SYNTHESES WITH ANHYDRO SUGARS. X.*

CLEAVAGE OF OXIRAN RING IN 1,6:2,3- AND 1,6:3,4-DIANHYDRO-β-D-HEXOPYRANOSES WITH POTASSIUM HYDROXIDE AND SULFURIC ACID

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1,6:2,3- and 1,6:3,4-dianhydro-β-D-hexopyranoses are cleaved diaxially with 5% aqueous potassium hydroxide under formation of 1,6-anhydro-β-D-hexopyranoses. If in dianhydrohexoses the oxiran ring and the hydroxyl group are trans oriented (compounds *I*—*IV*), their cleavage to 1,6-anhydro-β-D-hexopyranoses is preceded by "migration of epoxide"; if the mentioned groups are *cis*-arranged (compounds *V*— *VIII*) the cleavage is accompanied by deep degradation. On hydrolysis in 2% sulfuric acid, the "migration of epoxides" takes place only negligibly and the final products are reducing hexoses formed by diaxial cleavage of the oxiran ring, which precedes the hydrolysis of the 1,6-anhydride bond. Only in the case of 1,6:3,4-dianhydro-β-D-allopyranose unexpectedly the same amount of D-glucose and D-gulose is formed.

Recently the preparation of the last representatives of the eight isomeric 1,6:2,3- and 1,6:3,4-dianhydro-β-D-hexopyranoses[1] was described thus making the whole group of these substances accessible for further synthetic use[2]. The cleavage of the oxiran ring with various nucleophilic or electrophilic reagents still holds an important place among the most important synthetic methods in sugar chemistry. The first work of this type in the group of 1,6-anhydro-β-D-hexopyranoses consists of the preparation of 4-amino-4-deoxy-D-mannose from 1,6:3,4-dianhydro-β-D-talopyranose[3].

If the cleavage of the oxiran ring of 1,6-anhydro-β-D-hexopyranose always took place diaxially with high selectivity, as suggested by literature[3-8], then this would make the preparation of 2 and 3 monosubstituted derivatives of D-galactose (from dianhydro compounds *II* and *V*), 2,3, and 4 monosubstituted D-glucose derivatives (from dianhydro derivatives *I*, *III*, *VI*, and *VIII*), and 3 and 4 monosubstituted derivatives of D-mannose (from dianhydro compounds *IV* and *VII*) more accessible

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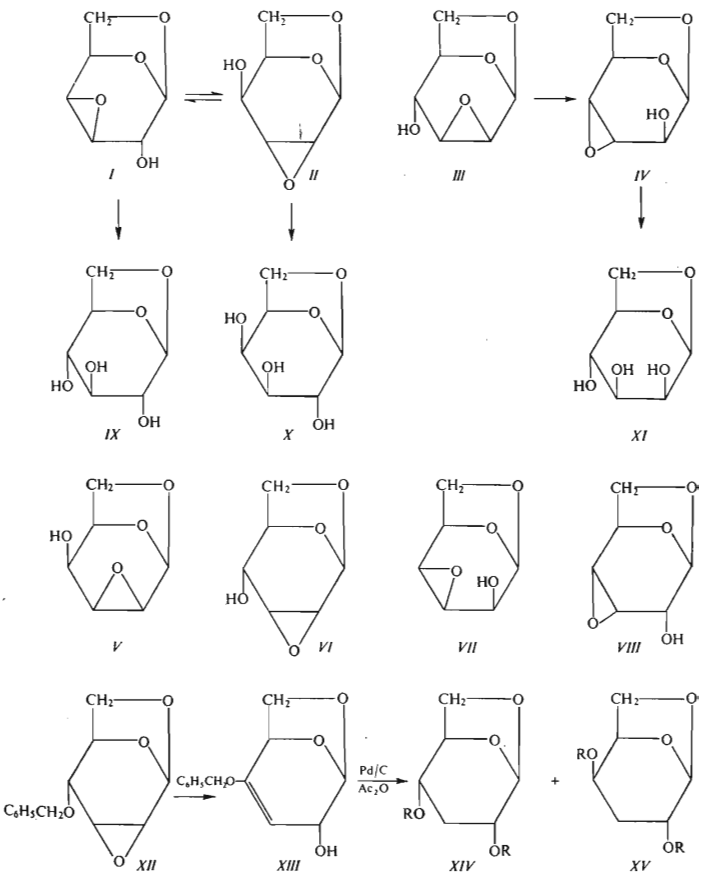
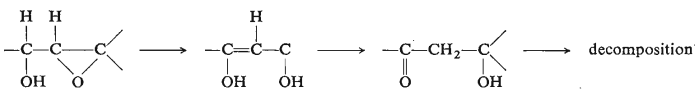
when other reagents than OH^- are used. With regard to the possibility of the "migration of epoxides"[9,10] which could complicate the cleavage of the oxirane ring, and to the fact that 1,6:2,3-dianhydro-4-deoxy-β-D-*lyxo*-hexopyranose[11] is cleaved by



