1058. *Carbonic Esters of Sucrose. Part III.*[1] *The Direct Preparation of Poly(sucrose Carbonates) from Sucrose.*

By R. S. Theobald.

Sucrose reacts with carbonyl chloride in the presence of pyridine to form poly(sucrose carbonate). Both soluble and insoluble polymers are more conveniently prepared by the action of diphenyl carbonate on sucrose in the presence of an alkaline catalyst. Soluble poly(sucrose carbonate) is almost inert towards invertase and shows a much higher stability to acid than sucrose does. The possible relevance of these properties and of some periodate oxidation studies to the structure of the polymer is discussed.

The formation of a carbonate polymer from sucrose and ethylene dichloroformate in the presence of aqueous alkali has been reported.[2] Carbonyl chloride provides an even simpler example of a difunctional reagent capable of forming intermolecular carbonate bridges, and has been employed for this purpose in both one-stage and two-stage condensation reactions with polyhydric alcohols [3] or phenols.[4,5] In their preparations of the monosaccharide carbonates by reaction of carbonyl chloride with the sugars in pyridine, Haworth and Porter [6] obtained amorphous by-products which, although not characterised, were probably polymeric.

The structural inability of sucrose to accommodate a five-membered cyclic carbonate group,[2] and, on the other hand, its high capacity for substitution, might be expected to favour the formation of a cross-linked polycarbonate with carbonyl chloride. Attempts to use aqueous alkali, under a variety of conditions, as the acid-acceptor in such a reaction were largely unsuccessful, the maximum yield of polymer achieved being about 4%. Whilst sodium hydroxide is an effective condensing agent in the preparation of aromatic polycarbonate resins,[5] its use with strongly hydrophilic derivatives such as carbohydrates appears to be limited by the rapid hydrolysis of the polycarbonate. In pyridine solution a polycarbonate was more easily obtained from sucrose, but the reaction tended to be uncontrollable and high molar ratios of carbonyl chloride to sucrose were required for satisfactory conversion.

The amorphous nature of the " carbonate " synthesised in 1912 by Hochstetter [7] from sucrose and diphenyl carbonate at 130° possibly indicated a polymeric structure, and it prompted a re-investigation of this largely neglected type of transesterification. Use of the recommended solvent, namely, molten resorcinol, gave no product with the characterstics claimed by Hochstetter, that is, a sparing solubility in water and alcohols. The

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[1] Part II, preceding paper.

[2] Part I, Theobald, *J.*, 1961, 5359.

[3] Muskat and Strain, U.S.P. 2,384,115, 2,385,930, 2,399,285, 2,399,287.

[4] Einhorn, *Annalen*, 1898, **300**, 135.

[5] Schnell, *Angew. Chem.*, 1956, **68**, 633; *Trans. J. Plastics Inst.*, 1960, **28**, 143.

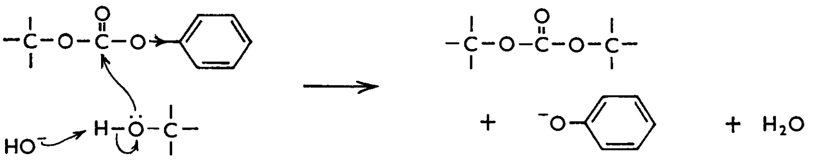
[6] Haworth and Porter, *J.*, 1930, 151.

[7] Hochstetter, G.P. 268,452/1912; *Friedländer*, 1913, **11**, 1211.

predominant reaction, even with very pure reagents, was hydrolysis of the sucrose. However, addition of a catalytic amount of sodium hydrogen carbonate caused rapid gelling of the mixture, and an amorphous substance with the correct physical properties resulted. This proved to be a cross-linked poly(sucrose carbonate) containing probably some *O*-phenoxycarbonyl groups and possibly resorcinol in a similar state of combination.

