

95. *Some Derivatives of Simple Carbohydrates Containing Unsaturated Substituents.**

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In this paper several acrylates and methacrylates of simple six-carbon chain carbohydrates are described and are shown to polymerise very readily to give transparent colourless resins of the thermosetting type. Acetal derivatives from hexahydric alcohols with unsaturated aldehydes, and a diallyl ester of a saccharic acid derivative have also been prepared but none of these undergoes polymerisation.

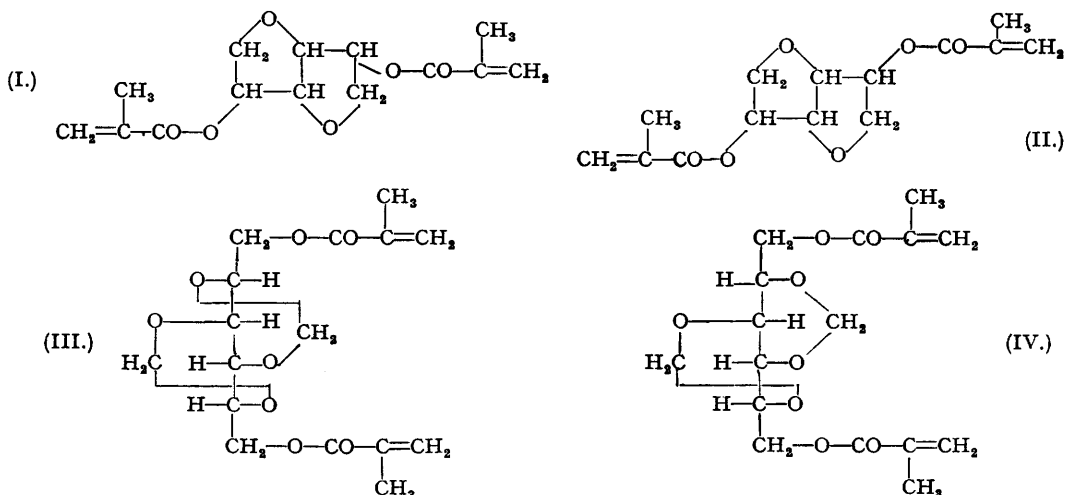
LITTLE success seems to have attended earlier endeavours to utilise carbohydrates as constituents of synthetic resins, and few appropriate derivatives of carbohydrates are known which can undergo polymerisation readily. Cellulose, starch, and sucrose, because of their great abundance, would appear to provide opportunities for this kind of investigation. Sucrose is the chief source of the initial material employed in this investigation; it is readily hydrogenated to give high yields of sorbitol and mannitol.

We have found that 1 : 6-diamino 2 : 4-3 : 5-dimethylene mannitol (Haworth, Heath, and Wiggins, *J.*, 1944, 155) and 2 : 4-3 : 5-dimethylene gluco- and *l*-ido-saccharic acids (Haworth, Jones, Stacey, and Wiggins, *J.*, 1944, 61), when appropriately mixed together or with other dibasic acids or diamines respectively, gave polyamides which were not sufficiently thermostable to compare with products of the Nylon type. In addition,

* Patent applied for.

sorbitol and mannitol partly substituted with formaldehyde residues, *e.g.*, 2 : 4-3 : 5-dimethylene sorbitol and mannitol (Haworth and Wiggins, *J.*, 1944, 58), were obtained with the object of forming polyesters with suitable dibasic acids, but again no useful products were obtained.