sodium hydroxide against expectation to 1,6-anhydro-4-deoxy-β-D-*xylo*- and *arabino*-hexopyranoses in a 1:1 ratio, we considered it useful to study the cleavage of oxiran rings of all dianhydrohexopyranoses, *I*—*VIII*, under identical conditions, *i.e.* with aqueous solutions of potassium hydroxide and sulfuric acid. Thus, using gas chromatography (Table I), paper and thin-layer chromatography we were able without difficulties to identify the products of the reaction by simple comparison with authentic samples, and also to determine to what extent the diaxial or diequatorial cleavage of epoxides is involved. We believe this reaction could also take place in a similar manner with other reagents, as for example alcoholates, thiolates, ammonia, potassium hydrogen fluoride, *etc.*

Alkaline cleavage of dianhydro derivatives was carried out in 5% potassium hydroxide at 100°C. The results are summarised in Table II. Dianhydro derivatives *I*—*IV* in which the oxiran ring is *trans* with respect to the hydroxyl group are cleaved practically quantitatively and diaxially to 1,6-anhydro-β-D-hexopyranoses. Compounds *I* and *II* give a mixture of 1,6-anhydro-β-D-glucopyranose (*IX*) and 1,6-anhydro-β-D-galactopyranose (X). Probably the "migration of epoxides" takes place rapidly in an alkaline medium under the formation of an equilibrium mixture (*I* ⇄ *II*) the composition of which was determined earlier[9] for 0·05N sodium hydroxide and 23°C. The mixture contained 80% *II* and 20% *I*. Both anhydrides *I* and *II* are evidently hydrolysed approximate at the same rate, because a mixture of 83% *X* and 17% *IX* is formed. From dianhydro derivatives *III* and *IV* only 1,6-anhydro-β-D-mannopyranose (*XI*) is formed which proves that *III* is isomerised to *IV*[10] rapidly, preceding the cleavage of the oxiran ring itself

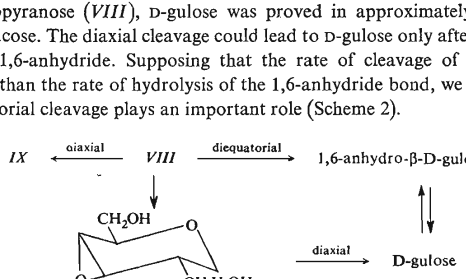
Unexpected behaviour was found in dianhydro derivatives *V*—*VIII*. Under identical reaction conditions the solutions of these substances in alkaline medium started to decompose after only a few minutes of heating, and after two hours 1,6-anhydro-β-D-hexopyranoses were isolated from the brown solutions in very low yield. As all 1,6-anhydro-β-D-hexopyranoses are stable in this medium the decomposition evidently takes place before the opening of the oxiran ring. In all instances in which we observed decomposition we were dealing with conformationally rigid dianhydro derivatives with the *cis*-arrangement of the oxiran cycle and the hydroxy group. Similar behaviour was also observed in 2,7:3,4-dianhydro-β-D-*allo*-heptulopyranose by Zissis[12]. We consider, therefore, that during this reaction a proton is eliminated under the formation of an enol group or a keto group according to Scheme 1.