The apparent necessity for an alkaline catalyst contrasts with Hochstetter's conclusion[7] that superior yields result from the omission of catalyst, and it seems not to be attributable to possible differences in the apparatus used. Soda glass was shown chromatographically to catalyse polymerisation very slightly and to decrease " inversion " of the sucrose, but its effect was undoubtedly masked by the feebly acid character of resorcinol ($k_1 = 3{\cdot}6 \times 10^{-10}$ at 18°). In the neutral solvent dimethyl sulphoxide, however, soda glass exerted a powerful catalytic action and rapid gelling occurred, with no hydrolysis of the sucrose. A sodium hydrogen carbonate catalyst (0·1% w/w) in dimethyl sulphoxide caused conveniently swift polymerisation even at 100°.

Under the last conditions, replacement of diphenyl carbonate, as the carbonate source, by the diethyl ester led mainly to the formation of *O*-ethoxycarbonylsucroses of low degrees of substitution, with negligible polymerisation. This difference in behaviour may reflect the higher electrophilic activity of the *O*-phenoxycarbonyl groups,[8] which participate spontaneously in intermolecular condensation until a semi-rigid structure is attained. Similar attempts to utilise ethylene carbonate for the production of cross-linked carbonate polymers were unsuccessful, the main reaction in this case probably being polyether formation.[9]



The effect of reducing the proportion of diphenyl carbonate relative to sucrose, from the 4 : 1 molar ratio employed by Hochstetter to a 0·5 : 1 ratio, is summarised in the Table.

Composition of polycarbonates obtained from sucrose and diphenyl carbonate in catalysed dimethyl sulphoxide.

Mol. of Ph_2CO_3 per mol. of sucrose	Gelling time (min.) at 135°	Yield of polymer (g.) from 14 g. of sucrose	Found (%)			*O*-Phenoxycarbonyl groups per sucrose unit (calc. from % phenol)
			C	H	Phenol	
0·5	No gelling in 1 hr.	13·7 (sol.)	Not analysed			—
0·9	No gelling in 1 hr.	13·1 ,,	,,	,,		—
1·0	6	11·3 (sol.)	42·1 [c]	5·4 [c]	—	—
		4·9 (insol.)	Not analysed			—
1·1	8 [a]	8·65 ,,	42·9	5·7	0·09	0·004
1·3	4	13·1 ,,	42·7	5·5	0·21	0·01
1·5	4	14·9 ,,	42·7	5·4	0·46	0·02
2·0	7 [a]	16·8 ,,	43·9	5·1	3·4	0·14
4·0	4 [b]	17·7 ,,	47·5	4·7	13·5 [d]	0·65

[a] At 130°. 17 min. at 100°. [c] After dialysis. [d] 13·3% in polymer from reaction heated 4 hr.

At the higher level the polymer contained an average of about 0·7 *O*-phenoxycarbonyl group per sucrose residue, irrespective of the duration of heating after gelling. The *O*-phenoxycarbonyl content fell significantly as the amount of reagent was reduced, until

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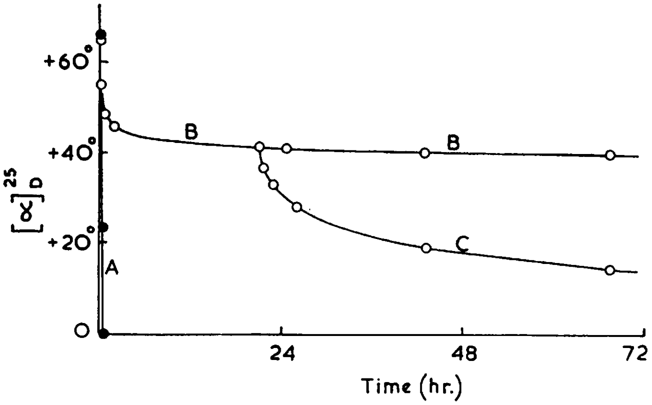
[8] Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, p. 211.