In the work herein reported we have sought to introduce unsaturated acyl groups into the sugar or polyhydric alcohol derivative, and have used acrylyl and methacrylyl* residues and have obtained polyacrylyl or methacrylyl sugar or sugar alcohol derivatives. As suitable compounds derived from sugar alcohols we investigated the dianhydrides of sorbitol and mannitol and the dimethylene and dibenzylidene derivatives of the hexahydric alcohols. Methods for preparing dianhydro mannitol and sorbitol have been described and their constitutions, as 1 : 4-3 : 6-dianhydrides of the hexitols, were determined by Wiggins (*J.*, 1945, 4) and Montgomery and Wiggins (this vol., p. 390). Since these substances were shown to have extremely stable structures they appear to be admirably suited for the purpose in view. On treating each substance, dissolved in sodium hydroxide solution, with *methacrylyl chloride* the 2 : 5-dimethacrylyl derivatives were precipitated. The derivative of the anhydride of mannitol, *i.e.* 2 : 5-dimethacrylyl 1 : 4-3 : 6-dianhydro mannitol (I), was obtained in crystalline form, whereas 2 : 5-dimethacrylyl 1 : 4-3 : 6-dianhydro sorbitol (II) was a liquid. Both compounds, however, were found to polymerise easily, and furnished hard, colourless, infusible and insoluble resins. The polymerisation was simply effected by heating the substances for a few minutes at 80°



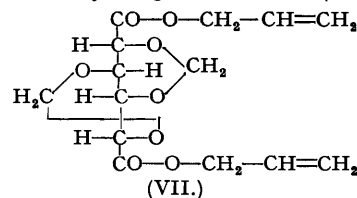
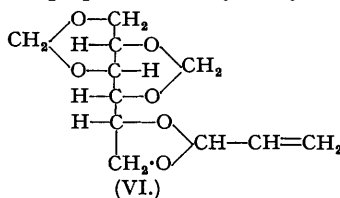
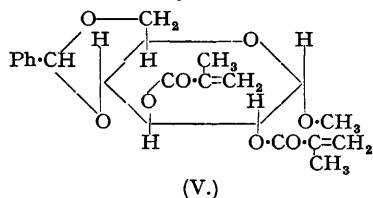
without the addition of peroxides. Apparently homogeneous co-polymers could also be formed by heating with methyl methacrylate in the presence of benzoyl peroxide. The effect of the added methacrylyl derivative of dianhydro hexitol was to harden methyl methacrylate polymers and to increase the rate of polymerisation. The methacrylate could also be made in pyridine solution if methacrylic anhydride (prepared according to U.S.P. 2,143,924, 1939) was used as the acylating agent, although by this method the yields were generally slightly lower. 2 : 5-Diacrylyl 1 : 4-3 : 6-dianhydro sorbitol was also obtained in crystalline form using sodium hydroxide and acrylyl chloride [prepared by Kohler's modification (*Amer. Chem. J.*, 1909, 42, 380) of Moureu's method (*Ann. Chim. Phys.*, 1894, 2, 161)]. This sorbitol derivative polymerised at 80° but the rate of polymerisation was rather slower than in the case of the corresponding methacrylyl derivative.

For effecting acrylylation and methacrylylation of derivatives of mannitol and sorbitol themselves the most useful starting materials were those in which the four central hydroxyl groups of the hexitol were substituted in acetal formation with formaldehyde. Other aldehydes might also be used but the formaldehyde compounds were found to be the most stable. Thus 1 : 6-dimethacrylyl 2 : 4-3 : 5-dimethylene mannitol (III), 1 : 6-diacrylyl 2 : 4-3 : 5-dimethylene mannitol, and 1 : 6-dimethacrylyl 2 : 4-3 : 5-dimethylene sorbitol (IV) were obtained, all in crystalline form. Similarly from a *dibenzylidene sorbitol* (prepared by benzoylation of the 1 : 6-dibenzoyl dibenzylidene sorbitol of Vargha, *Ber.*, 1935, 68, 1377) 1 : 6-dimethacrylyl 2 : 3 : 4 : 5-dibenzylidene sorbitol was obtained. All these compounds on being heated just above their melting points polymerised extremely easily without the use of catalysts to form hard, transparent, infusible, insoluble resins. One sugar derivative, namely 4 : 6-benzylidene α -methylglucoside, has been subjected to methacrylylation and crystalline 2 : 3-dimethacrylyl 4 : 6-benzylidene α -methylglucoside (V) obtained. This substance rapidly polymerised when heated above its melting point.

