CCCLXXVIII.—*Isolation of Crystalline α- and β-Ethylglucofuranosides (γ-Ethylglucosides) and Other Crystalline Derivatives of Glucofuranose.*

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FOLLOWING upon Fischer's discovery of γ-methylglucoside, unusual interest has been manifested in this novel variety of sugar derivative. Isolated as an uncrystallisable syrup possessing exceptional properties, γ-methylglucoside was clearly differentiated from the normal type represented by the crystalline α- and β-methylglucosides. Whilst the latter were analogous in constitution to α- and β-glucoses, the γ-glucoside appeared to be structurally related to a new form of glucose which had not been isolated. The method adopted by Fischer for the preparation of γ-methylglucoside did not exclude the possibility of the presence of traces of the normal α- and β-forms as impurity, and as ordinarily obtained these are undoubtedly present. Hitherto it has not been found possible to isolate the γ-glucosides as pure crystalline compounds.

Recent experiments in this laboratory have demonstrated (Haworth, Hirst, and Miller, J., 1927, 2436) that γ-glucosides and their derivatives are constituted as five-atom ring forms, to which the name *furanoses* has been given, and this class of sugar differs from the commoner six-atom ring forms, which are designated the *pyranoses*. To the latter type belong the crystalline α- and β-methylglucosides, which are consequently described as α- and β-methylglucopyranosides.

The formulation of the hypothetical γ-glucose as a glucofuranose requires for its complete expression the representation of two stereoisomeric forms of the sugar and of its alkylglucosides.

Two such stereoisomeric forms have now been isolated as crystalline substances. These are *α-ethylglucofuranoside* (VIII) and *β-ethylglucofuranoside* (VI), and their physical properties are here contrasted with the structurally different pair of stereoisomerides represented by the common α- and β-ethylglucopyranosides which

were obtained by Fischer (*Ber.*, 1895, **28**, 1154) and by Bourquelot and Bridel (*Compt. rend.*, 1912, **155**, 86):

	M. p.	$[\alpha]_D$.	
Ethylglucofuranoside (γ-variety):			
α-Modification	82— 83°	+ 98°	diff. 184°
β-Modification	59— 60	− 86	
Ethylglucopyranoside (normal variety):			
α-Modification	113—114	+150·3	diff. 183·7
β-Modification	73	− 33·4	

It is noteworthy that the range of the specific rotations exhibited by the parallel pairs is almost identical. This is represented by an interval of 184° and 183·7° respectively, and it is evident that to this extent the new pair of stereoisomerides conforms to the statistical rule for the "A" position at carbon atom 1, as originally enunciated by C. S. Hudson (*J. Amer. Chem. Soc.*, 1926, **48**, 1434). This author's more recent views have favoured the allocation of a five-atom ring structure to the normal variety, and he has credited the six-atom ring structure to a second hypothetical pair, for which he has calculated other rotational values. He remarks that the isolation of such a pair of isomerides possessing those rotations would be the best answer to objections which might be raised. Conversely, it can be said that the isolation of a pair of isomerides having rotations of different magnitude from those allotted would disprove his contention. We have now provided the necessary evidence by the isolation of this second pair of α- and β-ethylglucosides, which are seen to have the five-atom ring structure which Hudson allocates to the previously existing pair. This result is sufficient to invalidate the arguments based on the tables of "epimeric differences" which Hudson advanced as his chief evidence for the older ring structure of the normal forms of α- and β-methylglucosides (compare Haworth and Hirst, J., 1928, 1221).

In the determination of ring structure in the sugar group methylation methods, involving the use of alkali and methyl sulphate, have been largely applied. We have in no case experienced any tendency for the oxide ring of a glucoside to be displaced by this procedure, although we have emphasised the fact that acids do, under well-recognised conditions, effect ring displacements in glucosides and sugars.