[9] Monson and Dickson, U.S.P. 2,819,260/1958 (*Chem. Abs.*, 1958, **52**, 10,166).

with about 1·5 mol. an almost theoretical yield of cross-linked polymer, with negligible *O*-phenoxycarbonyl substitution, was obtained. Equimolar proportions of sucrose and diphenyl carbonate afforded a poly(sucrose carbonate) 70% of which was water-soluble, and a further decrease in the reagent (*e.g.*, to 0·9 mol. per mol. of sucrose) gave a wholly water-soluble polymer which could be purified by dialysis.

A dialysed water-soluble poly(sucrose carbonate), when incubated with invertase, exhibited a small rapid fall in optical rotation and was then attacked only extremely slowly by the enzyme. Although very little is known concerning the specificity of invertase towards substituted sucroses, it seems likely that a derivative substituted solely in the D-glucopyranose half of the molecule would undergo enzymic hydrolysis. Thus, sucrose 2-phosphate [10] is attacked, as also are methyl [11] and benzyl β-D-fructofuranoside.[12] Most of the fructose residues in the polymer therefore probably carry carbonate linkages, and the initial enzyme attack is possibly confined to chain-terminating sucrose units. Only fructose, and not glucose, is liberated in this step, but it may not be valid to conclude that substitution in D-fructofuranose is restricted to positions sterically shielding the glycoside bond. Mineral acids caused progressive hydrolysis of soluble poly(sucrose carbonate), but much more slowly than in the case of sucrose itself (see Figure). A positive optical rotation was still obtained after 1 week at 25° in N-acid, behaviour analogous to that already reported [2] for " tri-*O*-ethoxycarbonylsucrose."



Hydrolysis of poly(sucrose carbonate) by invertase and by N-hydrochloric acid.

(A) Upper section(s) of hydrolysis curves of sucrose in either aqueous invertase or N-hydrochloric acid (curves coincident in this range). (B) Undialysed poly(sucrose carbonate) in aqueous invertase. (C) Undialysed poly(sucrose carbonate) in aqueous invertase treated, after 21 hr., with hydrochloric acid (Calc. for complete hydrolysis: $[\alpha]_D$ −37·2°).

Oxidation of the dialysed polymer with sodium metaperiodate, followed by reduction with potassium borohydride, and hydrolysis with a cation-exchange resin provided much free glucose, indicating [13] appreciable substitution at $C_{(3)}$ of the D-glucopyranosyl residue. However, the total periodate consumption of about 2 mol. per sucrose unit (48 hr.) requires that an equal proportion of polymer linkages must occupy primary positions (6, 1′, or 6′). Further examination of the hydrolysis fragments also revealed fructose and a trace of erythritol, consistent with some secondary substitution, at positions 3′ or 4′, in the D-fructofuranosyl moiety, and at $C_{(4)}$ of D-glucopyranose. The failure to detect glyceraldehyde, a

[10] Courtois and Ramet, *Bull. Soc. Chim. biol.*, 1945, **27**, 610, 614.

[11] Hestrin and Avineri-Shapiro, *Biochem. J.*, 1944, **38**, 2; Purves and Hudson, *J. Amer. Chem. Soc.*, 1934, **56**, 1973.

[12] Purves and Hudson, *J. Amer. Chem. Soc.*, 1937, **59**, 49.

[13] Smith and Van Cleve, *J. Amer. Chem. Soc.*, 1955, **77**, 3091.

fragment indicative of 2-substitution in glucose, should not be regarded as conclusive, since the chromatographic standard of this compound was itself only weakly revealed.

