628. *Polyamides Containing Carbohydrate Residues. Part II.*[1] *Benzylidenedioxy-derivatives.*

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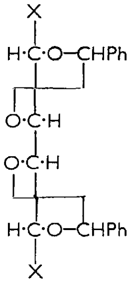
1,6-Diamino-di-*O*-benzylidene-1,6-dideoxy-galactitol and -D-mannitol and di-*O*-benzylidenegalactaric acid have been synthesised. Two benzylidenedioxy-polyamides are described.

In a preceding paper[1] a series of methylenedioxy-polyamides with high viscosities was prepared by interfacial polycondensation. Two benzylidenedioxy-derivatives are now reported.

1,6-Diamino-di-*O*-benzylidene-1,6-dideoxygalactitol was synthesised from 1,6-dichloro-1,6-dideoxygalactitol[2] essentially as described for the di-*O*-methylene[2] and di-*O*-isopropylidene[3] derivatives. Distillation of the diamine in this case was more difficult because of the high boiling point, and only small batches (about 0·5 g.) could be distilled without decomposition. This compound almost certainly has the 2,3:4,5-acetal structure



(I; X = $CH_2{\cdot}NH_2$)

(II; X = CO_2Me)

(I) with two α-*trans*-rings.[4] Attempts to convert the diamine (I) into its dihydrochloride by addition of a small excess of concentrated hydrochloric acid to an ethanolic solution were unsuccessful, loss of benzylidene residues occurring even at 0°.

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[1] Part I, *J.*, 1963, 1208.

[2] Butler and Cummings, *J.*, 1956, 636.

[3] Bird, Black, Dewar, and Hare, *Chem. and Ind.*, 1961, 1077.

[4] Mills, *Adv. Carbohydrate Chem.*, 1955, **10**, 1.

1,6-Diamino-di-*O*-benzylidene-1,6-dideoxy-D-mannitol was synthesised in the same way, zinc chloride and benzaldehyde being used for the complete introduction of benzylidene groups into 1,6-dichloro-1,6-dideoxy-D-mannitol;[5] hydrogen chloride as catalyst failed to give the fully substituted compound. The acetal ring structure of this diamine cannot readily be predicted.[4,6]

Polyamides were prepared from these two diamines by interfacial polycondensation with sebacoyl dichloride. Because of the insolubility of the reagents in water, the procedure had to be modified slightly; the diamine was dissolved in ethanol and converted into its dihydrochloride with the exact amount of 0·1N-hydrochloric acid. Ethanol was removed by distillation and the aqueous solution of the dihydrochloride condensed immediately with the acid chloride in carbon tetrachloride solution, the free diamine being liberated with the required amount of sodium hydroxide. Poly(di-*O*-benzylidene-1,6-dideoxy-1-sebacamidogalactitol), having an inherent viscosity of 0·42, was isolated in 65% yield, and the optically active mannitol polyamide, isolated in 36% yield, had a viscosity of 0·5. These viscosities are about one-half of those of the corresponding methylenedioxy-derivatives.[1]

An attempt was made to prepare 2,3:4,5-di-*O*-benzylidenegalactaroyl dichloride, which could be used as a source of benzylidenedioxy-polyamides by interfacial polycondensation with hexamethylenediamine and other diamines. Dimethyl galactarate[7] was readily converted into the fully substituted dimethyl di-*O*-benzylidenegalactarate, which has probably the 2,3:4,5-acetal structure (II).[4] Saponification of this ester with hot barium hydroxide gave di-*O*-benzylidenegalactaric acid, which crystallised from dioxan with one molecule of solvent; the dioxan was removed at 70°/0·1 mm. to give the pure dibasic acid. Repeated attempts were made to convert this into its diacid chloride by treatment with thionyl chloride, but the compound decomposed during isolation with the liberation of benzaldehyde.

EXPERIMENTAL

General Methods.—Specific rotations were measured at 20° in a 2-dm. tube. M. p.s and polymer-melt temperatures were measured on a Kofler hot-stage microscope. Inherent viscosities, $[\eta_{\text{inh.}} = \ln(\eta_{\text{soln.}}/\eta_{\text{solv.}})/c]$, were determined for solutions in *m*-cresol at 25° at a polymer concentration (c) of 0·5 g. per 100 ml.; results are expressed in dl./g.