Acetal derivatives of mannitol and sorbitol have also been made with aldehydes containing unsaturated linkages in the anticipation that these might polymerise. For this purpose acraldehyde and cinnamaldehyde were used. 1 : 3-2 : 4-Dimethylene sorbitol (Bourne and Wiggins, *J.*, 1944, 517) was treated with acraldehyde in the presence of zinc chloride and a small yield of 1 : 3-2 : 4-dimethylene 5 : 6-acrylidene sorbitol (VI) was obtained.

* Since this work was completed, Treadway and Yanovsky (*J. Amer. Chem. Soc.*, 1945, 67, 1038) have reported the preparation of the methacrylates of glucose, dextrin, and starch.

Again, mannitol on treatment with cinnamaldehyde gave *tricinnamylidene mannitol*. Finally an unsaturated ester of a dimethylene saccharic acid was prepared, namely *diallyl 2 : 4-3 : 5-dimethylene glucosaccharate* (VII).



None of these substances, however, showed any tendency to polymerise in the presence of benzoyl peroxide as catalyst.

EXPERIMENTAL.

Methacrylyl Chloride.—To dry potassium methacrylate (62 g.), prepared by hydrolysis of methyl methacrylate by aqueous-alcoholic potash, phosphorus oxychloride (38 g.) was slowly added, with good stirring (compare Moureu *loc. cit.*). After the addition the mixture was heated on a boiling water-bath for 1 hour and thereafter the product was distilled on an oil-bath. The crude product was purified by twice distilling over dry potassium methacrylate (1–2 g. portions). *Methacrylyl chloride* had b. p. 95° and was obtained in 64.0% yield as an extremely lachrymatory mobile liquid (Found : C, 45.8; H, 4.9; Cl, 33.3. C_4H_5OCl requires C, 45.9; H, 4.8; Cl, 33.9%).

Methacrylic Anhydride.—This was obtained according to the procedure given by Rubenstein in U.S.P. 2,143,924 (1939) in 80% yield. The only modification employed was in the use of potassium methacrylate instead of the sodium salt.

Acrylyl Chloride.—This was prepared from sodium acrylate (70 g.) and phosphorus oxychloride (33.6 c.c.) by Moureu's method (as modified by Kohler, *loc. cit.*). The yield was 60% of the theoretical and the product boiled at 76–77° after purification by distillation over anhydrous sodium acrylate.

2 : 5-Dimethacrylyl 1 : 4-3 : 6-Dianhydro Mannitol.—(a) Dianhydro mannitol (4.0 g.) was dissolved in sodium hydroxide (5N, 20 c.c.) and methacrylyl chloride carefully added at 0° with vigorous shaking. The crystalline product which rapidly separated was collected, washed with water, and dried in a vacuum. It recrystallised from ligroin (b. p. 100–120°) in colourless flakes (yield, 2.6 g.; 33% of the theoretical), m. p. 67°, $[\alpha]_D^{20} + 176.6^\circ$ in chloroform (*c*, 0.586) (Found : C, 59.7; H, 6.4. $C_{14}H_{18}O_8$ requires C, 59.6; H, 6.4%).

Some loss in yield is accounted for by the fact that polymerisation occurs during the initial reaction and during the recrystallisation of the product, since about 15% of the crude product remains insoluble in ligroin.

(b) To a solution of dianhydro mannitol (2.0 g.) in dry pyridine (10 c.c.) was added methacrylic anhydride (8.4 g.). After keeping for 24 hours at room temperature the mixture was poured into ice-water, and the crystalline product was filtered off, washed with water, dried in a vacuum, and recrystallised from ligroin (b. p. 100–120°) (yield, 1.1 g.; 28% of the theoretical). It had m. p. 67°, and was identical with the material obtained above.