A similar structural study commencing with periodate oxidation was carried out on " tri-*O*-ethoxycarbonylsucrose." For this and other related oxidations, 20% t-butyl alcohol in water was found to be a suitably inert solvent, though exerting the same inhibiting effect at higher concentrations as noted by Guthrie[14] for *NN*-dimethylformamide. The ester consumed only about 1 mol. of oxidant per mol. of sucrose in 5 days, but paper chromatograms of the fragments from subsequent reduction and hydrolysis were indistinguishable from those obtained from soluble poly(sucrose carbonate). These results, in conjunction with the observed acid-stability of the derivatives, suggest that in both poly(sucrose carbonate) and *O*-ethoxycarbonylsucrose substitution is partly random, but mainly preferential at positions 3, 6, 1′, and 3′. The strong possibility of acyl migration under slightly alkaline conditions[15] renders any structural investigation involving standard methylation techniques of little value.

In very few cases have the detailed structures of partly substituted sucrose derivatives been determined. Black, Dewar, and Rutherford[16] concluded that in a mono-*O*-methylsucrose, obtained from trisodium " sucrate," the ether groups occupy mainly, but not exclusively, positions 2, 6, 1′, and 3′. According to Gaver *et al.*,[17] a preference for initial attack at $C_{(2)}$ is also exhibited by sucrose in sodium hydroxide–butanol, further substitution involving, successively, positions 3′ and 3. However, Percival[18] claimed that potassium hydroxide forms an adduct ($C_{12}H_{22}O_{11}$,3KOH) with sucrose exclusively at the primary positions (6, 1′,6′). The difficulty of avoiding the selective isolation or detection of particular isomers in these researches may partly explain apparent inconsistencies. It also seems likely that, with larger attacking groups, steric factors may take precedence over hydroxyl acidities in deciding the positions of substitution.

EXPERIMENTAL

The following chromatographic solvents were employed with Whatman No. 1 paper: (i) butan-1-ol–pyridine–water (10 : 3 : 3 v/v), (ii) butan-1-ol–pyridine–water (3 : 2 : 1·5 v/v), (iii) butan-1-ol–ethanol–water (40 : 11 : 19 v/v), and (iv) ethyl acetate–acetic acid–water (9 : 2 : 2 v/v). Sprays used for detection were (*a*) methanolic potassium hydroxide–acidified *p*-anisidine reagent,[2] (*b*) 0·02M-sodium metaperiodate followed after 5 min. by 4% ammoniacal silver nitrate,[19] and (*c*) *p*-anisidine hydrochloride.[20]

Reaction of Sucrose with Carbonyl Chloride in Pyridine.—Carbonyl chloride (43·7 g., 5 mol.) in dry toluene (100 ml.) was added dropwise during 1 hr. to a cooled (ice–salt) stirred solution of sucrose (30·2 g.) in dry pyridine (500 ml.). The mixture was stirred for a further ½ hr. at room temperature, then poured into saturated aqueous sodium hydrogen carbonate (2 l.), and the precipitate was collected. After being washed thoroughly with water it was dried *in vacuo* over phosphoric oxide. The yield of cross-linked *poly*(*sucrose carbonate*) was 8·7 g. (26%) (Found: C, 42·4; H, 5·2. $[C_{12}H_{20}O_{11},CO]_n$ requires C, 42·4; H, 5·4; $[C_{12}H_{19}O_{11}\cdot(CO)_2]_n$ requires C, 42·5; H, 4·8%), $\nu_{max.}$ (C=O stretching) 1760 cm.$^{-1}$. A similar experiment with stirring overnight after addition of the reagent afforded a 28% yield of polymer, but recovery was negligible when only 2 mol. of carbonyl chloride was used per mol. of sucrose. An unknown excess of gaseous carbonyl chloride, passed into sucrose in pyridine, gave on one occasion a 50% yield of polymer.

The polymer was rapidly hydrolysed by an excess of aqueous ammonia at room temperature and sucrose was detected chromatographically in the solution.

Reaction of Sucrose with 4 *Mol. of Diphenyl Carbonate.*—(a) *In resorcinol.* Hochstetter's

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[14] Guthrie, *Chem. and Ind.*, 1960, 691.

[15] McKeown and Hayward, *Canad. J. Chem.*, 1957, **35**, 992.

[16] Black, Dewar, and Rutherford, *J.*, 1959, 3073.