SCHEME 1

The formed β-hydroxy ketone decomposes rapidly in basic medium, probably by retroaldolisation mechanism. As we were unable to prove this mechanism, directly we tried to prove the possibility of such a reaction with a compound in which the enol group formed is protected in the form of a benzyl ether. Heating of 4-O-benzyl-1,6:2,3-dianhydro-β-D-allopyranose (*XII*) with potassium *tert*-butoxide in *tert*-butyl alcohol gives rise to 1,6-anhydro-4-O-benzyl-3-deoxy-β-D-*erythro*-hex-3-enopyranose (*XIII*) as the main product in addition to traces of several so far unidentified compounds. The structure of *XIII* was proved by hydrogenation in the presence of palladium on charcoal when we were able to isolate from the reaction mixture the acetates of 1,6-anhydro-3-deoxy-β-D-*ribo*-hexopyranose (*XIV*) described earlier by Pratt and Richtmyer[13] and 1,6-anhydro-3-deoxy-β-D-*xylo*-hexopyranose (*XV*). The structure *XIII* was confirmed by PMR and IR spectra, which gave evidence of the presence of enol-ether double bond and hydroxyl group.

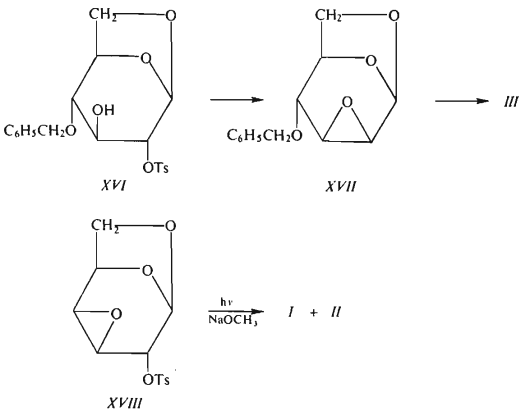
The acid cleavage was carried out with 2% sulfuric acid at 100°C (see Table III). Under these conditions not only the oxiran ring is cleaved, but the 1,6-glycoside bond is hydrolysed as well, giving rise to an equilibrium mixture of the hexose and its 1,6-anhydro derivative (*cf.*[14]). From Table III it follows that in analogy to their behaviour in alkaline medium epoxy derivatives *I*–*VII* are also hydrolysed diaxially in acid medium. Small amounts of hexoses which seem to be formed by diequatorial cleavage can be also formed, of course, by diaxial cleavage after the preceding hydrolysis of the 1,6-anhydride bond. However, in the case of 1,6:3,4-dianhydro-β-D-allopyranose (*VIII*), D-gulose was proved in approximately the same amount as D-glucose. The diaxial cleavage could lead to D-gulose only after preceding opening of the 1,6-anhydride. Supposing that the rate of cleavage of the oxirane ring is greater than the rate of hydrolysis of the 1,6-anhydride bond, we can assume that the diequatorial cleavage plays an important role (Scheme 2).



SCHEME 2

In contrast to the alkaline medium the so-called "migration of epoxides" does not take place in an acid medium to any great extent, because from dianhydride *I* D-glucose is formed practically exclusively, and from *II* D-galactose is formed to be accompanied by traces of D-glucose. Similar results were also observed with dianhydro derivatives *III* and *IV*. From the first predominantly D-glucose is formed, while from the second only D-mannose if formed in addition to traces of D-idose.