When 2 : 5-dimethacrylyl 1 : 4-3 : 6-dianhydro mannitol was heated above its m. p. (*i.e.*, at 80°) for only a few minutes, without the addition of benzoyl peroxide, polymerisation took place and a hard colourless transparent resin was obtained. Polymerisation also took place when the substance was heated with twice its weight of methyl methacrylate, but here benzoyl peroxide was necessary. After 1½ hours' heating at 100° an apparently homogeneous hard colourless resin was obtained.

2 : 5-Dimethacrylyl 1 : 4-3 : 6-Dianhydro Sorbitol.—Dianhydro sorbitol (5 g.) was dissolved in sodium hydroxide (5N, 20 c.c.), cooled to 0° and methacrylyl chloride added slowly. After being shaken for a few minutes, the reaction mixture was exhaustively extracted with ether, the ether extract dried ($MgSO_4$), and the ether removed. A thin colourless liquid remained which failed to crystallise (yield, 4 g.; 41% of the theoretical), $[\alpha]_D^{20} + 78.2^\circ$ in chloroform (*c*, 1.74) (Found : C, 59.5; H, 6.4. $C_{14}H_{18}O_8$ requires C, 59.6; H, 6.4%). Distillation under reduced pressure over quinol at 190° (bath temperature) could only be accomplished with large losses. The sorbitol compound polymerised to a hard colourless resin on keeping at room temperature for three days. It also polymerised very rapidly when heated on a boiling water-bath, but the product was a gel which did not harden on prolonged heating. Similarly polymerisation in toluene solution took place with precipitation of a gelatinous polymer, without there being any obvious increase in the viscosity of the solution. When 2 parts of the liquid dimethacrylyl dianhydro sorbitol were dissolved in 3 parts of methyl methacrylate and the solution heated at 100° for 15 minutes in the presence of benzoyl peroxide a hard infusible glass was obtained. All these resins were insoluble in organic solvents.

2 : 5-Diacrylyl Dianhydro Sorbitol.—Dianhydro sorbitol (2 g.) was dissolved in sodium hydroxide solution (5N, 20 c.c.), cooled in ice, and acrylyl chloride added slowly with shaking. The oily layer which rapidly separated was extracted with ether, the ether extract dried ($MgSO_4$), and the ether removed leaving a crystalline residue. After being recrystallised from ligroin (b. p. 100–120°) shining flakes of 2 : 5-diacrylyl dianhydro sorbitol were obtained (yield, 0.9 g.; 26% of the theoretical), m. p. 57°, $[\alpha]_D^{20} + 130.9^\circ$ in chloroform (*c*, 1.054) (Found : C, 56.8; H, 5.5. $C_{12}H_{14}O_8$ requires C, 56.6; H, 5.6%).

This substance polymerised to a hard transparent colourless resin when heated for 40 minutes on a boiling water-bath. Copolymerisation with an equal weight of methyl methacrylate to a hard durable resin took place in the presence of benzoyl peroxide within 2½ hours at 100°.

1 : 6-Dimethacrylyl 2 : 4-3 : 5-Dimethylene Sorbitol.—Dimethylene sorbitol (0.4 g.) prepared by the method of Haworth and Wiggins (*loc. cit.*) was dissolved in sodium hydroxide solution (10 c.c. of 5N) and a slight excess of methacrylyl chloride (0.5 g.) added at 0° with vigorous shaking. Colourless crystals rapidly separated, and were collected and recrystallised from ethyl alcohol from which the compound was obtained in fine needles, m. p. 90°, $[\alpha]_D^{18} + 93.2^\circ$ in chloroform (*c*, 2.236) (Found : C, 55.8; H, 6.6. $C_{16}H_{22}O_8$ requires C, 56.1; H, 6.5%).

This substance polymerised on heating for a few minutes above its m. p. to a hard colourless resin.

1 : 6-Dimethacrylyl 2 : 4-3 : 5-Dimethylene Mannitol.—(a) Dimethylene mannitol (4 g.) was treated with methacrylyl chloride (4.5 g.) in sodium hydroxide solution (5N, 20 c.c.) as in the previous preparation. The product, recrystallised from ligroin (b. p. 100–120°), formed prismatic crystals (yield, 4.3 g.; 65% of the theoretical), m. p. 85°, $[\alpha]_D^{18} + 88.7^\circ$ in chloroform (*c*, 1.065) (Found : C, 56.1; H, 6.3. $C_{16}H_{22}O_8$ requires C, 56.1; H, 6.5%).

