112. *Dithiols. Part VI. Ethers of 2 : 3-Dimercaptopropanol with Mannitol and Sorbitol.*

By Peter Bladon and L. N. Owen.

A description is given of experiments directed towards the synthesis of the following water-soluble ethers of "BAL" (2 : 3-dimercaptopropanol): 1- and 3-(2 : 3-dimercaptopropyl) mannitol; 6-(2 : 3-dimercaptopropyl) sorbitol; and 2-(2 : 3-*dimercaptopropyl*) 1 : 4-3 : 6-*di-anhydromannitol*. The *acetyl* derivatives were obtained in each case.

In Part II of this series (Evans and Owen, *J.*, 1949, 244), the preparations of the α- and β-glyceryl ethers of "BAL" (2 : 3-dimercaptopropanol) were described. This work has now been extended to the synthesis of compounds in which the hydroxyl group of "BAL" is etherified by one of the hydroxyl groups of mannitol or sorbitol. The general method was the same as in the earlier work, and involved the preparation of the corresponding fully acetylated allyl ethers. These were made by three general methods:

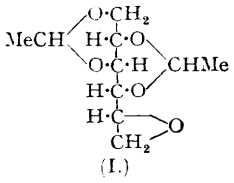
(*a*) Direct allylation of a suitably protected derivative of the hexitol with allyl bromide in the presence of sodium hydroxide. This method has been studied by Yanovsky and his co-workers (*J. Amer. Chem. Soc.*, 1944, **66**, 1625; 1945, **67**, 46), who applied it to the complete allylation of carbohydrates. In the present work, it was necessary to allylate only one of the two hydroxyl groups usually available in the protected hexitols, and the procedure adopted was therefore the addition of allyl bromide to a solution of the hexitol derivative in concentrated aqueous sodium hydroxide.

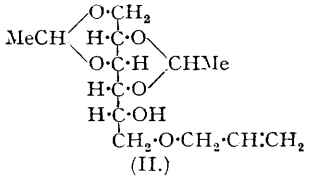
(*b*) Reaction of the sodium derivative of the hydroxy-compound (prepared by treatment with sodium in liquid ammonia) with allyl bromide.

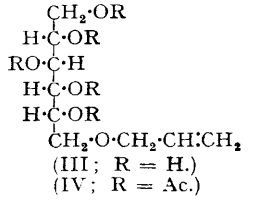
(*c*) Ring-opening of an ethylene oxide anhydro-compound with sodium allyl oxide in allyl alcohol. In the case of terminal epoxides, ring opening proceeds mainly in such a way that the allyloxy-group becomes attached to the terminal carbon atom (cf. the analogous case of ring opening with sodium methoxide, Vargha and Puskás, *Ber.*, 1943, **76**, 859). No Walden inversion occurs, and the product has the configuration of the initial epoxide. With a non-terminal epoxide, the ring opening can occur in two ways, and, since Walden inversion takes place in both cases, neither of the two products has the configuration of the initial epoxide.

The allyl ethers were then subjected to acid hydrolysis to remove the protecting groups (*iso*propylidene or ethylidene), and then fully acetylated, the products being treated with bromine in carbon tetrachloride solution, to yield the dibromopropyl ethers. These compounds, on treatment with potassium thiolacetate in boiling ethanol, gave the corresponding bisthiol-acetates. Deacetylation of these was carried out with either barium methoxide or methanolic hydrogen chloride.

The starting material for the preparation of the 6-sorbitol ether of 2 : 3-dimercaptopropanol was 1 : 3-2 : 4-diethylidene sorbitol (Appel, *J.*, 1935, 425; Hockett and Nickerson, *J. Amer. Chem. Soc.*, 1947, **69**, 850). Attempts at the direct allylation of this compound with allyl


(I.)


(II.)

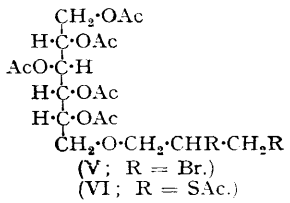

(III; R = H.)
(IV; R = Ac.)

bromide and alkali, aimed at the formation of a monoallyl derivative, gave mixtures of mono- and di-allyl compounds. Accordingly, the route *via* the anhydro-compound was used. 1 : 3-2 : 4-Diethylidene 5 : 6-anhydrosorbitol (I) was prepared by the method of Vargha and Puskás (*loc. cit.*) (see also Sullivan, *J. Amer. Chem. Soc.*, 1946, **67**, 837; Wiggins, *J.*, 1946, 388). An improved yield (93%) was obtained in the conversion of the intermediate 6-tosyl compound into the anhydro-compound. It was also possible to avoid isolation of the tosyl derivative by treatment of the crude syrup with sodium methoxide, and to isolate the anhydro-compound by sublimation, with little alteration in the overall yield.

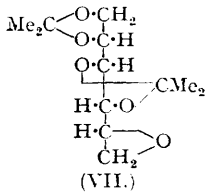
Ring opening of (I) with sodium allyl oxide in allyl alcohol at 100° gave 1 : 3-2 : 4-*diethylidene* 6-*allyl sorbitol* (II). The crude 6-allyl sorbitol (III) obtained by removal of the ethylidene

residues by acid hydrolysis was a syrup, which was acetylated to give *penta-acetyl* 6-*allyl sorbitol* (IV) as a liquid which could be distilled in a high vacuum.

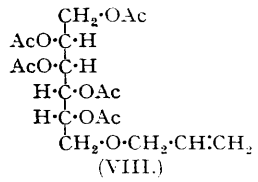
Addition of bromine to this compound gave *penta-acetyl* 6-(2 : 3-*dibromopropyl*) *sorbitol* (V), which, on reaction with potassium thiolacetate in boiling ethanol furnished *hepta-acetyl* 6-(2 : 3-*dimercaptopropyl*) *sorbitol* (VI). Deacetylation with barium methoxide furnished a crude barium salt of the dithiol, but, as previously found with the barium salt of dimercaptopropylglucoside (cf. Evans and Owen, *J.*, 1949, 244), this could not be purified.



(V; R = Br.)
(VI; R = SAc.)

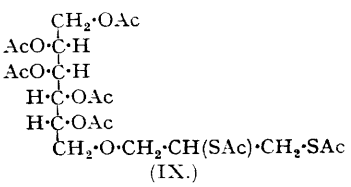


(VII.)

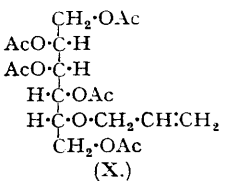


(VIII.)