The starting substances for this study were prepared generally by known procedures. Dianhydro derivative *III* was prepared by catalytic debenzylation of 4-O-benzyl-1,6:2,3-dianhydro-β-D-mannopyranose (*XVII*) obtained from 1,6-anhydro-4-O-benzyl-2-O-*p*-toluenesulfonyl-β-D-glucopyranose (*XVI*) on reacting with sodium methoxide. Epoxide *II* was prepared by isomerisation of epoxide *I* or directly from 1,6:3,4-dianhydro-2-O-*p*-toluenesulfonyl-β-D-galactopyranose (*XVIII*) by photolytic detosylation with sodium methoxide according to Zen, Tashima, and Koto[15], leading to isomerisation of the dianhydro derivative *I* to an equilibrium mixture of *I* and *II*.



EXPERIMENTAL

Melting points were measured on a Boetius micro melting point apparatus. Optical rotations were measured on an automatic polarimeter Bendix-Ericson, Ltd., type 143 A. The samples for analysis were dried at room temperature and 0·1 Torr, over phosphorus pentoxide. Paper chromatography of reducing sugars was carried out by multiple development technique at 20—25°C on Whatman No 1 paper in ethyl acetate–pyridine–water (2 : 1 : 2); detection was carried out with ammoniacal silver nitrate and heating at 90°C. Chromatography of acetylated derivatives of 1,6-anhydro-β-D-hexopyranoses was carried out on thin layers (0·25 mm) of silica gel containing 5% of gypsum (Lachema), in benzene–acetone (9 : 1). Detection was carried out by carbonisation after previous spraying with 50% sulfuric acid. For gas chromatography Chrom III apparatus (Laboratorní přístroje) was employed. Gas chromatography of acetates of 1,6-anhydrohexoses was carried out on a 280 cm long column, 4 mm in diameter, filled with Chromosorb W—AW 60—80 mesh, coated with 3% of phase SE — 30. Trimethylsilyl ethers were chromatographed on a 182 cm long column, 4 mm in diameter, filled with Chromosorb G (40—60 mesh), coated with 2·5% of phase SE — 52. The solutions were concentrated on a vacuum rotatory evaporator at 30—40°C.

4-O-Benzyl-1,6:2,3-dianhydro-β-D-mannopyranose (*XVII*)*

To a solution of 10 g of 1,6-anhydro-4-O-benzyl-2-O-*p*-toluenesulfonyl-β-D-glucopyranose[16] in 100 ml of chloroform a solution of sodium (2·5 g) in 50 ml of methanol was added within 3 minutes under external cooling. The mixture was allowed to stand at room temperature for 24 hours. It was poured into 400 ml of water and the formed emulsion was separated by filtration through filter paper. The chloroform layer was separated and the aqueous layer extracted 5 times with 50 ml of chloroform. The combined organic extracts were dried over magnesium sulfate and evaporated. Crystallisation from ether–light petroleum gave 5·1 g (89%) of product, m.p. 64°C, $[\alpha]_D^{20}$ −27° (*c* 1·1; chloroform). For $C_{13}H_{14}O_4$ (234·3) calculated: 66·65% C, 6·02% H; found: 66·30% C, 5·99% H.

1,6:2,3-Dianhydro-β-D-mannopyranose (*III*)

Benzyl derivative *XVII* (1·0 g) was hydrogenolysed in 10 ml of ethanol in the presence of 0·3 g of 10% palladium on charcoal at 40°C. After approximately 4 hours the reaction was over and the reaction mixture was filtered and the filtrate evaporated to dryness, affording 0·66 g (98%) of crude crystalline product. On crystallisation from a mixture of acetone–light petroleum, or ethyl acetate–light petroleum a product was obtained with m.p. 68—70°C, $[\alpha]_D^{20}$ −35° (*c* 0·8; water), in agreement with the literature[10].