[17] Gaver, Lasure, and Tieszen, U.S.P. 2,572,923 (*Chem. Abs.*, 1952, **46**, 1786).

[18] Percival, *J.*, 1935, 648.

[19] Dr. A. C. Richardson, personal communication.

[20] Hough, Jones, and Wadman, *J.*, 1950, 1702.

method [7] was modified as follows: Sucrose (7 g.) was dissolved in a magnetically-stirred mixture of molten resorcinol (35 g.) and sodium hydrogen carbonate (0·035 g.) at 135° (oil-bath). Diphenyl carbonate (18 g.) was added and heating continued for about 45 min.; sudden cessation of stirring then denoted gelling of the mixture. The cooled mass was macerated with ether (500 ml.), and the polymer was collected, washed with more ether, and air-dried. After being triturated with water and collected, it was continuously extracted (Soxhlet) over boiling aqueous dioxan (1 : 1 v/v) for 8 hr., and vacuum-dried (60°; silica gel). The poly(sucrose carbonate) (5·4 g.) was insoluble in ethanol and other common organic solvents, but rapidly dissolved in cold aqueous alkalis with hydrolysis to sucrose. Continuous ether-extraction of the acidified (dilute sulphuric acid) hydrolysate afforded a small quantity of dark oil containing resorcinol (fluorescein test) and probably phenol. Analysis of the polymer also supported the presence of some aromatic residues (Found: C, 44·0; H, 4·8%).

With 1% of catalyst (w/w of resorcinol) gelling occurred in about 10 min. With the omission of catalyst and the use of purified reagents ("AnalaR" sucrose; resorcinol recrystallised three times from ethanol–benzene; diphenyl carbonate recrystallised three times from ethanol) in a Pyrex flask no gelling took place in 4 hr. at 135°. Addition of ether precipitated a pinkish solid (101% w/w of sucrose used) consisting almost exclusively of sucrose and its hydrolysis products, as indicated by paper chromatography. A duplicate experiment did not give a gel in 20 hr. at 130°, and the residue remaining from subsequent distillation at 150°/10^{-4} mm. was totally ethanol-soluble.

(b) *In dimethyl sulphoxide, catalysed by soda glass.* Sucrose (14 g.) in warm dimethyl sulphoxide (20 ml.; redistilled from K_2CO_3) was treated with recrystallised diphenyl carbonate (36 g.). The stirred solution was kept at 135° and powdered soda glass (1 g.) added. Gelling occurred suddenly after 5 min. The use of coarsely ground soda glass (1 g.) as the catalyst prolonged the gelling time to 30 min. Pyrex glass (1 g.) caused no gelling in 2 hr., and paper chromatography of the brown syrup precipitated by ether indicated almost complete decomposition to glucose, fructose, and 5-hydroxymethylfurfuraldehyde.

Alkaline Hydrolysis of Cross-linked Poly(sucrose Carbonate).—Polycarbonate gels, prepared by method (b) above but with sodium hydrogen carbonate (0·02 g.) as the catalyst, with varying molar ratios of diphenyl carbonate to sucrose (see Table), were purified and dried as in (a) [$\nu_{max.}$ (C=O) 1760 cm.$^{-1}$ for all samples].

The polymers (*ca.* 2 g., accurately weighed) were hydrolysed at 60° with 2N-sodium hydroxide (100 ml.) for 30 min., and the clear solutions carefully acidified with dilute sulphuric acid. Bromine water was added slowly (shaking) until a faint yellow colour persisted in the aqueous phase. The precipitated 2,4,6-tribromophenol (m. p. 91—93°; mixed m. p 93—95°) was collected (suction), washed with water (50 ml.), and dried at room temperature and pressure over phosphoric oxide. The average number of *O*-phenoxycarbonyl groups per sucrose unit of polymer was calculated from the yield of tribromo-derivative obtained. No correction was made for the slight solubility of tribromophenol (7×10^{-3}% in water at 15°, equivalent to *ca.* 0·008 *O*-phenoxycarbonyl group per 200 ml. of hydrolysate).