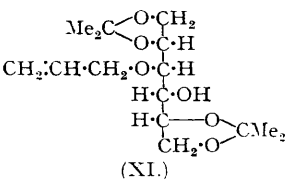
For the preparation of 2 : 3-dimercaptopropyl 1(or 6)-mannitol ether, 1 : 2-3 : 4-di*iso*propylidene mannitol was used (Wiggins, *J.*, 1946, 13); this was converted into 1 : 2-3 : 4-di-*iso*propylidene 5 : 6-anhydromannitol (VII) by a modification of the method of Wiggins (*J.*, 1946, 388), the intermediate 6-tosyl compound not being isolated, but treated directly, in the crude state, with sodium methoxide; the anhydro-compound was then purified by sublimation. Treatment of (VII) with sodium allyl oxide in boiling allyl alcohol gave 6-*allyl* 1 : 2-3 : 4-*di*-iso*propylidene mannitol*, converted by acid hydrolysis into crystalline 1(or 6)-*allyl mannitol*, acetylation of which gave the solid *penta-acetyl* derivative (VIII). With bromine, this gave *penta-acetyl* 1-(2 : 3-*dibromopropyl*) *mannitol* and thence, with potassium thiolacetate, *hepta-acetyl* 1-(2 : 3-*dimercaptopropyl*) *mannitol* (IX) was obtained. Deacetylation with barium methoxide gave a crude barium salt.



(IX.)



(X.)



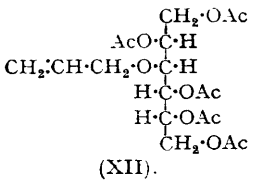
(XI.)

An attempt was made to prepare the above 1-allyl mannitol by direct allylation of 1 : 2-3 : 4-di*iso*propylidene mannitol with a limited amount of allyl bromide and excess alkali. Removal of the *iso*propylidene residues from the product by acid hydrolysis gave a syrup from which 1-allyl mannitol was obtained in small yield. Acetylation of the material remaining in the mother-liquors gave a syrupy product, and determination of the acetyl content and of the unsaturation showed that this was a mixture of mono- and di-allyl compounds. On long storage, crystals separated, and after purification these were found to have the analysis expected for a penta-acetyl monoallyl mannitol. The material was not identical with penta-acetyl 1-allyl mannitol (VIII), and must therefore be *penta-acetyl* 2(or 5)-*allyl mannitol* (X).

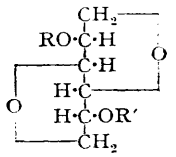
For the projected preparation of 3-(2 : 3-dimercaptopropyl) mannitol, the starting material was 1 : 2-5 : 6-di*iso*propylidene mannitol (Baer, *J. Amer. Chem. Soc.*, 1945, **67**, 338). This was allylated with 1·4 moles of allyl bromide and excess of alkali, to give 3-*allyl* 1 : 2-5 : 6-*di*iso-*propylidene mannitol* (XI). Monoallylation in this case is facilitated by the fact that only one monoallyl derivative is possible, since the 3- and the 4-position in mannitol are identical. Acid hydrolysis of (XI) gave crystalline 3-allyl mannitol, the properties of which agreed well with those given by Wrigley and Yanovsky (*J. Amer. Chem. Soc.*, 1948, **70**, 2194) who obtained it as a by-product in the preparation of 3 : 4-diallyl mannitol. It was converted into the *penta-acetyl* derivative (XII) and thence into *penta-acetyl* 3-(2 : 3-*dibromopropyl*) *mannitol*. The corresponding bisthiolacetate was not obtained pure.

The starting material for the preparation of the 2 : 3-dimercaptopropyl ether of 1 : 4-3 : 6-dianhydromannitol was 1 : 4-3 : 6-dianhydromannitol (XIII) itself, which was prepared from mannitol by the methods of Wiggins (*J.*, 1945, 5) and of Bladon and Owen (preceding paper). Attempts at the direct monoallylation of this compound, with allyl bromide and excess of alkali, all yielded mainly the diallyl compound. The method which was finally used involved conversion

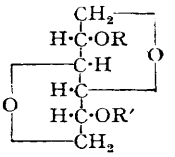
of the dianhydromannitol into its monosodium derivative by treatment with sodium in liquid ammonia, and refluxing of the dry sodium salt with excess of allyl bromide in benzene. A mixture of mono- and di-allyl compounds again resulted, but the proportion of monoallyl compound was considerably higher. The mixture was heated with phthalic anhydride in pyridine (method of Levene and Mikeska, *J. Biol. Chem.*, 1927, **75**, 587), and the reaction product was treated with aqueous sodium carbonate solution; the alkali-insoluble portion consisted of 2 : 5-diallyl 1 : 4-3 : 6-dianhydromannitol, whilst the alkali-soluble portion, on acidification, gave solid 2-*allyl* 1 : 4-3 : 6-*dianhydromannitol* 5-(*hydrogen phthalate*) (XIV). The diallyl compound had properties agreeing with those described by Gregory and Wiggins (*J.*, 1947, 1405). The hydrogen phthalate on hydrolysis gave 2-*allyl* 1 : 4-3 : 6-*dianhydromannitol* (XV) as a liquid,



(XII).



(XIII; R = H, R′ = H.)
(XIV; R = $CH_2{\cdot}CH{:}CH_2$, R′ = $CO{\cdot}C_6H_4{\cdot}CO_2H$.)
(XV; R = $CH_2{\cdot}CH{:}CH_2$, R′ = H.)
[XVI; R = $CH_2{\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc$, R′ = Ac.]
[XVII; R = $CH_2{\cdot}CH(SH){\cdot}CH_2{\cdot}SH$, R′ = H.]



(XVIII; R = R′ = H.)
(XIX; R = $CH_2{\cdot}CH{:}CH_2$, R′ = H.)
(XX; R = H, R′ = $CH_2{\cdot}CH{:}CH_2$.)

only slightly more viscous than the diallyl compound and of almost identical boiling point. Acetylation of (XV) gave the *acetyl* derivative, which readily took up bromine in carbon tetrachloride solution to give 5-*acetyl* 2-(2 : 3-*dibromopropyl*) 1 : 4-3 : 6-*dianhydromannitol*; treatment of this with potassium thiolacetate in boiling alcohol gave *triacetyl* 2-(2 : 3-*dimercaptopropyl*) 1 : 4-3 : 6-*dianhydromannitol* (XVI). Finally, almost pure 2-(2 : 3-*dimercaptopropyl*) 1 : 4-3 : 6-*dianhydromannitol* (XVII) was obtained by deacetylation of the thiolacetate with methanolic hydrogen chloride. The free dithiol was a viscid liquid, readily soluble in water.