1,6:2,3-Dianhydro-β-D-gulopyranose (*II*)

A suspension of 3·0 g of tosyl derivative *XVIII* in 150 ml of a solution of sodium (0·7 g) in methanol was irradiated in a quartz reactor with a 100 W high-pressure mercury lamp. Irradiation was

TABLE I

Gas Chromatography of Derivatives of 1,6-Anhydro-β-D-hexopyranoses

Configuration	Acetates ret. time, min		Trimethylsilyl ethers ret. time, min
	a	*b*	*c*
allo	6·98	4·9	10·40
altro	6·18	5·0	11·55
gluco	6·50	4·4	10·70
manno	6·98	5·7	9·55
gulo	6·08	4·0	9·10
ido	5·66	4·3	12·70
galacto	7·25	5·2	8·55
talo	7·16	8·0	11·55

[a] Column 280 cm, diameter 4 mm; filling 3% SE 30 on Chromosorb W AW 60—80 mesh; 205°C; 46 ml N_2/min. [b] Column 100 cm, diameter 2·5 mm; filling 3·0% OV — 17 on Shimalite W 80 to 100 mesh; 155°C; 23 ml N_2/min. [c] Column 182 cm, diameter 4 mm; filling: 2·5% SE 52 on Chromosorb G HMDS 40—60 mesh; 171°C; 48 ml N_2/min.

* The synthesis was performed by Dr J. Halbych.

carried out at 25°C under stirring with a stream of nitrogen for 14 hours. When all initial material had disappeared the reaction mixture was neutralised with 5% sulfuric acid and evaporated to dryness. The residue was extracted with warm acetone and the combined extracts were concentrated and inoculated with an authentic sample *II*. Yield 0·9 g (62%) of dianhydro derivative *II*, m.p. 135–137°C, and $[\alpha]_D^{20}$ +30° (*c* 0·9; water) were in agreement with those of an authentic specimen[9].

1,6-Anhydro-4-O-benzyl-3-deoxy-β-D-*erythro*-hex-3-enopyranose (*XIII*)

The benzyl derivative *XII* (500 mg), prepared according to literature[1], was refluxed with a solution of 200 mg of potassium in 10 ml of tert-butyl alcohol for 5 hours. Then the reaction mixture was poured into 15 ml of water and extracted with benzene. The benzene extract was dried over anhydrous magnesium sulphate and evaporated to dryness. Crystallisation of the residual syrup from ether–light petroleum mixture gave 350 mg (70%) of compound *XIII*, m.p. 100–102°C, $[\alpha]_D^{25}$ −45° (*c* 0·8; chloroform). PMR spectrum (deuteriochloroform, 60 Mc): 2·62τ (5 H singlet, aromatic nucleus); 4·50τ (1 H complex singlet, anomeric H); 5·21τ (2 H singlet, CH_2-benzylic); 6·24τ (2 H multiplet, CH_2—O of the 1,6-anhydro bridge); 8·25τ (1 H doublet, C—OH). IR spectrum (chloroform): 1665 cm^{-1}, (—O—C=C—), 3580 cm^{-1} (free —OH), 3460 cm^{-1} (—OH assoc.). For $C_{13}H_{14}O_4$ (234·3) calculated: 66·65% C, 6·02% H; found: 66·36% C, 5·91% H.

TABLE II

Reaction of Dianhydro-β-D-hexopyranoses with 5% KOH at 100°C

Starting compound	Products	Starting compound	Products
	1,6:2,3-Dianhydro-β-D-hexopyranoses		
III *manno*	1,6-anhydro-β-D-mannopyranose (100%)	*II* *gulo*	1,6-anhydro-β-D-galactopyranose (83%) 1,6-anhydro-β-D-glucopyranose (17%)
V *talo*	decomposition 1,6-anhydro-β-D-galactopyranose (~1%)	*VI* *allo*	decomposition 1,6-anhydro-β-D-glucopyranose (~5%)
	1,6:3,4-Dianhydro-β-D-hexopyranoses		
I *galacto*	1,6-anhydro-β-D-glucopyranose (17%) 1,6-anhydro-β-D-galactopyranose (83%)	*IV* *altro*	1,6-anhydro-β-D-mannopyranose (100%)
VII *talo*	decomposition 1,6-anhydro-β-D-mannopyranose (9%)	*VIII* *allo*	decomposition 1,6-anhydro-β-D-glucopyranose (8%)