There can be no doubt as to the facts that the normal forms of α- and β-methylglucosides give rise, on methylation either by the Purdie method or by the use of alkali and methyl sulphate, to methylated derivatives which are six-atom ring forms. Hudson's contention seems to depend on the assumption of a change, during this methylation process, of ring structure from a five-atom to a six-atom ring. It is, however, equally well established that the

γ-methylglucosides give rise on methylation by the same reagents to methylated derivatives which are five-atom ring forms. Here Hudson's views require the hypothesis that ring displacement in this second case has occurred in the other direction, from a six-atom ring to a five-atom ring. Since the above methylations proceed almost quantitatively, the same experimental conditions can scarcely be responsible for both ring changes in opposite directions. Our theoretical position is the simple and natural one, that the experimental facts are consistently clear and convincing, and require no conception so hypothetical or accommodating as ring displacement for their rational interpretation or acceptance. Were such a displacement to occur, it would be amenable to experimental detection, since in the above examples it would lead to an equilibrium mixture containing each type of ring compound, and these are readily identified by their marked difference in properties. There is indeed on record in the literature one example of a ring change from γ-methylmannoside to α-methylmannoside, occurring either spontaneously or on the application of methylation agents in an alkaline medium (Irvine and Burt, J., 1924, **125**, 1343). But we are convinced, by experiments which will be communicated later, that in these observations the authors have mistaken the nature of their products. We have been interested in this example because, hitherto, we have derived the constitution of γ-methylmannoside solely from a study of the lactone obtainable from γ-mannose-diacetone (Goodyear and Haworth, J., 1927, 3136). Even if Irvine and Burt's observation had received confirmation, this or any other solitary example of ring displacement would not invalidate the constitutional arguments we have developed, inasmuch as the glucosides of individual sugars have been separately investigated in the many cases included in our purview. There appears to be, however, no authentic case on record of ring displacement in an alkylglucoside by the agency of alkaline solutions.

For the above and other reasons we decided to attempt the formation of homogeneous ethylglucosides in the γ-glucose series by selecting methods which would involve the application of alkali in the final stages of the isolation. If any tendency existed for displacement of a five-atom ring to a six-atom ring, then we should expect to find evidence of it from the character of our products; especially as it is a comparatively simple matter to detect such a change experimentally. Such evidence is, however, entirely lacking.

If it be the case, as C. S. Hudson suggests, that the normal varieties of α- and β-alkylglucosides are five-atom ring forms, then by the experimental procedure we have adopted we should expect to obtain these normal forms and not the labile or γ-forms of the alkylgluco-

sides, since glucose-acetone carbonate, the initial substance we have used in these transformations, resembles in structure glucose-diacetone, which possesses in its sugar nucleus a five-atom ring (Freudenberg and Brauns, *Ber.*, 1922, **55**, 3233; Freudenberg and Doser, *Ber.*, 1923, **56**, 1243; Levene and Meyer, *J. Biol. Chem.*, 1922, **54**, 805; 1923, **57**, 317; 1924, **60**, 173; Anderson, Charlton, and Haworth, this vol., p. 1329). It is evident that the new alkyl-glucosides belong to the γ-glucose (glucofuranose) series, since they are clearly differentiated both in physical and in chemical properties from the alkylglucosides of the normal (pyranose) series, and resemble closely γ-methylglucoside. But the final proof of the constitution of pyranose and furanose forms is reached quite independently of the structure allocated to glucose-diacetone.

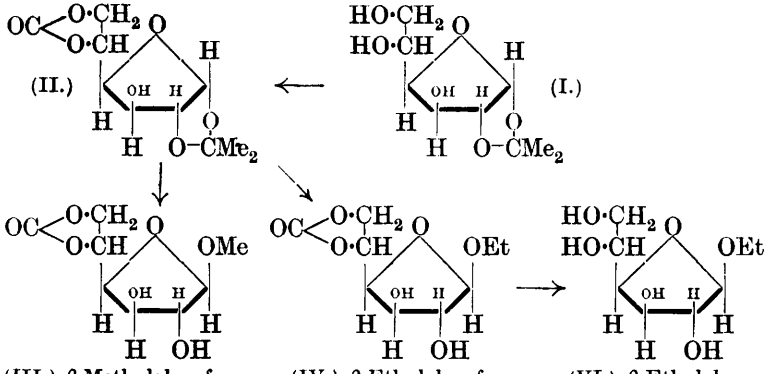
Glucose-diacetone was converted into glucose-monoacetone by acetic acid, and the positions previously occupied by the eliminated acetone residue were re-occupied when the glucose-monoacetone (I) was condensed with carbonyl chloride in acetone solution, which led to the introduction of a carbonate group. This crystalline product, *glucose-acetone carbonate* (II), is hydrolysable by dilute acids to give the crystalline glucose 5 : 6-monocarbonate (VII), which is the first authentic crystalline derivative of glucofuranose (γ-glucose) possessing a free reducing group. From this compound the crystalline *phenylosazone* and *anilide* were prepared, and when the carbonate residue was eliminated from these two derivatives they reverted to the ordinary glucosazone and glucose-anilide.