The analogous allylation of the monosodium derivative of 1 : 4-3 : 6-dianhydrosorbitol (XVIII) (Montgomery and Wiggins, *J.*, 1946, 390) gave, by use of the hydrogen phthalate method of separation, 2 : 5-diallyl 1 : 4-3 : 6-dianhydrosorbitol (Gregory and Wiggins, *loc. cit.*) and a liquid which was probably a mixture of the isomeric 2- (XIX) and 5-allyl 1 : 4-3 : 6-dianhydrosorbitol (XX); this mixture yielded a mixture of the corresponding acetyl derivatives on acetylation. Since the two isomers could not be separated, the synthesis was not carried beyond this stage.

Experimental.

(Light absorptions, in ethanol, were determined by Dr. E. A. Braude.)

1 : 3-2 : 4-*Diethylidene Sorbitol*.—Appel's method of preparation (*J.*, 1935, 425) was slightly modified and applied to sorbitol (500 g.), paraldehyde (500 c.c.), and concentrated hydrochloric acid (170 c.c.). After 8 hours' stirring, the mixture was extracted twice with chloroform (300 c.c., 100 c.c.), and the extracts were washed with 200-c.c. portions of water, 10% aqueous sodium hydroxide (twice), and with water again, and dried ($CaCl_2$). The chloroform and most of the excess of paraldehyde were removed by distillation under reduced pressure. The residual syrup was heated with acetic acid (400 c.c.) and water (400 c.c.) on the steam-bath under reflux and under reduced pressure (*ca.* 150 mm.) for 2 hours, the liberated acetaldehyde being removed by a current of air drawn through a capillary leak. The solution was concentrated under reduced pressure until solid began to separate; dilution with water then precipitated triethylidene mannitol (30—40 g.), m. p. 165—167° (after recrystallisation from ethanol), derived from mannitol present as impurity in commercial sorbitol (cf. Bourne and Wiggins, *J.*, 1948, 1933). Evaporation of the aqueous solution gave a syrup, which was taken up in methanol (250 c.c.), and treated with ether (100 c.c.) and light petroleum (b. p. 40—60°) (50 c.c.). 1 : 3-2 : 4-Diethylidene sorbitol crystallised as a fine powder when the solution was kept at 0° for a few days; yield, 120—170 g.; m. p. 210—214°.

Allylation of 1 : 3-2 : 4-*Diethylidene Sorbitol*.—A mixture of the diethylidene sorbitol (23·5 g., 0·1 mol.), acetone (105 c.c.), sodium hydroxide (32 g.), and water (82 g.) was stirred vigorously in a 1-l. 3-necked flask, fitted with mercury-sealed stirrer, reflux condenser, and dropping-funnel, and surrounded by a water-bath at 70°, whilst a solution of allyl bromide (15 g., 0·125 mol.) in acetone (25 c.c.) was added during 2 hours. Heating and stirring were continued for a further 2 hours, and the condenser was then rearranged for distillation; the water-bath was slowly heated to 100°, whilst a stream of nitrogen was blown through the solution to remove volatile material. The contents of the flask were diluted with water (250 c.c.), and the alkali was partly neutralised with sulphuric acid (16·2 c.c. of concentrated acid in 50 c.c. of water). The reaction product was isolated by 5 extractions with ether (total, 350 c.c.), and the dried (K_2CO_3) extracts were evaporated; distillation of the residue gave 12·3 g. (45%) of a very viscous oil, b. p. 120°/0·005 mm., n_D^{25} 1·4730, $[\alpha]_D^{28}$ −7·5° (*c*, 4 in chloroform), $[\alpha]_D^{22}$ −4·2° (*c*, 4 in ethanol), which was

a mixture of mono- and di-allyl compounds (Found: C, 58·2; H, 8·1. Calc. for $C_{13}H_{22}O_6$: C, 56·9; H, 8·1. Calc. for $C_{16}H_{26}O_6$: C, 61·1; H, 8·3%).

1 : 3-2 : 4-*Diethylidene* 5 : 6-*Anhydrosorbitol*.—6-Tosyl 1 : 3-2 : 4-diethylidene sorbitol was prepared by the method of Vargha and Puskás (*Ber.*, 1943, **76**, 859) and crystallised from ethyl acetate–light petroleum (b. p. 60—80°) (cf. Sullivan, *J. Amer. Chem. Soc.*, 1945, **67**, 837); yield, 32%; m. p. 87—90° (Vargha and Puskás, *loc. cit.*, give m. p. 92°).

1 : 3-2 : 4-Diethylidene 5 : 6-anhydrosorbitol was made by the action of sodium methoxide on the 6-tosyl compound (Vargha and Puskás, *loc. cit.*). The yield of almost pure material (m. p. 129—130°) (93%) was much higher than that obtained by these workers, and by Sullivan (*loc. cit.*) (see also the method of preparation given by Wiggins, *J.*, 1946, 388). The anhydro-compound was also made, in almost identical overall yield (28%), by treatment of the crude tosyl compound (syrup) with sodium methoxide; in this case it was isolated by sublimation at 120—140° (bath)/10 mm.

1 : 3-2 : 4-*Diethylidene* 6-*Allyl Sorbitol*.—1 : 3-2 : 4-Diethylidene 5 : 6-anhydrosorbitol (11·5 g.) was heated on the steam-bath for 6½ hours under reflux with a solution of sodium (1 g.) in allyl alcohol (50 c.c.). After addition of water (100 c.c.), the alkali was neutralised with carbon dioxide. Most of the allyl alcohol was removed by distillation under reduced pressure, and after the addition of sodium chloride the solution was extracted 7 times with ether (total 290 c.c.). The extracts were dried (K_2CO_3) and the solvent was removed. Distillation of the very viscous oil gave 1 : 3-2 : 4-*diethylidene* 6-*allyl sorbitol* (10·2 g., 55%), b. p. 115—130° (bath)/0·0001 mm., n_D^{19} 1·4780, $[\alpha]_D^{20}$ −1·3° (*c*, 3 in ethanol) (Found: C, 56·7; H, 8·35. $C_{13}H_{22}O_6$ requires C, 56·9; H, 8·1%).

