from ethanol to give needles, m. p. 207—208° (decomp.) undepressed on admixture with *NN*-dimethylhepta-*O*-acetyl-β-cellobiosylamine.

N-β-*Cellobiosyltrimethylammonium Chloride.*—A solution of *N*-hepta-*O*-acetyl-β-cellobiosyltrimethylammonium bromide (2·5 g.) in water (5 ml.) was added to saturated aqueous sodium chloride (13 ml.). The mixture was extracted with chloroform, and the extract dried (Na_2SO_4) and concentrated under reduced pressure. Addition of light petroleum (b. p. 40—60°) caused separation of needles of N-*hepta*-O-*acetyl*-β-*cellobiosyltrimethylammonium chloride*, which, recrystallised from chloroform–light petroleum, had m. p. 192° (decomp.), $[\alpha]_D^{21}$ −5·7° (*c* 4·2 in water), −13·2° (*c* 4·5 in chloroform) (Found: C, 43·4; H, 5·7; Ionic Cl, 4·5. $C_{29}H_{44}O_{17}NCl,CHCl_3$ requires C, 43·2; H, 5·4; Ionic Cl, 4·3%). The acetate (2·0 g.) was deacetylated in the normal manner, to give N-β-*cellobiosyltrimethylammonium chloride*, m. p. 227° (decomp.), $[\alpha]_D^{22}$ +7·7° (*c* 1·5 in water) (Found: C, 42·5; H, 7·2; Cl, 8·2. $C_{15}H_{30}O_{10}NCl$ requires C, 42·9; H, 7·2; Cl, 8·5%).

N-β-*Cellobiosyltrimethylammonium Nitrate.*—A solution of the bromide (4·0 g.) in water (10 ml.) was added to saturated aqueous ammonium nitrate (40 ml.). The mixture was extracted with chloroform, and the extract dried (Na_2SO_4) and concentrated under reduced pressure. The residual syrup crystallised on trituration with ethyl acetate. The crystals (2·44 g., 60%), m. p. 205° (decomp.), were recrystallised from acetone solution by addition of ethyl acetate, giving needles of N-*hepta*-O-*acetyl*-β-*cellobiosyltrimethylammonium nitrate* containing ethyl acetate of crystallisation, m. p. 208° (decomp.), $[\alpha]_D^{21}$ −6·8° (*c* 6·5 in water). After removal of ethyl acetate at 78° over phosphoric oxide, the material had m. p. 202° (decomp.) (Found: C, 46·6; H, 6·0. $C_{29}H_{44}O_{20}N_2$ requires C, 47·0; H, 6·0%). The acetate was deacetylated in the normal manner to give N-β-*cellobiosyltrimethylammonium nitrate*, m. p. 215° (decomp.), $[\alpha]_D^{20}$ +7·5° (*c* 9·7 in water) (Found: C, 40·0; H, 7·0. $C_{15}H_{30}O_{13}N_2$ requires C, 40·4; H, 6·8%).

Reaction of Acetobromocellobiose with Trimethylamine at Room Temperature. Isolation of N-*Hepta*-O-*acetyl*-β-*cellobiosyldimethylamine.*—Trimethylamine (3·0 g.) was added to acetobromocellobiose (10 g.) in chloroform (40 ml.), kept at room temperature for 16 days with occasional shaking, and then evaporated, and the resulting residue crystallised twice from ethanol to give *N*-hepta-*O*-acetyl-β-cellobiosyldimethylamine (4·16 g., 44%), m. p. 207—209° (decomp.). Zemplén and Bruckner [7] give m. p. 203°. Addition of water to the ethanol mother-liquors gave hepta-*O*-acetyl-2-hydroxycellobial as plates, which after two recrystallisations from ethanol had m. p. and mixed m. p. 127—128° (0·55 g., 6%).

Reaction of Acetobromocellobiose with Trimethylamine at 90°.—Ethanolic trimethylamine (*ca.* 40%; 80 ml.) and acetobromocellobiose (10 g.) were heated at 85—95° for 2 hr. The white crystals produced were fractionally crystallised, to give, as the main product, *N*-hepta-*O*-acetyl-β-cellobiosyldimethylamine (2·72 g., 29%), m. p. 210—211° (decomp.), $[\alpha]_D^{21}$ −11·5° (*c* 2·9 in chloroform) (Found: C, 50·7; H, 6·1; N, 1·9; Ac, 45·8. Calc. for $C_{28}H_{41}O_{17}N$: C, 50·8; H, 6·2; N, 2·1; Ac, 45·4%). Zemplén *et al.*[6] give m. p. 205° (decomp.), $[\alpha]_D^{20}$ −11·5° (in chloroform). Distillation of the product (0·45 g.) with alcoholic 2% sodium hydroxide (15 ml.) and collection of the distillate in hydrogen bromide gave needles of dimethylammonium bromide (0·04 g., 47%), m. p. *ca.* 150° (Found: Br, 63·9. Calc. for C_2H_8NBr: Br, 63·5%). A sample (0·10 g.) was heated in methyl bromide (*ca.* 1 g.) at 100° for 5 min., then cooled to room temperature during 2 hr. Excess of methyl bromide was evaporated and the residue crystallised from chloroform–light petroleum (b. p. 40—60°), to give needles (0·07 g., 44%) of *N*-hepta-*O*-acetyl-β-cellobiosyltrimethylammonium bromide, m. p. 180° (effervesce at 80°, resolidify at 150°), undepresed on admixture with the previously prepared salt.