(b) Dimethylene mannitol (2 g.) dissolved in dry pyridine (40 c.c.) was treated with methacrylic anhydride (6 g.; 100% excess) and the mixture set aside for 24 hours at room temperature. On pouring into water a solid product separated which recrystallised from ligroin (b. p. 100–120°) and was identical with the 1 : 6-dimethacrylyl 2 : 4-3 : 5-dimethylene mannitol obtained above.

During the recrystallisation of the crude material from these experiments an insoluble solid was always obtained which could not be melted and was doubtless polymerised material (Found: C, 56.4; H, 6.5. $(C_{16}H_{22}O_8)_n$ requires C, 56.1; H, 6.5%). Dimethacrylyl dimethylene mannitol polymerised extremely quickly on heating above its m. p. After 2 minutes' heating at 90° the melt sets to a hard, transparent, infusible resin. In appearance the resin resembles polymerised methyl methacrylate but it is much harder and quite insoluble in organic solvents. It was only decomposed slowly on boiling with concentrated mineral acid. Apparently no polymerisation occurred on heating the monomer in toluene solution until the toluene had been removed by evaporation. Homogeneous co-polymerisation occurred with an equal weight of methyl methacrylate in the presence of benzoyl peroxide. The product, a hard infusible glass, was insoluble in all solvents.

1 : 6-Diacrylyl 2 : 4-3 : 5-Dimethylene Mannitol.—To a solution of 2 : 4-3 : 5-dimethylene mannitol in 5*N*-sodium hydroxide (20 c.c.) cooled to 0° there was added, slowly and with vigorous shaking, acrylyl chloride (2 g.). A thick oily liquid separated which slowly solidified. Recrystallisation from ligroin (b. p. 100—120°) gave 1 : 6-diacrylyl dimethylene mannitol (1.1 g.; 36.4% of the theoretical), m. p. 86°, $[\alpha]_D^{25} + 89.8^\circ$ in chloroform (*c*, 0.512) (Found: C, 53.4; H, 5.8. $C_{16}H_{18}O_8$ requires C, 53.4; H, 5.8%). The pure product polymerised on heating just above its m. p. to form first a soft gel, then a brittle transparent gel. The polymerisation was complete in 10 minutes without the addition of a catalyst. When an equal weight of methyl methacrylate was added to the diacrylyl dimethylene mannitol and the mixture heated on the boiling water-bath in a sealed tube in the presence of benzoyl peroxide a polymer was obtained which did not appear to be homogeneous.

2 : 4-3 : 5-Dibenzylidene Sorbitol.—1 : 6-Dibenzoyl dibenzylidene sorbitol (v. Vargha, *loc. cit.*) (5 g.) (m. p. 208°) was shaken overnight with dry methyl alcohol containing sodium (50 mg.). Complete solution occurred and on evaporation under reduced pressure a solid product was obtained which after recrystallisation from acetone–ligroin had m. p. 208° (the m. p. was depressed in admixture with starting material), $[\alpha]_D - 14.8^\circ$ in acetone (*c*, 0.945). Yield, 2.8 g. (Found: C, 66.6; H, 6.2. $C_{26}H_{32}O_8$ requires C, 67.0; H, 6.1%).

1 : 6-Dimethacrylyl 2 : 3 : 4 : 5-Dibenzylidene Sorbitol.—2 : 3 : 4 : 5-Dibenzylidene sorbitol (2 g.) was dissolved in dry pyridine (40 c.c.) and methacrylic anhydride (3.5 g.) added. The mixture was kept at room temperature for 24 hours. On pouring into ice-water a precipitate was obtained which was collected and recrystallised from ligroin (b. p. 100—120°). The product, 1 : 6-dimethacrylyl 2 : 3 : 4 : 5-dibenzylidene sorbitol, had m. p. 135° and $[\alpha]_D^{25} - 26.2^\circ$ in chloroform (*c*, 0.535) (Found: C, 68.2; H, 6.1. $C_{28}H_{36}O_8$ requires C, 68.0; H, 6.1%).