Penta-acetyl 6-*Allyl Sorbitol*.—6-Allyl 1 : 3-2 : 4-diethylidene sorbitol (10·2 g.) was heated with 4% sulphuric acid (100 c.c.) and ethanol (25 c.c.) on the steam-bath for 5 hours, the liberated acetaldehyde being allowed to escape. The solution was extracted once with ether to remove oily impurities, and then neutralised with barium carbonate (20 g.). The barium salts were removed, and the aqueous solution was evaporated under reduced pressure. The syrup was dried by several evaporations with small amounts of ethanol, and was then dissolved in ethanol (20 c.c.), filtered from a small quantity of insoluble matter, evaporated, and finally dried over phosphoric oxide under reduced pressure. This 6-allyl sorbitol (8·35 g.) failed to crystallise, and it was therefore heated with acetic anhydride (42 c.c.) and fused sodium acetate (4·2 g.) on the steam-bath for 8 hours. Excess of anhydride was removed by distillation under reduced pressure, and the residue was stirred with water for 1½ hours. The product was an oil (14·9 g., 92%) which failed to crystallise, and was distilled. *Penta-acetyl* 6-*allyl sorbitol* had b. p. 140° (bath)/0·0001 mm., n_D^{22} 1·4548, $[\alpha]_D^{21}$ +0·86° (*c*, 2·7 in chloroform) (Found: C, 52·1; H, 6·8; Ac, 48·4. $C_{19}H_{28}O_{11}$ requires C, 52·8; H, 6·5; Ac, 49·4%).

Penta-acetyl 6-(2 : 3-*Dibromopropyl*) *Sorbitol*.—A solution of penta-acetyl 6-allyl sorbitol (13·9 g.) in carbon tetrachloride (60 c.c.) was stirred vigorously and cooled whilst a solution of bromine (5·4 g.) in carbon tetrachloride (20 c.c.) was added during 4 hours, the temperature being kept at −6° to −8°. Stirring was continued for 15 minutes after all the bromine had been added. The carbon tetrachloride solution was washed with sodium hydrogen carbonate solution (50 c.c.), containing sodium thiosulphate (0·5 g.), and dried (Na_2SO_4). The solvent was removed by distillation, and the syrup evaporated several times with methanol, and finally heated at 80°/0·0001 mm. for an hour; yield of *dibromide*, 17·6 g. (93%) (Found: Br, 27·2. $C_{19}H_{28}O_{11}Br_2$ requires Br, 27·0%).

Hepta-acetyl 6-(2 : 3-*Dimercaptopropyl*) *Sorbitol*.—The above dibromide (17 g.), potassium thiolacetate (8 g.), ethanol (60 c.c.), and thiolacetic acid (0·2 c.c.) were heated together on the steam-bath in a 3-necked flask, fitted with reflux condenser, mercury-sealed stirrer, and nitrogen-inlet tube. Vigorous stirring was necessary to prevent violent bumping (caused by precipitated potassium bromide). A slow stream of dry nitrogen was passed through the apparatus during the reaction (6 hours); the deep-yellow solution was then treated with water (300 c.c.), and the insoluble oil was isolated by extraction with ether. The dried (Na_2SO_4) extracts were evaporated in a stream of nitrogen, and the residual syrup was heated to constant weight at 70°/0·0001 mm., to give *hepta-acetyl* 6-(2 : 3-*dimercaptopropyl*) *sorbitol* (16·1 g., 97%) (Found: S, 11·2. $C_{23}H_{34}O_{13}S_2$ requires S, 11·0%). Light absorption: max. 2280 A.; $\varepsilon = 7800$.

Deacetylation. A solution of the hepta-acetate (15·6 g.) in dry methanol (150 c.c.) was cooled to *ca.* −20° and vigorously stirred during addition of methanolic barium methoxide (62 c.c.; 1·04N.), air being excluded by a slow stream of dry nitrogen. After 25 minutes, a fine yellow precipitate suddenly appeared, and after a further 40 minutes it was filtered off in an atmosphere of nitrogen, washed well with methanol and with dry ether, and dried under reduced pressure, first over calcium chloride and finally over phosphoric oxide. The crude barium salt of 6-(2 : 3-dimercaptopropyl) sorbitol (8·4 g.) had $[\alpha]_D^{17}$ +3·15° (*c*, 5 in water) (Found: C, 32·0; H, 6·3; S, 11·2; thiol S, 10·7; Ba, 24·3. Calc. for $C_9H_{18}O_6S_2Ba$: C, 25·5; H, 4·3; S, 15·1; Ba, 32·4%). It formed a fine yellow deliquescent powder, easily soluble in water, and was used without further purification for pharmacological tests. The analytical figures suggest either tenacious retention of solvent or incomplete deacetylation; a triacetate, $C_{15}H_{24}O_9S_2Ba$, requires C, 32·7; H, 4·4; S, 11·7; Ba, 25·0%. The high thiol value, compared with the total sulphur content, indicates almost complete deacetylation of the acetylthio-groups, however.

1 : 2-3 : 4-*Diisopropylidene* 5 : 6-*Anhydromannitol*.—1 : 2-3 : 4-Di*iso*propylidene mannitol (Wiggins, *J.*, 1946, 13) (50 g.) was dissolved in dry pyridine (100 c.c.), and a solution of toluene-*p*-sulphonyl chloride (38 g.) in pyridine (70 c.c.) was added, with stirring, during 1 hour, the temperature being kept below 10° by ice-cooling. The mixture was set aside overnight and then concentrated under reduced pressure. Water and chloroform were added, and the chloroform layer was removed and washed successively with dilute hydrochloric acid, water, and sodium hydrogen carbonate solution, and then dried (Na_2SO_4). This solution was cooled to 0° and gradually treated below 5° with a solution of sodium (4·5 g.) in dry methanol (80 c.c.); after a further 10 minutes at 5°, water was added to dissolve the precipitated sodium toluene-*p*-sulphonate, the chloroform layer was removed, and the aqueous portion was extracted once more with chloroform. The combined chloroform extracts were washed with water, dried (Na_2SO_4), and evaporated to a syrup. Distillation then furnished 1 : 2-3 : 4-di*iso*propylidene 5 : 6-anhydromannitol (27 g., 63%), b. p. 98°/0·003 mm., n_D^{20} 1·4500.

6-*Allyl* 1 : 2-3 : 4-*Diisopropylidene Mannitol*.—A solution of the anhydro-compound (25 g.) in allyl alcohol (100 c.c.) containing sodium (4 g.) was boiled under reflux for 6 hours and then concentrated to small bulk. After dilution with water, and neutralisation with hydrochloric acid, the lower oily layer was taken up in chloroform, and the aqueous portion was extracted twice with chloroform. The combined extracts were washed with water, dried (Na_2SO_4), and evaporated to an oil, which on distillation gave 6-*allyl* 1 : 2-3 : 4-*diisopropylidene mannitol* (28 g., 90%), b. p. 140—142°/0·003 mm., n_D^{20} 1·4570 (Found: C, 59·9; H, 8·7. $C_{15}H_{26}O_6$ requires C, 59·6; H, 8·7%).