Re-extraction of the polymers with aqueous dioxan for a further 8 hr. caused no decrease in the phenol obtained by hydrolysis.

Reaction of Sucrose with 1 *Mol. of Diphenyl Carbonate.*—Sucrose (14·0 g.; dried over H_2SO_4) and diphenyl carbonate (8·76 g., 1 mol.; recryst.) were heated together at 135° in dimethyl sulphoxide (20 ml.) containing sodium hydrogen carbonate (0·02 g.) in the usual way. The solution gradually became more viscous, finally appearing to gel in 6 min. After a further 5 min., the mixture was cooled and transferred to acetone (250 ml.), and the precipitated product collected when granular, triturated with acetone and ether, and dried *in vacuo* (over H_2SO_4) (yield 18·4 g.).

The gelatinous suspension obtained by stirring the solid with water (200 ml.) was centrifuged (2000 rev./min.), giving 4·86 g. of insoluble polycarbonate (A). De-ionisation of the supernatant solution by electrodialysis [21] (B.D.H. "Permaplex" membranes A-20 and C-20; ~250 v) and evaporation *in vacuo* afforded 11·13 g. of crude water-soluble polymers (B). Multiple development paper chromatography [22] of the soluble fraction [four overnight developments with solvent (ii), the paper being dried after each run; spray (*a*)] separated sucrose and at least five other components from the virtually non-mobile high-polymer spot.

[21] Anderson and Wylam, *Chem. and Ind.*, 1956, 191.

[22] Jeanes, Wise, and Dimler, *Analyt. Chem.*, 1951, **23**, 415.

Dialysis (Cellophane membrane) of the water-soluble fraction removed low polymers and a trace of sucrose, leaving soluble *poly*(*sucrose carbonate*) (C), recovered as a brittle resin, insoluble in non-polar solvents, but soluble in water, *NN*-dimethylformamide, and dimethyl sulphoxide, with $[\alpha]_D^{25}$ +70·3° (*c* 2·2 in H_2O), $\nu_{max.}$ (C=O) 1750 cm.$^{-1}$ (Found: C, 42·1; H, 5·4. $[C_{13}H_{20}O_{12}]_n$ requires C, 42·4; H, 5·4%).

Action of Invertase on Soluble Poly(*sucrose carbonate*).—(a) *Polarimetric study.* A solution of the de-ionised, but undialysed, polymer B (2 g.) in water (40 ml.) was treated with B.D.H. invertase concentrate (0·5 ml.), quickly diluted to 50 ml., and kept at 25°. The optical rotation was measured at intervals (see Figure).

A solution of the dialysed polymer C (0·219 g.) and invertase concentrate (0·1 ml.) in water (10 ml.) was similarly examined. The fall in rotation in 24 hr. ($[\alpha]_D^{25}$ $+70{\cdot}3° \longrightarrow +64{\cdot}0°$) was equivalent to the hydrolysis of about 7% of the total sucrose content of the polymer.

(b) *Examination of products.* Dialysed polymer C (0·4 g.) in water (2 ml.) was treated with invertase concentrate (0·1 ml.) and kept 24 hr. at room temperature. This solution, and that from a simultaneous hydrolysis of sucrose (0·02 g.), were examined on paper chromatograms [solvents (i) and (iv); sprays (*a*) and (*b*)]. Fructose, but not glucose, was detected in the polymer hydrolysate whereas both were easily detected in the sucrose hydrolysate.

Subsequent dialysis of the polymer hydrolysate removed fructose, as shown by paper chromatography, leaving a polymer solution that was weakly reducing towards Fehling's reagent. The initial polymer C was non-reducing.

Acid Hydrolysis of Soluble Poly(*sucrose carbonate*).—The invertase hydrolysate (9 ml.) of polymer B, after 21 hr. at 25°, was mixed with concentrated hydrochloric acid (1 ml.) and kept at 25°. The optical rotation was measured at intervals and plotted (see Figure).