When the acetone residue in glucose-acetone carbonate was removed by an alcoholic solution of hydrogen chloride or sulphuric acid, the alkylglucosides of the monocarbonate were obtained, and the β-form was at once isolated as the crystalline substance. In this way we have prepared the compounds (III–VI) indicated on p. 2800.

The β-methyl- and β-ethyl-glucoside carbonates were readily isolated at this stage as homogeneous crystalline forms.

The α- and β-*ethylglucofuranoside* 5 : 6-*monocarbonates* also gave rise, in contact with acetic anhydride and pyridine, to their crystalline *diacetyl* derivatives. By repeated crystallisation of crude diacetyl-α-ethylglucofuranoside 5 : 6-monocarbonate we were able to ensure its separation from the β-isomeride. Digestion of this diacetyl-α-isomeride with hot barium hydroxide solution effected the simultaneous removal of the acetyl and carbonate residues with formation of the crystalline α-ethylglucofuranoside (VIII).

Returning now to the β-ethylglucofuranoside 5 : 6-monocarbonate (IV), we found that elimination of the carbonate residue by sodium hydroxide led to the isolation of crystalline β-ethylglucofuranoside (VI). The α- and β-ethylglucofuranosides have properties corre-



(II.) (I.)

(III.) β-Methylglucofuranoside 5 : 6-monocarbonate. (IV.) β-Ethylglucofuranoside 5 : 6-monocarbonate. (VI.) β-Ethylglucofuranoside.

(VIII.) α-Ethylglucofuranoside. (V.) α-Ethylglucofuranoside 5 : 6-monocarbonate. (VII.) Glucofuranose 5 : 6-monocarbonate.

sponding to those of γ-glucosides and these are given in detail in the experimental section. It is seen that they undergo rapid and complete hydrolysis with $N/100$-hydrochloric acid during ½ hour at 95°. Under these conditions the α- and β-ethylglucopyranosides are not appreciably changed.

An indication of the structure of the glucose-acetone carbonate from which the present series of compounds is derivable was revealed by the following series of transformations. The introduction of a *p*-toluenesulphonyl residue into glucose-acetone carbonate was followed by the elimination of the carbonate residue with the aid of barium hydroxide. This gave 3-*p*-toluenesulphonylglucose-monoacetone, and into this compound a second acetone residue was subsequently introduced. The product was identical with the crystalline *p*-toluenesulphonyl derivative of glucose-diacetone. It would thus appear that, since glucose-diacetone has been shown to possess a furanose structure, the same structure can be allocated also to glucose-acetone carbonate and to glucofuranose 5 : 6-monocarbonate, as well as to the two isomeric forms of ethylglucofuranoside.

Although acid reagents have been utilised in some of the above reactions, the 5-position has been closed, owing to the presence of the carbonate residue, to the entry of other groups during this acid

treatment. In order to supplement these arguments an independent proof of ring structure of the glucofuranosides is provided in the oxidation of the methylated methylglucofuranoside to 2 : 3 : 5 : 6-tetramethyl γ-gluconolactone, and finally to *d*-dimethoxysuccinic acid, which is characterised as the crystalline methylamide (Haworth, Hirst, and Miller, *loc. cit.*).

EXPERIMENTAL.

Glucose-acetone Carbonate (II).—(a) *From glucose.* Gaseous carbonyl chloride was admitted to a suspension of glucose (8 g.) in dry acetone (70 c.c.), the operation being accompanied with vigorous mechanical stirring until all the glucose had dissolved (3 hours). After being kept over-night, the solution was neutralised by agitation with basic lead carbonate and filtered, and the residue washed with acetone. The combined filtrate and washings were evaporated nearly to dryness at 35°, and again filtered. The crystalline solid deposited (3 g.) was recrystallised from ethyl alcohol and gave colourless needles, which sintered at 215° and melted and decomposed with effervescence at 223—224°. $[\alpha]_{5780}^{20°}$ −36° (Found: C, 48·7; H, 6·0; CO_2, 17·7; *M*, 250. $C_{10}H_{14}O_7$ requires C, 48·8; H, 5·7; CO_2, 17·9%; *M*, 246).