1-*Allyl Mannitol*.—6-Allyl 1 : 2-3 : 4-diisopropylidene mannitol (26 g.), suspended in N-sulphuric acid (50 c.c.), was heated on the steam-bath for 4 hours (the solution became homogeneous after ½ hour). The cooled solution was neutralised with barium carbonate, filtered, and evaporated to a solid residue (18 g., 94%) of 1-*allyl mannitol*, which could be crystallised in small quantities from ethanol in the form of plates, m. p. 99—101°, $[\alpha]_D^{22}$ +18° (*c*, 1 in water) (Found: C, 48·0; H, 8·3. $C_9H_{18}O_6$ requires C, 48·6; H, 8·2%). When heated in ethanol for several minutes it appeared to undergo polymerisation, a flocculent precipitate being slowly formed.

Penta-acetyl 1-*Allyl Mannitol*.—1-Allyl mannitol (17 g.) was heated on the steam-bath for 2 hours with acetic anhydride (70 c.c.) and fused sodium acetate (10 g.). The solution was concentrated under reduced pressure and then stirred with water to decompose any remaining anhydride. The oil was taken up in chloroform, and the aqueous solution was extracted once more with chloroform. The combined extracts were washed with water, and with sodium hydrogen carbonate solution, and were then dried (Na_2SO_4) and evaporated to an oil (31 g., 94%), which slowly crystallised. Recrystallisation from methanol gave needles of *penta-acetyl* 1-*allyl mannitol*, m. p. 63—64°, $[\alpha]_D^{17}$ +30° (*c*, 2·3 in chloroform) (Found: C, 52·4; H, 6·7. $C_{19}H_{28}O_{11}$ requires C, 52·7; H, 6·5%).

Penta-acetyl 1-(2 : 3-*Dibromopropyl*) *Mannitol*.—The above penta-acetate (30·2 g.) was dissolved in carbon tetrachloride (100 c.c.) and treated at 0° with bromine (11 g.), added slowly during 1½ hours with stirring. Chloroform (20 c.c.) was then added to dissolve a small amount of oil which had separated, and the solution was washed with sodium hydrogen carbonate solution and then with sodium hydrogen sulphite solution, and finally dried (Na_2SO_4) and evaporated to a pale yellow syrup (41 g., 99%), which consisted essentially of *penta-acetyl* 1-(2 : 3-*dibromopropyl*) *mannitol* (Found: Br, 26·6. $C_{19}H_{28}O_{11}Br_2$ requires Br, 27·0%).

Hepta-acetyl 1-(2 : 3-*Dimercaptopropyl*) *Mannitol*.—The dibromide (41 g.) and potassium thiolacetate (19 g.) in ethanol (200 c.c.) were heated under reflux for 6 hours and then set aside overnight. Water (600 c.c.) was added, most of the alcohol was removed by distillation under reduced pressure, and the product was extracted with ether. The dried ($CaCl_2$) extracts were evaporated to a brown syrup of the *hepta-acetyl* compound (40·5 g., 100%) (Found: S, 10·5. $C_{23}H_{34}O_{13}S_2$ requires S, 11·0%).

Deacetylation. The hepta-acetate (20 g.) in dry methanol (55 c.c.) was treated, as previously described, with 1·13N-barium methoxide (80 c.c.) and gave a crude barium salt (15 g.) (Found: S, 11·2; thiol S, 9·5. Calc. for $C_9H_{16}O_6S_2Ba$: S, 15·1%).

Direct Allylation of 1 : 2-3 : 4-*Diisopropylidene Mannitol*.—1 : 2-3 : 4-Diisopropylidene mannitol (7 g.) in acetone (40 c.c.), sodium hydroxide (10 g.), and water (15 c.c.) was treated at 70° with allyl bromide (4·6 g.) in acetone (10 c.c.) under conditions similar to those described above for 1 : 3-2 : 4-diethylidene sorbitol. The product, isolated by ether-extraction, was distilled, and gave an oil (5·3 g.), b. p. 160°/0·007 mm., n_D^{25} 1·4570, $[\alpha]_D^{22}$ +14·2° (*c*, 5 in chloroform), which was a mixture of mono- and di-allyl compounds (Found: C, 60·8; H, 8·6. Calc. for $C_{15}H_{26}O_6$: C, 59·6; H, 8·7. Calc. for $C_{18}H_{30}O_6$: C, 63·2; H, 7·0%).

This mixture (5 g.) was hydrolysed by being heated with 3% aqueous sulphuric acid for 1½ hours, a little alcohol being added to effect dissolution. The cooled solution was extracted once with ether to remove oily impurities, and the acid was neutralised with barium carbonate (4 g.). The barium salts were removed by filtration, and the aqueous solution was evaporated under reduced pressure from a water-bath at 75°. The syrup was taken up in hot ethanol and filtered. Evaporation of the solvent, and addition of ethyl acetate to the residue, gave a solid (2·6 g.), m. p. 59—80°, which on recrystallisation from acetone, and ethanol–ethyl acetate, gave 1-allyl mannitol, m. p. 98—101°, $[\alpha]_D^{22}$ +17·6° (*c*, 0·8 in water), identical with that prepared *via* the 5 : 6-anhydro-compound.

Evaporation of the mother-liquors gave a syrup (2·6 g.), which was acetylated by being heated on the steam-bath with acetic anhydride (10 c.c.) and fused sodium acetate (2 g.) for 4 hours. Excess of anhydride was decomposed by stirring the mixture with water (100 c.c.) for 2 hours, and the acetyl derivative was isolated by 3 extractions with chloroform. The extracts were washed with sodium hydrogen carbonate solution, the washings being extracted twice with fresh chloroform. The dried (Na_2SO_4) extracts were evaporated, and the residue was distilled to give a colourless syrup (4·1 g.), b. p. 140°/0·0001 mm., n_D^{20} 1·4534, $[\alpha]_D^{18}$ +24·4° (*c*, 4 in chloroform) (Found: Ac, 43·8; equiv., from unsaturation value with ICl, 158. Calc. for monoallyl penta-acetate, $C_{19}H_{28}O_{11}$: Ac, 49·8; equiv., 216. Calc. for diallyl tetra-acetate, $C_{20}H_{30}O_{10}$: Ac, 40·0%; equiv., 107·5). After one month, the syrup deposited crystals (0·6 g.), m. p. 39—54°, which were drained on porous tile. Six recrystallisations from light petroleum (b. p. 60—80°) gave *penta-acetyl* 2-*allyl mannitol*, m. p. 78—79°, $[\alpha]_D^{21}$ +18·2° (*c*, 1 in chloroform) (Found: C, 52·9; H, 6·4. $C_{19}H_{28}O_{11}$ requires C, 52·8; H, 6·5%). The material depressed the m. p. of penta-acetyl 1-allyl mannitol (m. p. 63—64°) to 54—55°.

