527. *Ionic Halogen Derivatives of Cellotriose and Cellotetraose.*

By W. M. Corbett and J. Kidd.

The approach to the problem of the crystal structure of cellulose II by a study of the crystal structure of the cellodextrins has led to the preparation of cellobiose compounds in which a heavy atom is present to facilitate the analysis of *X*-ray diffraction patterns.[1] We now record the preparation of *N*-β-cellotriosyltrimethylammonium bromide and *N*-β-cellotetraosyltrimethylammonium iodide. The prerequisite that the presence of the group containing the heavy atom should not greatly alter the crystal structure has been met in the case of the cellotetraose derivative, the principal reflections of its *X*-ray powder photograph being very similar to those of cellotetraose itself. The crystal structures of these derivatives will be determined by Dr. W. Ferrier and colleagues at Queen's College, Dundee, and will be reported elsewhere.

The water-solubilising power of the quaternary ammonium halide group noted for the fully acetylated cellobiose derivatives [1] is still present in the polyacetates of these higher dextrins: *N*-(tredeca-*O*-acetyl-β-cellotetraosyl)trimethylammonium bromide readily dissolves in water to a soapy solution. The presence of one mol. of water in the crystalline deacetylated compounds appears to be fairly common, and is evidently not detrimental in the cellotetraose compound in that it does not alter the crystal structure.

Experimental.—Acetobromocellotriose. Cellotriose (3·28 g.) was added in small portions to a mixture of acetic anhydride (12 ml.) and perchloric acid (0·1 ml.) at 30—40°. The mixture was poured on ice and extracted with chloroform. The combined extracts were washed with water and sodium hydrogen carbonate solution, dried ($CaCl_2$), and evaporated to a syrup which crystallised from chloroform–ether. The undeca-*O*-acetyl-α-cellotriose (5·26 g.) had m. p. 221—222°. Dickey and Wolfrom [2] give m. p. 223—224°. Bromine (4·04 ml.), followed by water (1·98 ml.), was added dropwise to a stirred mixture of glacial acetic acid (30 ml.) and red phosphorus (3·2 g.) at <20°. To this was added a solution of cellotriose acetate (4·78 g.) in chloroform (5 ml.) and the mixture was kept at room temperature for 4½ hr. It was then poured on ice, and the aqueous layer extracted with chloroform. The combined organic layers were washed twice with ice-water, once with sodium hydrogen carbonate solution, then dried ($CaCl_2$). Evaporation *in vacuo* afforded a syrup which crystallised from chloroform–ether to give needles of *acetobromocellotriose* (3·50 g., 54% based on cellotriose), m. p. 183° (decomp.), $[\alpha]_D^{18}$ +58·0° (*c* 11·4 in chloroform) (Found: C, 46·5; H, 5·5. $C_{38}H_{51}O_{25}Br$ requires C, 46·3; H, 5·2%).

N-β-*Cellotriosyltrimethylammonium bromide.* Anhydrous trimethylamine (*ca.* 10 ml.) was added to a solution of acetobromocellotriose (3·46 g.) in chloroform (20 ml.). After being kept at 30° for 3 hr., it was extracted with water (5 ml.). The chloroform layer was separated, combined with five successive chloroform extractions of the aqueous layer, and evaporated *in vacuo* to a syrup which crystallised from ether–ethyl acetate to give N-(*deca*-O-*acetyl*-β-*cellotriosyl*)*trimethylammonium bromide* (1·86 g., 51%), m. p. 180° (decomp.), $[\alpha]_D^{20}$ −16·1° (*c* 6·0 in chloroform) (Found: C, 46·8; H, 5·8. $C_{41}H_{60}O_{25}NBr$ requires C, 47·0; H, 5·8%). A solution of the acetate (1·12 g.) in dry methanol (6 ml.) was deacetylated by the addition of methanolic ~0·5M-sodium methoxide (0·3 ml.). The solution was kept for 2 hr. at room temperature, then neutralised with solid carbon dioxide and diluted with a little acetone, to yield small colourless crystals of N-β-*cellotriosyltrimethylammonium bromide* (0·43 g., 64%), m. p. 205° (decomp.) (effervesce at 150°), $[\alpha]_D^{19}$ +3·7° (*c* 5·6 in water) (Found: C, 39·1; H, 6·6. $C_{21}H_{40}O_{15}NBr,H_2O$ requires C, 39·1; H, 6·6%).