2,4-di-O-Acetyl-1,6-anhydro-3-deoxy-β-D-*ribo*-hexopyranose (*XIV*) and
2,4-di-O-Acetyl-1,6-anhydro-3-deoxy-β-D-*xylo*-hexopyranose (*XV*)

A solution of 66 mg of benzyl enol ether *XIII* in 1 ml of ethanol was hydrogenated in the presence of 20 mg of 10% palladium on charcoal at 30°C and atmospheric pressure. When absorption of hydrogen was terminated (approx. 3 hours), the solution was filtered and the filtrate evaporated to dryness. The remaining syrup (35 mg) was acetylated with 0·5 ml of acetic anhydride and 25 mg of anhydrous sodium acetate at 140°C in a sealed tube for 5 minutes. The reaction mixture was poured into water and extracted with chloroform. The organic layer was washed with sodium hydrogen carbonate solution and water, dried over anhydrous calcium chloride, filtered, and evaporated to dryness. Thin-layer chromatography in benzene–acetone (9 : 1) showed the presence of two substances in an approximate 1 : 1 ratio determined gas chromatographically (SE — 30; 163°C). Both substances were separated by crystallisation from ether–light petroleum mixture. The substance melting at 114—116°C, $[\alpha]_D^{25}$ —71·5° (*c* 0·7; chloroform) was identified as deoxy derivative *XIV*, because its properties coincided with the literature data[13]: m.p. 114—116°C, $[\alpha]_D^{25}$ —74° (*c* 0·9; chloroform). To the other substance, m.p. 74—75°C $[\alpha]_D^{24}$ +14° (*c* 0·9; chloroform), we assigned the structure *XV* on the basis of its synthesis and optical rotation. For $C_{10}H_{14}O_6$ (230·2) calculated: 52·17% C, 6·13% H; found: 52·24% C, 6·08% H.

Alkaline Cleavage of Dianhydro Derivatives *I*— *VIII*

A solution of 200 mg of dianhydro derivative in 4 ml of 5% potassium hydroxide was heated in a sealed tube placed in a boiling water bath for 5 hour. The solution was then filtered through a column of Dowex 50 W in H^+ cycle and the filtrate was evaporated to dryness. In the case

TABLE III
Reaction of Dianhydro-β-D-hexopyranoses with 2% H_2SO_4 at 100°C

Starting compound	Products (%)	Starting compound	Products (%)
	1,6:2,3-Dianhydro-β-D-hexopyranoses		
III *manno*	D-glucose (90%) D-altrose (10%)[a] D-mannose[b]	*II* *gulo*	D-galactose (100%) D-glucose[b]
V *talo*	D-galactose (100%) D-idose[b]	*VI* *allo*	D-glucose (100%)
	1,6:3,4-Dianhydro-β-D-hexopyranoses		
I *galacto*	D-glucose (100%) D-galactose[b]	*IV* *altro*	D-mannose D-idose[b]
VII *talo*	D-mannose (100%)	*VIII* *allo*	D-glucose (50%) D-gulose (50%)

[a] This number includes the quantity of the corresponding 1,6-anhydro derivative. [b] Traces only.

of dianhydro derivative *V— VIII* the brown coloured solutions were decolorised with charcoal before concentration. Gas chromatography: 3—4 mg of the residue were dissolved in 1 ml of anhydrous pyridine and 0·2 ml of hexamethyldisilazane and 0·1 ml of trimethylsilyl chloride were added to the solution. After thorough shaking for 1 minute the reaction mixture containing trimethylsilyl derivatives of 1,6-anhydro-β-D-hexopyranoses was injected into the column[17]. Paper chromatography: approximately 5 mg of the residue were hydrolysed in 1 ml water in the presence of 100 mg of Amberlite IR 120 in H^+ cycle by heating at 100°C for 3 hours. The solution was then applied onto the paper. Thin-layer chromatography: 5 mg of the residue were acetylated with 0·1 ml of acetic anhydride and 10 mg of anhydrous sodium acetate at 120°C for 5 minutes. After cooling 0·2 ml of water were added followed by 0·1 ml of chloroform, the mixture was shaken, and the organic extract was applied on the start. The results are presented in Table II.