Periodate Oxidation of Dialysed Polymer.—Dialysed, dried poly(sucrose carbonate) (0·2046 g.) in water (20 ml.) was treated with 0·1M-sodium metaperiodate (15 ml.), and the solution diluted to 50 ml. with water and kept in the dark at room temperature. After 48 hr. an aliquot part (5 ml.) was removed and the periodate uptake estimated by the potassium iodide–thiosulphate method [23] (Found: 1·97 mol. per sucrose unit). After 3 days, excess of saturated aqueous barium chloride was added to the bulk of the oxidation medium, the mixture made faintly alkaline with saturated aqueous barium hydroxide, and then neutrality was restored with carbon dioxide. The inorganic precipitate was collected, the filtrate evaporated *in vacuo* below 40°, and the residue treated with ethanol (50 ml.). After a further evaporation to remove traces of water, the white solid was extracted at room temperature with absolute ethanol (4 × 50 ml.), and the extracts were filtered and evaporated below 40° to an almost clear syrup (0·23 g.). This was dissolved in water (10 ml.), and treated, in ½ hr., with potassium borohydride (0·5 g.). The solution, after being kept overnight, was diluted to 50 ml. with water and slowly percolated through a column (35 × 2 cm.) of Amberlite IR-120 (H^+) resin. The eluate and column washings (200 ml.) were together evaporated *in vacuo* below 40° to about 10 ml., treated with methanol (50 ml.), and taken almost to dryness. After three further evaporations with methanol, to remove boric acid, a syrup (0·15 g.) remained.

Paper chromatography of the syrup was carried out with dihydroxyacetone, glycerol, erythritol, glyceraldehyde, glycolaldehyde, sucrose, glucose, and fructose as reference compounds, with solvents (i), (iii), and (iv), and sprays (*b*) and (*c*). The following components were detected: glucose (strong), glycerol (strong), dihydroxyacetone (fairly strong), fructose (fairly strong), and erythritol (trace). Whilst glycollaldehyde and glyceraldehyde were not detected, the corresponding standards were only weakly revealed.

*Periodate Oxidation of "Tri-*O*-ethoxycarbonylsucrose."*—The dried derivative (D.S. 3·2; 0·210 g.) was dissolved in warm t-butyl alcohol (10 ml.), cooled, and treated with 0·1M-sodium metaperiodate (15 ml.), followed by water to a volume of 50 ml. The solution was kept in the dark at room temperature for 5 days (uptake 1·08 mol. per mol. of sucrose), then worked up as above except that (i) the residue of barium salts was washed with 50% aqueous t-butyl alcohol in place of water, (ii) borohydride reduction was conducted in 50% aqueous ethanol, and (iii) the resin column was washed before and after use with 50% ethanol. The final syrup (0·104 g.) was chromatographed exactly as before. The same hydrolysis fragments were detected as for the polycarbonate, in approximately the same proportions.

Sucrose itself consumed 2·97 mol. of periodate in 5 days in 20% t-butyl alcohol.

Action of Diethyl Carbonate on Sucrose.—Sucrose (7 g., 1 mol.), diethyl carbonate (10·2 ml.,

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[23] Neumüller and Vasseur, *Arkiv Kemi*, 1953, **5**, 235.

4 mol.), and sodium hydrogen carbonate (0·02 g.) in dimethyl sulphoxide (20 ml.) were stirred under reflux at 130° for 2 hr. The solution was cooled and poured into an excess of ether, and a sample of the syrupy precipitate chromatographed on paper [solvent (iii); spray (*a*)]. Much unchanged sucrose was detected, but strong spots (R_F 0·41 and 0·66) corresponding to the low-substituted esters found previously [2] in " tri-*O*-ethoxycarbonylsucrose " were also revealed. Slow-moving polymeric components were present in traces only.

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