The aqueous layer coming from the previously described benzene extraction was extracted with three 150-cc. portions of ether and the combined extracts were dried (sodium sulfate). Evaporation of the ether left a residue (0.2 g.) which was very soluble in water. It was crystallized from a mixture of ethyl acetate and petroleum ether (b.p., 60–68°), when it formed white plates melting at 276–280° (dec.). The value for the neutral equivalent indicated that this substance was a dimethyldicarboxyphenol.

Anal. Calcd. for $C_{10}H_{10}O_6$: neut. equiv. (two), 105. Found: neut. equiv., 107.

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Esters of Glucose and Lactose

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A number of straight-chain aliphatic acid esters of glucose and lactose were prepared. The crystalline compounds are described below; the others are listed in Table I.

Table I

Properties of Polysubstituted Glucose and Lactose Esters

Ester	Acyl groups per mol.[a]	Elementary analyses, % Calcd.[b] C	H	Found[c] C	H	Free acidity,[d] %	$[\alpha]^{25}D$ (c, 2.5) in $CHCl_3$	M.p., °C. (cor.)	$n^{20}D$	Physical state and color
A. Glucose										
Caprylate	4.7	67.7	10.2	68.2	10.2	1.1	+46.8		1.4587	Light-amber sirup
Caprate	4.8	70.5	10.8	70.9	10.8	1.1	+40.3		1.4612	Light-amber sirup
B. Lactose										
Caproate	7.2	63.2	9.0	63.2	9.0	0.85	+15.3		1.4646	Light-yellow sirup
Caprylate	6.9	66.5	9.9	66.7	10.2	1.5	+14.5		1.4650	Amber sirup
Caprate	7.0	69.3	10.5	69.6	10.7	2.0	+12.6		1.4657	Amber sirup
Laurate	6.5	70.7	10.9	70.2	11.1	Trace	+13.4	110–112		White, waxy solid
Myristate	7.2	73.0	11.4	73.3	11.4	0	+ 9.4	43.4–46.0		White, waxy solid
Palmitate	7.5	74.5	11.7	74.5	11.7	Trace	+ 9.0	55.6–58.2		White, waxy solid
Stearate	7.2	75.4	11.9	75.3	12.0	Trace	+ 7.9	62.5–64.5		White, waxy solid

[a] Calculated from free hydroxyl values obtained by the method of Ogg, Porter and Willits, *Ind. Eng. Chem., Anal. Ed.*, **17**, 394 (1945). [b] Based on the number of acyl groups per mol. found. [c] Microanalyses by C. L. Ogg and Mary Jane Welsh. [d] By Mrs. R. B. Kelly.

All the esters but the lactose butyrate were prepared by slowly adding a chloroform solution of acid chloride (10% excess) to a stirred mixture of the sugar (β-lactose, or anhydrous α-glucose), pyridine (1.1 moles/mole of acid chloride), and chloroform.[1] After initially cooling with an ice-salt mixture (until one hour after the acid chloride was added) the reaction was carried out six to eight hours at room temperature for the glucose esters and four to thirteen hours at 50–70° for the lactose, depending upon the reaction rate.

α-D-Glucose Pentamyristate.—After three recrystallizations from an alcohol–chloroform mixture the ester formed long, fine needles, insoluble in 95% alcohol and acetone, soluble in Skellysolve C and very soluble in ether, chloroform and benzene; m.p. 59.0–59.8° (cor.), $[\alpha]^{25}D$ +38.3° (*c* 2.5, chloroform), +33.5° (*c* 2.5, benzene).

Anal. Calcd. for $C_6H_7O_6(COC_{13}H_{27})_5$: free hydroxyl, none; C, 74.09; H, 11.62. Found: free hydroxyl, none[2a]; free acidity, none[2a]; C, 74.19; H, 11.63.[2b]

Lactose Octabutyrate[3] (β?).—β-Lactose was stirred with a mixture of butyric anhydride (70% excess) and pyridine (1.9 moles/mole of butyric anhydride) for eight hours at room temperature, eight hours at 50°, and 23 hours at 90°. After separating the crystals which formed in the sirupy product and recrystallizing four times from a 3:1 alcohol-water mixture, the ester was obtained as fine needles very soluble in 95% alcohol, acetone, Skellysolve C, ether, chloroform and benzene; m.p. 77.0–77.4° (cor.), $[\alpha]^{25}D$ + 4.6° (*c* 2.5, chloroform), −14.2° (*c* 2.5, benzene).

Anal. Calcd. for $C_{12}H_{14}O_{11}(COC_3H_7)_8$: free hydroxyl, none; C, 58.52; H, 7.81. Found: free hydroxyl, none[2a]; free acidity, none[2a]; C, 58.55; H, 8.17.[2b]

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[1] *Cf.* G. Zemplén and E. D. Laszlo, *Ber.*, **48**, 915 (1915).

[2] (a) By Mrs. R. B. Kelly. (b) Microanalyses by C. L. Ogg and Mary Jane Welsh.

[3] An apparently unsuccessful preparation was recorded by M. Berthelot, *Ann. chim. phys* [3] **60**, 98 (1860).

[4] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

X-Ray Investigation of *t*-Butyl Chloride and *t*-Butyl Bromide[1]

By Robert S. Schwartz, Benjamin Post and I. Fankuchen

Thermal measurements indicate that both *t*-butyl chloride and *t*-butyl bromide undergo two transitions in the solid state. The sum of the entropies of the transitions is 8.7 e.u./mole for the chloride, and 7.6 e.u./mole for the bromide. The dielectric constants of the crystalline solids just below the melting point are higher than those of the liquids.[2,3] These data indicate that both crystalline solids are highly disordered above the transition temperatures. The nature of the disorder has been investigated using low temperature single crystal X-ray diffraction techniques.

Experimental

Eastman Kodak Co. "white label" *t*-butyl chloride and *t*-butyl bromide were fractionally distilled in a column packed with glass helices. The fraction of *t*-butyl chloride boiling between 50.0–50.5° was used; $n^{20}D$ 1.3852. The *t*-butyl bromide boiled at 72.7–73.0°; $n^{20}D$ 1.4278.

Optical observations indicate that both compounds are isotropic at temperatures above transition II and strongly birefringent below this transition. Baker and Smyth,[2] however, have reported that below this transition crystalline *t*-butyl bromide is isotropic.

Samples of the compounds were sealed in thin-walled Pyrex capillary tubes and mounted on the goniometer arcs of a low temperature X-ray camera.[4] Single crystals of the

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[1] This work supported by the Office of Naval Research.

[2] W. O. Baker and C. P. Smyth, This Journal, **61**, 2798 (1939).

[3] L. M. Kushner, R. W. Crowe and C. P. Smyth, *ibid.*, **72**, 1091 (1950).

[4] B. Post, R. S. Schwartz and I. Fankuchen, *Rev. Sci. Inst.*, **22**, 218 (1951).