Allylation of 1 : 2-5 : 6-*Diisopropylidene Mannitol*.—1 : 2-5 : 6-Diisopropylidene mannitol (Baer, *loc. cit.*) (22·6 g., 0·09 mol.) in water (20 c.c.) and acetone (85 c.c.) was treated with sodium hydroxide solution (32 g. of NaOH in 32 c.c. of water). The mixture, which formed two layers, was vigorously stirred and heated in a water-bath at 75° during addition (4 hours) of a solution of allyl bromide (15·1 g., 0·125 mol.) in acetone (20 c.c.). After working up in the usual way, ether extraction gave an oil, which on distillation furnished 3-*allyl* 1 : 2-5 : 6-*diisopropylidene mannitol* (23 g., 87%), b. p. 139°/0·001 mm., n_D^{19} 1·4562, $[\alpha]_D^{19}$ +5·3° (*c*, 1·0 in chloroform) (Found: C, 59·9; H, 8·7. $C_{15}H_{26}O_6$ requires C, 59·6; H, 8·7%).

3-*Allyl Mannitol*.—3-Allyl 1 : 2-5 : 6-diisopropylidene mannitol (23 g.) was heated with 6% aqueous sulphuric acid (100 c.c.) on the steam-bath for 4 hours. The solution was cooled, and extracted once with ether to remove oily impurities, and then neutralised with barium carbonate (40 g.) and filtered;

the residue was well washed with hot water. The aqueous solution was evaporated under reduced pressure from a water-bath at 75°, and the residue so obtained was dried by evaporation several times with ethanol. The semi-solid product (16 g.) was dissolved in hot ethanol and filtered from a small amount of insoluble material. Evaporation of the alcoholic solution until crystals formed, and addition of ethyl acetate, gave 3-allyl mannitol (10 g., 59%), m. p. 112—114°; when recrystallised from ethanol–ethyl acetate it formed hard rosettes, m. p. 117°, $[\alpha]_D^{20}$ +15·3° (*c*, 1·0 in water) (Found: C, 48·3; H, 8·2. Calc. for $C_9H_{18}O_6$: C, 48·6; H, 8·2%). Wrigley and Yanovsky (*loc. cit.*) give m. p. 119—120° (corr.), $[\alpha_D^{25}]$ +15·8° (*c*, 4 in water). Evaporation of the mother-liquors gave a syrup (4·5 g.).

Penta-acetyl 3-Allyl Mannitol.—3-Allyl mannitol (9·5 g.), acetic anhydride (38 c.c.), and fused sodium acetate (4·25 g.) were heated together on the steam-bath for 2½ hours. Most of the excess anhydride was removed by distillation under reduced pressure, and the residue was stirred with water for 30 minutes. The insoluble syrup was taken up in chloroform (5 × 50 c.c.), and the extracts were washed with sodium hydrogen carbonate solution, the washings being extracted twice more with chloroform. The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure to yield *penta-acetyl 3-allyl mannitol* (18·4 g., 100%), which distilled as a colourless oil, b. p. 120—150° (bath)/0·001 mm., n_D^{20} 1·4532, $[\alpha]_D^{22}$ +33·3° (*c*, 3 in chloroform) (Found: C, 52·4; H, 6·4; Ac, 51·0; equiv., by ICl titration, 214. $C_{19}H_{28}O_{11}$ requires C, 52·8; H, 6·5; Ac, 49·4; equiv., 216).

Penta-acetyl 3-(2 : 3-Dibromopropyl) Mannitol.—A solution of penta-acetyl 3-allyl mannitol (2·2 g.) in carbon tetrachloride (15 c.c.) was treated with bromine (0·85 g.) in carbon tetrachloride (15 c.c.), added with vigorous stirring during 2 hours, the temperature being kept below 0°. The solution was then shaken with aqueous sodium thiosulphate, dried (Na_2SO_4), and evaporated, to yield *penta-acetyl 3-(2 : 3-dibromopropyl) mannitol* as a syrup (2·8 g., 94%), n_D^{23} 1·4794 (Found: Br, 27·4. $C_{19}H_{28}O_{11}Br_2$ requires Br, 27·0%).

Treatment of the dibromide with potassium thiolacetate in the usual way, followed by deacetylation of the liquid bisthiolacetate with barium methoxide, gave the crude barium salt of the dithiol as a pale yellow powder, readily soluble in water. The analysis was typical of this type of compound (Found: S, 11·5; thiol S, 10·1; Ba, 28·1. Calc. for $C_9H_{18}O_6S_2Ba$: S, 15·15; Ba, 32·4%).

Allylation of 1 : 4-3 : 6-Dianhydromannitol.—(*a*) A mixture of 1 : 4-3 : 6-dianhydromannitol (Wiggins, *J.*, 1945, 5; Bladon and Owen, preceding paper) (14·6 g., 0·1 mol.), acetone (100 c.c.), sodium hydroxide (36 g.), and water (70 c.c.) was treated at 60—70° with a solution of allyl bromide (15·1 g., 0·125 mol.) in acetone (30 c.c.) during 1½ hours with vigorous stirring. Heating and stirring were continued for a further 2 hours, and the product was then isolated as previously described, giving an oil (4·2 g.), b. p. 160°/10 mm., n_D^{23} 1·4850 (Found: equiv., by ICl titration, 54. Calc. for diallyl derivative, $C_{12}H_{18}O_4$: equiv., 56·5).

The aqueous solution from the ether-extraction was evaporated to dryness under reduced pressure, and the solid residue was extracted with chloroform (Soxhlet). Evaporation of the dried (Na_2SO_4) extracts gave unchanged 1 : 4-3 : 6-dianhydromannitol (8 g.), m. p. and mixed m. p. 83—85°, after recrystallisation from ethyl acetate.