From the mother-liquors were also isolated (*a*) tetramethylammonium bromide (1·04 g., 47·5%) (Found: Br, 52·0. Calc. for $C_4H_{12}NBr$: Br, 52·0%), (*b*) trimethylammonium bromide (0·01 g., 0·5%) (Found: Br, 57·5. Calc. for $C_3H_{10}NBr$: Br, 57·2%), (*c*) a compound (0·19 g.), m. p. 177—178° (decomp.), $[\alpha]_D^{22}$ −11·7° (*c* 0·2 in chloroform) (Found: C, 50·9; H, 6·5; N, 2·1. Calc. for $C_{28}H_{41}O_{17}N$: C, 50·8; H, 6·2; N, 2·1%), which was a lower-melting form of *N*-hepta-*O*-acetyl-β-cellobiosyldimethylamine. Recrystallisation from ethanol and seeding with the higher-melting form gave the higher-melting form, m. p. and mixed m. p. 209—210° (decomp.), (*d*) an unidentified halogen- and nitrogen-free compound (0·04 g.), m. p. 214—215° (Found: C, 49·6; H, 5·6%), and (*e*) hepta-*O*-acetyl-2-hydroxycellobial (0·35 g., 4%), m. p. and mixed m. p. 128—129° (Found: C, 50·5; H, 5·4. Calc. for $C_{26}H_{34}O_{17}$: C, 50·6; H, 5·6%).

Hepta-*O*-acetyl-2-hydroxycellobial (0·0686 g.) in dioxan (5 ml.) was saponified with 0·01N-sodium hydroxide (10 ml.) at room temperature for 80 min. Alkali consumed was 7·90 equiv. An authentic sample under similar conditions consumed 7·80 equiv. The titration solution was stirred with Amberlite Resin IR-120(H), filtered, stirred with barium carbonate, filtered, again stirred with resin, filtered, and concentrated. Chromatography of the resultant syrup in ethyl acetate–pyridine–water (8 : 2 : 1) revealed the presence of glucose, and in ethyl acetate–acetic acid–water (10 : 1·3 : 1) an acid with R_{Lactic} 0·51 was detected with " B.D.H. 4·5 " indicator spray.[18] It slowly reacted with permanganate–periodate spray,[19] and gave no reaction with hydroxylamine–ferric chloride spray for lactones.[20]

Reaction of N-*Hepta*-O-*acetyl*-β-*cellobiosyltrimethylammonium Halides with Inorganic Salts.* —(a) *Calcium chloride.* A solution of calcium chloride (30 g.) in water (20 ml.) was added to one of *N*-hepta-*O*-acetyl-β-cellobiosyltrimethylammonium bromide (5 g.) in water (10 ml.), and the mixture was extracted with chloroform (6 × 50 ml.). The chloroform extracts were dried ($CaCl_2$), concentrated under reduced pressure to 100 ml., and diluted with light petroleum (b. p. 40—60°; *ca.* 40 ml.). The solution yielded hygroscopic needles (4·1 g.) of a *complex*, m. p. 170° (decomp.). Recrystallised from chloroform–light petroleum (b. p. 40—60°) this had m. p. 177° (decomp.) (effervesces at 150°; resolidifies), $[\alpha]_D^{22}$ −12·2° (*c* 5·7 in chloroform) (Found: Ionic Cl, 8·1; Ca, 2·2. $C_{29}H_{44}O_{17}NCl,CHCl_3,\frac{1}{2}CaCl_2$ requires Ionic Cl, 8·0; Ca, 2·3%).

(b) *Mercuric bromide.* Solid mercuric bromide (0·21 g.), added to a solution of *N*-hepta-*O*-acetyl-β-cellobiosyltrimethylammonium bromide–chloroform complex (0·50 g.) in chloroform (3 ml.), dissolved at room temperature in a few seconds. The solution was filtered from the slight excess of mercuric bromide and evaporated under reduced pressure. The residue crystallised from hot absolute methanol (15 ml.) as prisms (0·37 g.), m. p. 160—162°, $[\alpha]_D^{21}$ −8·7° (*c* 9·0 in chloroform). To estimate the bromine present, a solution of the *complex* (0·252 g.) in acetone (2·5 ml.) was treated dropwise with sodium iodide in acetone (5%; 2 ml.) and kept for 10 min. at room temperature. The sodium bromide precipitated was filtered off, washed with acetone, and titrated in aqueous solution against silver nitrate (Found: Br, 15·4. $C_{29}H_{44}O_{17}NBr,CHCl_3,\frac{1}{2}HgBr_2$ requires Br, 15·2%). The acetone filtrate from the sodium bromide precipitate was concentrated, diluted with chloroform to precipitate excess of sodium iodide, filtered, and concentrated under reduced pressure to a green syrup which crystallised from hot absolute methanol as yellow-green needles, m. p. 184—185°, undepressed on admixture with the iodide compound described below.

(c) *Mercuric iodide.* Red mercuric iodide (0·33 g.) was dissolved in a solution of *N*-hepta-*O*-acetyl-β-cellobiosyltrimethylammonium iodide–chloroform complex (0·66 g.) in chloroform (3 ml.). The olive-green solution was worked up in the same way as in the mercuric bromide experiment, the product crystallising from hot absolute methanol as yellow-green needles, m. p. 183° (sinter at 180°).

The authors thank Drs. W. Ferrier and J. Mann for valuable discussions, and Mr. A. T. Masters for most of the microanalyses. This work forms part of the fundamental research programme undertaken by the Council of the British Rayon Research Association.

BRITISH RAYON RESEARCH ASSOCIATION, HEALD GREEN LABORATORIES,
WYTHENSHAWE, MANCHESTER, 22. [*Received, November 25th,* 1958.]

[18] Nair and Muthe, *Naturwiss.*, 1956, **43**, 106.
[19] Lemieux and Bauer, *Analyt. Chem.*, 1954, **26**, 920.
[20] Abdel-Akher and Smith, *J. Amer. Chem. Soc.*, 1951, **73**, 5859.