1,6:3,4-*Dianhydro*-β-D-*galactopyranose* (I): After 5 hours of reaction the optical rotation value was stabilised at $[\alpha]_D^{25}$ −29·5°. The presence of 1,6-anhydro-β-D-glucopyranose (*IX*) and 1,6-anhydro-β-D-galactopyranose (*X*) was proved in the reaction mixture. From optical rotation its composition was calculated: 17% of *IX* and 83% of *X*. (*IX*: $[\alpha]_D^{25}$ −66·5° (ref.[18]); *X*: $[\alpha]_D^{25}$ −21·9° (ref.[19]). This was corroborated by quantitative gas chromatography of trimethylsilyl ethers of the mentioned anhydrohexopyranoses. The yield was quantitative.

1,6:2,3-*Dianhydro*-β-D-*gulopyranose* (II): Qualitative and quantitative results were identical with those obtained for *I*.

1,6:2,3-*Dianhydro*-β-D-*mannopyranose* (III): After 5 hours reaction time the optical rotation value was stabilised at $[\alpha]_D^{25}$ −127° corresponding to the optical rotation of 1,6-anhydro-β-D-mannopyranose (*XI*) ($[\alpha]_D^{25}$ −127·6° (ref.[20]). According to chromatography the mixture contained only this one substance. The yield was quantitative.

1,6:3,4-*Dianhydro*-β-D-*altropyranose* (IV): All results were in agreement with the results obtained for *III*.

1,6:2,3-*Dianhydro*-β-D-*talopyranose* (V): 1·9 mg of 1,6-anhydro-β-D-galactopyranose (*X*) was obtained only.

1,6:2,3-*Dianhydro*-β-D-*allopyranose* (VI): 9·1 mg of 1,6-anhydro-β-D-glucopyranose (*IX*) were isolated.

1,6:3,4-*Dianhydro*-β-D-*talopyranose* (VII): 17·9 mg of 1,6-anhydro-β-mannopyranose (*XI*) were isolated.

1,6:3,4-*Dianhydro*-β-D-*allopyranose* (VIII): 15·7 mg of 1,6-anhydro-β-D-glucopyranose (*IX*) were obtained.

Acid Cleavage of Dianhydro Derivatives *I— VIII*

A solution of 100 mg of dianhydro derivative in 2 ml of 2% sulfuric acid was heated in a sealed tube in a boiling water bath for 3 hours. The reaction mixture was neutralised with barium carbonate and the insoluble precipitate was separated by centrifugation. A part of the solution was chromatographed on paper. The remaining part was evaporated to dryness and transformed to trimethylsilyl ethers by the procedure described in the general part of the section on alkaline cleavage. These derivatives were analysed by gas chromatography. The results are summarised in Table III.

Cleavage of 1,6:3,4-*dianhydro*-β-D-*allopyranose* (VIII): After 3 hours hydrolysing as described above the reaction mixture was neutralised with Dowex 2 W in OH^- cycle and the solution was evaporated to dryness. The remaining syrup (95 mg) was acetylated by heating it with 1 ml of acetic anhydride and 200 mg of anhydrous sodium acetate at 100°C for 15 minutes. After dilution with water the acetates were isolated by extraction with chloroform which was then washed with sodium hydrogen carbonate and dried over anhydrous calcium chloride. After

evaporation a syrup was obtained which contained, according to thin-layer chromatography, two substances which were separated by preparative chromatography on a column of silica gel (15 g) with benzene–acetone (12 : 1). The first eluted substance was identified as D-glucose penta-acetate. The second substance was a syrup which after deacetylation with sodium methoxide in ethanol gave a syrupy D-gulose. This was transformed to its phenylhydrazone, m.p. 143°C. Lit.[21] gives m.p. 142°C.

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