2,3:4,5-*Di-*O*-benzylidene*-1,6-*dichloro*-1,6-*dideoxygalactitol.*—Dry hydrogen chloride was passed through an agitated suspension of 1,6-dichloro-1,6-dideoxygalactitol[2] (6·06 g.) in benzaldehyde (42 ml.) for 4 hr. The product was washed with light petroleum (b. p. 40—60°) and water, and recrystallised twice from ethanol (800 ml.), to give 2,3:4,5-*di*-O-*benzylidene*-1,6-*dichloro*-1,6-*dideoxygalactitol* (5·95 g., 54·5%) as needles, m. p. 153—154° (Found: C, 61·2; H, 5·3; Cl, 18·2. $C_{20}H_{20}Cl_2O_4$ requires C, 60·8; H, 5·1; Cl, 17·9%).

1,6-*Diamino*-2,3:4,5-*di*-O-*benzylidene*-1,6-*dideoxygalactitol* (I).—Dibenzylidenedichlorogalactitol (4·28 g.) was treated with dry methanol, saturated with ammonia at 0°, (160 ml.) at 145—150° for 72 hr. in an autoclave. The solution was evaporated to dryness, the solid dissolved in methanol (120 ml.) and water (60 ml.), and chloride removed by passage through a column of Amberlite resin IRA-401(OH$^-$). The eluate was decolorised with charcoal (4 g.) and concentrated, to give the crude diamine (1·835 g.), which was distilled (bath-temp. 250—270°/0·005 mm.) in 0·5-g. batches, giving 1,6-*diamino*-2,3:4,5-*di*-O-*benzylidene*-1,6-*dideoxygalactitol* (1·24 g., 32·2%), n_D^{21} 1·5685, m. p. 102—104° (Found: C, 67·0; H, 6·7; N, 7·7. $C_{20}H_{24}N_2O_4$ requires C, 67·4; H, 6·8; N, 7·9%).

2,3,4,5-*Di*-O-*benzylidene*-1,6-*dichloro*-1,6-*dideoxy*-D-*mannitol.*—1,6-Dichloro-1,6-dideoxy-D-mannitol[5] (1 g.), benzaldehyde (2 ml.), and powdered fused zinc chloride (1 g.) were shaken for 15 min. and then left at 20° for 11 days. The syrupy mixture was extracted with light petroleum (b. p. 40—60°; 5 × 20 ml.) and with water (2 × 20 ml.), and the crude product crystallised from ethanol (20 ml.)–water (6 ml.), to give 2,3,4,5-*di*-O-*benzylidene*-1,6-*dichloro*-1,6-*dideoxy*-D-*mannitol* (451 mg., 24·9%), m. p. 165—166°, $[\alpha]_D$ +66° (*c* 0·5 in $CHCl_3$) (no infrared OH band in

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[5] Haworth, Heath, and Wiggins, *J.*, 1944, 155.
[6] Barker and Bourne, *Adv. Carbohydrate Chem.*, 1952, **7**, 137.
[7] Butler, Lawrance, and Stacey, *J.*, 1958, 740.

Florube mull) (Found: C, 60·8; H, 5·3; Cl, 17·7. $C_{20}H_{20}Cl_2O_4$ requires C, 60·8; H, 5·1; Cl, 17·9%).

*1,6-Diamino-2,3,4,5-di-O-benzylidene-1,6-dideoxy-*D*-mannitol.*—Dibenzylidenedichloromannitol (3·94 g.) was treated with methanolic ammonia as described for the galactitol derivative, and the crude diamine (3 g.) sublimed at 180°/0·005 mm. in 0·5-g. batches to give *1,6-diamino-2,3,4,5-di-O-benzylidene-1,6-dideoxy-*D*-mannitol* (1·56 g., 44%) as yellow needles, m. p. 179—181°, $[\alpha]_D$ +59·3° (*c* 1 in $CHCl_3$) (Found: C, 67·3; H, 7·0; N, 7·8. $C_{20}H_{24}N_2O_4$ requires C, 67·4; H, 6·8; N, 7·9%).

Dimethyl 2,3:4,5-Di-O-benzylidenegalactarate.—A rapid stream of dry hydrogen chloride was passed through an agitated suspension of pure dimethyl galactarate [7] (5 g.) in benzaldehyde (20 ml.) for 5 hr. The solid (5·67 g.) was washed with light petroleum (b. p. 60—80°) and with water, ethanol, and ether, and recrystallised from ethanol (1·5 l.), to give *dimethyl 2,3:4,5-di-O-benzylidenegalactarate* (5·27 g., 60·6%), m. p. 173·5° (Found: C, 63·9; H, 5·4; OMe, 15·1. $C_{22}H_{22}O_8$ requires C, 63·75; H, 5·35; 2OMe, 15·0%) (no infrared OH absorption). A 2% solution in chloroform showed no optical activity.