(*b*) A mixture of 1 : 4-3 : 6-dianhydromannitol (29·2 g., 0·2 mol.), dioxan (100 c.c.), sodium hydroxide (72 g.), and water (92 c.c.) was similarly treated at 70° with allyl bromide (30 g., 0·25 mol.) in dioxan (30 c.c.), and gave a product (14·5 g.), b. p. 145°/16 mm., n_D^{26} 1·4802, $[\alpha]_D^{26}$ +157° (*c*, 2 in chloroform), which also consisted largely of 2 : 5-diallyl 1 : 4-3 : 6-dianhydromannitol (Found: C, 62·6; H, 8·2; equiv., by ICl titration, 59·6. Calc. for $C_{12}H_{18}O_4$: C, 63·7; H, 8·0%; equiv., 56·5). Gregory and Wiggins (*J.*, 1947, 1405) give b. p. 173°/10 mm., n_D^{21} 1·4847, $[\alpha]_D^{23}$ +160° (*c*, 1·5 in chloroform).

(*c*) Sodium (4·6 g., 0·2 atom), in small pieces, was added to a solution of 1 : 4-3 : 6-dianhydromannitol (29·2 g., 0·2 mol.) in liquid ammonia (500 c.c.) contained in a 1-l. flask. The sodium dissolved with evolution of hydrogen. After 1 hour, the small amount of undissolved sodium was removed, the ammonia was boiled off on the steam-bath, and the residual solid was heated under reduced pressure to remove the last traces of ammonia. The fine white powder was transferred to a 500-c.c. flask, fitted with a mercury-sealed stirrer and reflux condenser, and was heated on the steam-bath with dry benzene (100 c.c.) and allyl bromide (50 g.) for 22 hours, with stirring, a further 25 g. of allyl bromide being added after 12 hours. The reaction mixture was treated with water (200 c.c.), the benzene layer was separated, and the aqueous solution was acidified with hydrochloric acid and continuously extracted with ether for 12 hours. The benzene and the ether extracts were dried (Na_2SO_4) and evaporated, yielding oils weighing, respectively, 10·75 g. and 13·1 g. Distillation of the combined oils gave a main fraction (20·5 g.), b. p. 107—115°/1 mm., n_D^{20} 1·4901 (Found: equiv., by ICl titration, 77; corresponding to a mixture containing *ca.* 45% of monoallyl derivative).

This mixture (20 g.) was heated under reflux with phthalic anhydride (16·8 g.) and dry pyridine (50 c.c.) for 23 hours. The excess of pyridine was removed by distillation under reduced pressure, and the residue was taken up in chloroform (100 c.c.) and washed successively with 2N-hydrochloric acid, water, 2N-sodium carbonate, and water. The chloroform solution was dried (Na_2SO_4) and evaporated to a mobile liquid (7·1 g.), which on distillation gave 2 : 5-diallyl 1 : 4-3 : 6-dianhydromannitol (6·3 g.), b. p. 87—89°/0·05 mm., n_D^{22} 1·4842, $[\alpha]_D^{21}$ +160° (*c*, 1·7 in chloroform), $[\alpha]_D^{21}$ +141° (*c*, 5·7 in chloroform) (Found: C, 63·6; H, 8·0; equiv., by ICl titration, 57·4. Calc. for $C_{12}H_{18}O_4$: C, 63·7; H, 8·0%; equiv., 56·5).

The acid washings of the chloroform solution were discarded. The sodium carbonate extracts and the final water-washing were acidified to Congo-red with hydrochloric acid and extracted 4 times with chloroform (100-c.c. portions). The extracts were washed once with water, dried (Na_2SO_4), and evaporated to a very viscous syrup (23·1 g.), which solidified on being stirred with ether. The solid (16·9 g.), m. p. 105—110°, was filtered off, and a portion was recrystallised 4 times from ethyl acetate (with charcoal) to give hard prisms of *2-allyl 1 : 4-3 : 6-dianhydromannitol 5-(hydrogen phthalate)*, m. p. 110°, $[\alpha]_D^{23}$ +80° (*c*, 0·9 in chloroform) (Found: C, 61·05; H, 5·7. $C_{17}H_{18}O_7$ requires C, 61·05; H, 5·4%). The rotation in 2N-sodium hydroxide, $[\alpha]_D^{20}$ +92° (*c*, 0·8), was unchanged after 12 hours at room temperature, showing that the ester was not appreciably hydrolysed under these conditions.

2-Allyl 1 : 4-3 : 6-Dianhydromannitol.—The foregoing hydrogen phthalate (16·8 g.) was boiled under reflux with sodium hydroxide (6·5 g.) in water (10 c.c.) for 2 hours, and then heated for a further 6 hours

on the steam-bath. The solution, diluted with water (50 c.c.) and treated with sodium hydrogen carbonate (4 g.), was exhaustively extracted with ether (12 hours). The dried (Na_2SO_4) extracts yielded, on evaporation, an oil (9·3 g.), which on distillation furnished *2-allyl* 1 : 4-3 : 6-*dianhydromannitol* (8·1 g., 86%) as a colourless mobile liquid, b. p. 85°/0·01 mm., n_D^{24} 1·4920, $[\alpha]_D^{20}$ +113° (*c*, 2·2 in chloroform) (Found: C, 58·0; H, 7·7; equiv., by ICl titration, 93. $C_9H_{14}O_4$ requires C, 58·05; H, 7·6%; equiv., 93).

5-Acetyl 2-Allyl 1 : 4-3 : 6-*Dianhydromannitol*.—2-Allyl 1 : 4-3 : 6-dianhydromannitol (8 g.), acetic anhydride (25 c.c.), and fused sodium acetate (2·5 g.) were heated together on the steam-bath overnight. The mixture was shaken with water (50 c.c.) until the excess of anhydride was destroyed, and the product was isolated by 4 extractions with chloroform. The extracts were washed with sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated, to give an oil (9·3 g.) which on distillation yielded *5-acetyl 2-allyl* 1 : 4-3 : 6-*dianhydromannitol* as a colourless mobile liquid (7·7 g., 82%), b. p. 92—93°/0·01 mm., n_D^{19} 1·4769, $[\alpha]_D^{23}$ +185·6° (*c*, 2·5 in chloroform) (Found: C, 58·1; H, 6·9; equiv., by ICl titration, 114·5. $C_{11}H_{16}O_5$ requires C, 57·9; H, 7·1%; equiv., 114).