On heating to 150° the crystals melted and rapidly polymerised to a hard insoluble resin.

2 : 3-Dimethacrylyl 4 : 6-Benzylidene α -Methylglucoside.—4 : 6-Benzylidene α -methylglucoside (2 g.), dissolved in dry pyridine, was treated with methacrylic anhydride (4.4 g.) and the mixture set aside for 24 hours. Thereafter it was poured into ice-water, and the precipitate was collected, washed with water, dried, and recrystallised from ligroin. The compound had m. p. 181°, $[\alpha]_D^{25} + 90.4^\circ$ in chloroform (*c*, 0.509) (Found: C, 62.8; H, 6.4. $C_{22}H_{28}O_8$ requires C, 63.1; H, 6.3%). Polymerisation occurred as soon as the compound melted, yielding a hard, transparent glass. The methacrylyl residues in this substance could be removed by treatment with alcoholic sodium methoxide at room temperature, the original 4 : 6-benzylidene α -methylglucoside being isolated.

1 : 3-2 : 4-Dimethylene 5 : 6-Acrylydene Sorbitol.—A mixture of dimethylene sorbitol (1.5 g.) (Bourne and Wiggins, *loc. cit.*), zinc chloride (1.5 g.), and acraldehyde (20 c.c.) was shaken for 5 hours. The solution obtained was poured into a ligroin–water mixture and a solid product separated. This was recrystallised several times from ethyl alcohol (yield, 0.6 g.; 32% of the theoretical), m. p. 160, $[\alpha]_D^{25} + 280.5^\circ$ in chloroform (*c*, 0.82) (Found: C, 54.5; H, 6.6. $C_{11}H_{16}O_6$ requires C, 54.1; H, 6.6%).

Attempts to polymerise this substance with or without benzoyl peroxide were unsuccessful.

Tricinnylamylidene Mannitol.—Mannitol (5 g.), zinc chloride (5 g.), and cinnamaldehyde (30 c.c.) were shaken together for 3 days, and the resulting solution poured into a water–ligroin mixture. The syrup which separated was washed with water and triturated with alcohol; crystallisation then took place. On being recrystallised from alcohol *tricinnylamylidene mannitol* separated in fine needles, m. p. 209°. Yield, 1.6 g.; 12% of the theoretical, $[\alpha]_D^{25} - 36.3^\circ$ in chloroform (*c*, 1.048) (Found: C, 75.3; H, 6.0. $C_{33}H_{32}O_8$ requires C, 75.5; H, 6.1%).

Attempts to polymerise this substance by heating in a sealed tube at 235° in the presence of benzoyl peroxide failed.

Diallyl 2 : 4-3 : 5-Dimethylene Glucosaccharate.—A solution of dimethylene glucosaccharic acid (1 g.) (Haworth, Jones, Stacey, and Wiggins, *loc. cit.*) in 1% allyl alcoholic hydrogen chloride (5 c.c.) was boiled for 6 hours. Thereafter it was neutralised with silver carbonate, the solution filtered, the residue washed with acetone, and the combined filtrates decolourised with animal charcoal and evaporated to dryness. The syrup obtained crystallised on trituration with alcohol. After being recrystallised from ether–ligroin the diallyl ester of 2 : 4-3 : 5-dimethylene glucosaccharic acid separated in fine needles. Yield, 0.75 g., m. p. 60°, $[\alpha]_D + 65.0$ in chloroform (*c*, 0.40) (Found: C, 53.9; H, 6.0. $C_{14}H_{18}O_8$ requires C, 53.5; H, 5.8%).

This product could not be polymerised on heating at 100° for 12 hours.

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