Acetobromocellotetraose. Cellotetraose (4·16 g.) was added gradually with stirring to a mixture of acetic anhydride (15 ml.) and perchloric acid (0·14 ml.) at 30—40°. The usual process of isolation yielded a syrup which crystallised from chloroform–ether to give needles of tetradeca-*O*-acetyl-α-cellotetraose, m. p. 238—239°. Dickey and Wolfrom [2] give m. p. 230—234°. A solution of the acetate (5·0 g.) in chloroform (7 ml.) was added to a hydrogen bromide solution

[1] Corbett and Kidd, *J.*, 1959, 1594.
[2] Dickey and Wolfrom, *J. Amer. Chem. Soc.*, 1949, **71**, 825.

(50 ml.) prepared as before, and kept for 4 hr. at room temperature. The *acetobromocellotetraose* (3·85 g., 76%) isolated in the usual way contained one mol. of chloroform of crystallisation and had m. p. 182—183° (decomp.), $[\alpha]_D^{19}$ 36·8° (*c* 7·3 in chloroform) (Found: C, 42·9; H, 4·9; Br, 5·4. $C_{50}H_{67}O_{33}Br,CHCl_3$ requires C, 43·1; H, 4·8; Br, 5·7%).

N-β-*Cellotetraosyltrimethylammonium iodide*. Addition of anhydrous trimethylamine (*ca.* 15 ml.) to a solution of acetobromocellotetraose (3·48 g.) in chloroform (16 ml.) caused a white solid to be deposited which, overnight, reverted to a sticky yellow material. Further product separated on addition of ether. The combined product was dissolved in chloroform and washed with a little water, the water layer being extracted three times with chloroform. The organic layers were combined, dried (Na_2SO_4), and evaporated *in vacuo*. The residual syrup in ethyl acetate gave N-(*tredeca*-O-*acetyl*-β-*cellotetraosyl*)*trimethylammonium bromide* (1·26 g., 35%), m. p. 189° (decomp.), $[\alpha]_D^{21}$ −16·8° (*c* 4·4 in chloroform) (Found: C, 47·4; H, 6·1; Br, 6·0. $C_{53}H_{76}O_{33}NBr$ requires C, 47·7; H, 5·7; Br, 6·0%). To a solution of the ammonium bromide derivative (1·04 g.) in acetone (4 ml.) was added with stirring a solution of sodium iodide (0·13 g.) in acetone (1·0 ml.). The solution was kept for 10 min. at room temperature, filtered from the sodium bromide produced, and evaporated *in vacuo* to a syrup. This was dissolved in chloroform and filtered from sodium iodide, and the filtrate was evaporated to a syrup which from ethyl acetate solution gave N-(*tredeca*-O-*acetyl*-β-*cellotetraosyl*)*trimethylammonium iodide* (0·61 g., 57%), m. p. 200° (decomp.), $[\alpha]_D^{20}$ −18·3° (*c* 4·9 in chloroform) (Found: C, 45·5; H, 5·5. $C_{53}H_{76}O_{33}NI$ requires C, 46·1; H, 5·5%). The acetate was deacetylated to N-β-*cellotetraosyltrimethylammonium iodide* (0·09 g., 88%), m. p. 212° (decomp.), $[\alpha]_D^{20}$ 0·0° (*c* 1·7 in water) (Found: C, 38·2; H, 6·3; I, 14·2. $C_{27}H_{50}O_{20}NI,H_2O$ requires C, 38·0; H, 6·1; I, 14·9%).

The authors acknowledge the valuable advice of Drs. W. Ferrier and J. Mann, and thank Dr. K. J. Heritage for samples of cellotriose and cellotetraose, Dr. J. Mann for the *X*-ray powder photograph, and Mr. A. T. Masters for the microanalyses. This work forms part of the fundamental research programme of the British Rayon Research Association.

British Rayon Research Association, Heald Green Laboratories,
Wythenshawe, Manchester, 22. [*Received, March* 13*th*, 1959.]