5-Acetyl 2-(2 : 3-Dibromopropyl) 1 : 4-3 : 6-*Dianhydromannitol*.—5-Acetyl 2-allyl 1 : 4-3 : 6-dianhydromannitol (7·4 g.) in carbon tetrachloride (80 c.c.) was treated with bromine (6 g.) in the same solvent (30 c.c.), added with cooling and stirring during ½ hour, the temperature being kept below −20°. The solution was allowed to warm to room temperature and was diluted with chloroform (40 c.c.) and stirred for a further 20 minutes in order to dissolve some viscid material which had separated. The solution was then washed with sodium hydrogen carbonate solution (50 c.c.) containing sodium thiosulphate (1 g.), then dried (Na_2SO_4) and evaporated. The viscous syrup (11·6 g., 92%) on distillation from a wide-necked retort gave *5-acetyl 2-(2 : 3-dibromopropyl)* 1 : 4-3 : 6-*dianhydromannitol* (9·3 g.), b. p. 120—170° (air-bath)/0·0001 mm., n_D^{26} 1·5241, $[\alpha]_D^{21}$ +116° (*c*, 2·3 in chloroform) (Found: C, 34·1; H, 4·4; Br, 40·9. $C_{11}H_{16}O_5Br_2$ requires C, 34·0; H, 4·2; Br, 41·2%).

Triacetyl 2-(2 : 3-Dimercaptopropyl) 1 : 4-3 : 6-*Dianhydromannitol*.—The above 5-acetyl compound (8·5 g.), potassium thiolacetate (6 g.), and ethanol (30 c.c.) were heated under reflux, with vigorous stirring, under nitrogen for 7 hours. The mixture was poured into water, and the product was isolated by 6 extractions with ether. The extracts were dried (Na_2SO_4) and evaporated, and the product on distillation gave *triacetyl 2-(2 : 3-dimercaptopropyl)* 1 : 4-3 : 6-*dianhydromannitol* (6·2 g.), b. p. 170—180° (air-bath)/0·0001 mm., n_D^{17} 1·5286, $[\alpha]_D^{19}$ +133° (*c*, 2·0 in chloroform) (Found: C, 46·8; H, 5·7; S, 16·7. $C_{15}H_{22}O_7S_2$ requires C, 47·6; H, 5·9; S, 17·0%). Light absorption: max. 2310 A., ε = 8300.

Deacetylation. The bisthiolacetate (5·2 g.) was heated under reflux with 2% methanolic hydrogen chloride (50 c.c.) for 4 hours under nitrogen. During this time, a brilliant purple colour appeared in the solution, reached a maximum intensity after 2 hours, and then faded, so that it had almost disappeared after 4 hours. The solvent was removed by distillation under reduced pressure and the residual syrup was kept for several hours over solid potassium hydroxide, under reduced pressure. On distillation from a retort, it gave, with slight decomposition, *2-(2 : 3-dimercaptopropyl)* 1 : 4-3 : 6-*dianhydromannitol* (2·9 g., 83%), as a yellow, viscous, cloudy liquid, b. p. 150° (air-bath)/0·0001 mm., n_D^{21} 1·5492, $[\alpha]_D^{21}$ +84° (*c*, 2·3 in chloroform) (Found: S, 22·7; thiol S, 21·4. $C_9H_{16}O_4S_2$ requires S, 25·4%). It was readily soluble in water.

Allylation of 1 : 4-3 : 6-*Dianhydrosorbitol*.—(*a*) Under conditions similar to those used for the direct allylation of 1 : 4-3 : 6-dianhydromannitol in acetone solution, 1 : 4-3 : 6-dianhydrosorbitol (14·6 g.) and allyl bromide (15·1 g.) gave an oil (2·1 g.), b. p. 90°/0·1 mm., n_D^{19} 1·4818 (Found: equiv., by ICl titration, 58), consisting mainly of diallyl derivative. Unchanged dianhydrosorbitol (7 g.) was recovered.

(*b*) 1 : 4-3 : 6-Dianhydrosorbitol (14·6 g., 0·1 mol.) was converted into the sodium derivative by reaction with sodium (2·3 g., 0·1 atom) in liquid ammonia. The dried salt was then treated with allyl bromide (25 g.) in boiling benzene (50 c.c.) as previously described, and the product (9·3 g.), on distillation, gave a mixture of the mono- and di-allyl derivatives, b. p. 100°/0·5 mm., n_D^{20} 1·4850 (Found: equiv., by ICl titration, 72), which was heated with phthalic anhydride (7·15 g.) in dry pyridine (20 c.c.) as before. There were obtained 2 : 5-diallyl 1 : 4-3 : 6-dianhydrosorbitol (3·6 g.), b. p. 90°/0·1 mm., n_D^{17} 1·4804, $[\alpha]_D^{19}$ +99° (*c*, 4·8 in chloroform) (Found: C, 63·8; H, 7·9; equiv., by ICl titration, 57. Calc. for $C_{12}H_{18}O_4$: C, 63·7; H, 8·0%; equiv., 56·5), and allyl 1 : 4-3 : 6-dianhydrosorbitol hydrogen phthalate, a dark brown glass (probably a mixture of isomers) (9·3 g.) which failed to yield any crystalline salts (Found: equiv., by alkali titration, 313·5. Calc. for $C_{17}H_{18}O_7$: equiv., 334). Gregory and Wiggins (*loc. cit.*) for 2 : 5-diallyl 1 : 4-3 : 6-dianhydrosorbitol give b. p. 185°/40 mm., n_D^{21} 1·4812, $[\alpha]_D^{22}$ +93·4° (*c*, 1·8 in chloroform).

The allyl 1 : 4-3 : 6-dianhydrosorbitol hydrogen phthalate (8·7 g.) was boiled under reflux with a solution of sodium hydroxide (2·7 g.) in water (11 c.c.) for 2 hours. The mixture was then diluted with water (30 c.c.), sodium hydrogen carbonate (2 g.) was added, and the liquid was continuously extracted with ether for 40 hours. The extracts were dried (Na_2SO_4) and evaporated to an oil (3·35 g., 70%), which was distilled, and gave allyl 1 : 4-3 : 6-dianhydrosorbitol as a colourless mobile liquid, b. p. 87—90°/0·05 mm., n_D^{21} 1·4891, $[\alpha]_D^{20}$ +15·1° (*c*, 2·5 in chloroform) (Found: C, 58·1; H, 7·75; equiv., by ICl titration, 97. Calc. for $C_9H_{14}O_4$: C, 58·05; H, 7·6%; equiv., 93·1).

On acetylation, by the method previously described, using acetic anhydride and sodium acetate, it gave acetyl allyl 1 : 4-3 : 6-dianhydrosorbitol, b. p. 160°/6 mm., n_D^{20} 1·4730, $[\alpha]_D^{20}$ +115° (*c*, 2 in chloroform) (Found: C, 57·65; H, 7·0. Calc. for $C_{11}H_{16}O_5$: C, 57·9; H, 7·1%).

These substances were probably mixtures of the 2- and the 5-allyl compound.

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