2,3:4,5-Di-O-benzylidenegalactaric Acid.—Dimethyl dibenzylidenegalactarate (8 g.) was heated for 3 hr. at 100° with barium hydroxide octahydrate (8 g.) in water (1·5 l.), whence a small residue separated; the cold filtrate was diluted with an equal volume of ethanol, and the solution stirred with Amberlite resin IR-120(H^+) to remove barium. The solution was concentrated and the product (6·20 g.) crystallised from dioxan (40 ml.) to yield needles of *2,3:4,5-di-O-benzylidenegalactaric acid* containing one molecule of dioxan (5·98 g., 65·3%) (Found: C, 61·6; H, 5·3%; equiv., 241·3. $C_{20}H_{18}O_8,C_4H_8O_2$ requires C, 60·7; H, 5·5%; equiv., 237·2). The dioxan was removed at 70°/0·1 mm. over phosphoric oxide (Loss: 18·3. $C_{20}H_{18}O_8,C_4H_8O_2$ requires $C_4H_8O_2$; 18·6%). The solvent-free *acid* had m. p. 203—204° (Found: C, 61·8; H, 4·7%; equiv., 192·5. $C_{20}H_{18}O_8$ requires C, 62·2; H, 4·7%; equiv., 193·2).

Attempted Preparation of 2,3:4,5-Di-O-benzylidenegalactaroyl Dichloride.—Dioxan-free dibenzylidenegalactaric acid (1 g.) was refluxed with pure thionyl chloride [8] (25 ml.) for 12 hr., the excess of chloride removed, and the crude product extracted with boiling light petroleum (b. p. 60—80°; 50 ml.) and filtered hot. The filtrate deposited small crystals (418 mg.; m. p. 145—150°), which darkened on drying and contained only 89·2% of the calculated chlorine content. The product failed to produce a polyamide with hexamethylenediamine in the interfacial reaction.

Poly(di-O-benzylidene-1,6-dideoxy-1-sebacamidogalactitol).—Diaminodibenzylidenegalactitol (516 mg., 1·45 mmole) in ethanol (30 ml.) was titrated to pH 6·0 with 0·1N-hydrochloric acid (29 ml.) and concentrated under reduced pressure at 40° to about 20 ml. To this residue at 0° was added a cold solution of sebacoyl dichloride (1·45 mmole) in carbon tetrachloride (30 ml.), followed immediately by 0·5N-sodium hydroxide (11·6 ml.; 5·8 mmole) and the solutions were mixed for 10 min. in a high-speed macerator. Polymer was washed with 0·1N-hydrochloric acid, 0·1N-sodium hydroxide, and water, and purified by dissolution in dimethylformamide (200 ml.) and reprecipitation in water (1·5 l.). The product was finally washed with ethanol and ether and dried over phosphoric oxide (20°/0·5 mm.), to give *poly(di-O-benzylidene-1,6-dideoxy-1-sebacamidogalactitol)* (494 mg., 65·2%), $\eta_{\text{inh.}}$ 0·42, polymer-melt temperature 210—220° [Found: C, 69·5; H, 7·5; N, 5·5. $(C_{30}H_{38}N_2O_6)_n$ requires C, 68·9; H, 7·3; N, 5·4%], soluble in hot dimethylformamide or dimethyl sulphoxide, and in formic acid or *m*-cresol, but insoluble in chloroform.

*Poly(di-O-benzylidene-1,6-dideoxy-1-sebacamido-*D*-mannitol).*—Diaminodibenzylidenemannitol (452 mg.) was condensed with sebacoyl dichloride as described above for the galactitol derivative; the crude product was extracted with boiling ethanol (100 ml.) and filtered hot. The insoluble fraction (241 mg., 36·2%) was *poly(di-O-benzylidene-1,6-dideoxy-1-sebacamido-*D*-mannitol)*, $\eta_{\text{inh.}}$ 0·50, $[\alpha]_D$ +86° (*c* 0·5 in *m*-cresol), polymer-melt temperature 130—140° (Found: C, 69·1; H, 7·7; N, 5·2%). The polymer was soluble in cold chloroform, dimethylformamide, dimethyl sulphoxide, formic acid, and *m*-cresol.

This research is supported with funds provided by the U.S. Department of Agriculture. We thank Dr. E. E. Percival for advice.

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[*Received, December 13th, 1962.*]

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[8] Cottle, *J. Amer. Chem. Soc.*, 1946, **68**, 1380.