The substance gave with barium hydroxide solution an immediate precipitate of barium carbonate and formed iodoform when warmed with hydrochloric acid and subsequently treated with alkali and iodine. It did not reduce Fehling's solution before hydrolysis with dilute acid. These properties are in agreement with those required for a *glucose-acetone carbonate*.

From the original acetone mother-liquor, glucose-monoacetone (3 g.) and glucose-diacetone (1 g.) were obtained together with unchanged glucose and a small amount of a syrupy product.

(b) *From glucose-monoacetone.* The procedure was as in (a), glucose-monoacetone being the initial material. The yield was similar to that mentioned above, 8 g. of the monoacetone yielding 3 g. of crystalline glucose-acetone carbonate. The close structural relationship of the latter substance to glucose-monoacetone was illustrated by the ease with which, in contact with aqueous alkali, the acetone-carbonate was converted into crystalline glucose-monoacetone.

p-*Toluenesulphonyl Derivative of Glucose-acetone Carbonate.*—Glucose-acetone carbonate (0·35 g.) was gradually dissolved in pyridine (0·7 c.c.) containing *p*-toluenesulphonyl chloride (0·41 g.) and the solution was heated at 60° during 3—4 hours. Addition of water precipitated an oil which solidified; after being washed with water and recrystallised five times from ethyl alcohol, this gave

colourless needles (0·42 g.), m. p. 103—105°. The yield was 75% of the theoretical. $[\alpha]_{5789}^{23°}$ −36°, $[\alpha]_{5461}^{23°}$ −39° in acetone (*c*, 0·6) (Found: C, 51·1; H, 5·15. $C_{17}H_{20}O_9S$ requires C, 51·0; H, 5·05%).

Conversion of p-*Toluenesulphonylglucose-acetone Carbonate into* p-*Toluenesulphonylglucose-diacetone.*—The above derivative of glucose-acetone carbonate (0·75 g.) was dissolved in aqueous alcohol (50% by volume), and to the warm solution *N*/3-barium hydroxide (1 mol.) was slowly added. The solution did not at any period become more than very faintly alkaline. The filtered solution was evaporated to dryness under diminished pressure, and the residue dissolved in a mixture of ether and water. The aqueous layer yielded a little glucose-monoacetone, and the ethereal layer gave a transparent glass (Ohle and Dickhäuser, *Ber.*, 1925, **58**, 2593). The latter was separated, and vigorously shaken with acetone and anhydrous copper sulphate for some time. From this solution there was isolated in almost theoretical yield the crystalline *p*-toluenesulphonylglucose-diacetone, m. p. 120—121° either alone or in admixture with a specimen which had been prepared direct from glucose-diacetone (Freudenberg and Ivers, *Ber.*, 1922, **55**, 929).

Preparation of β-*Ethylglucofuranoside* 5 : 6-*Monocarbonate* (IV).—To a rapidly cooled solution of glucose-acetone carbonate (2·75 g.) (dissolved by boiling in 150 c.c. of ethyl alcohol which had been dried over calcium), ethyl-alcoholic hydrogen chloride (21 c.c. of 5*N*) was rapidly added, thus making the concentration of acid 2·25% and that of the sugar derivative 1·6%. By rapid cooling of the alcoholic solution the glucose-acetone carbonate separated in minute crystals which redissolved on heating for 1 hour at 45—50°. The subsequent reaction was followed polarimetrically. A point of inflexion was observed in the rotation–time curve usually after about 6—8 hours, when the rotation was still slightly negative. Beyond this stage positive rotations were quickly reached, and in order to avoid the latter condition the solution was immediately neutralised with silver carbonate, and the filtrate evaporated at 35° under diminished pressure. The syrupy residue crystallised partly and was dissolved in ethyl alcohol containing dry ether. From the solution, β-*ethylglucofuranoside* 5 : 6-*monocarbonate* crystallised. This substance was extremely soluble in water, ethyl alcohol, acetone, and chloroform, but sparingly soluble in dry ether. It was best purified from ether which had not been specially dried, and separated in long silky needles on cautious addition of light petroleum. The ethylglucofuranoside 5 : 6-monocarbonate sintered and melted at 164—165°, and showed $[\alpha]_{5780}^{19°}$ −50·6°, $[\alpha]_{5461}^{19°}$ −55·0° (*c*, 1·1 in water) (Found: C, 46·2; H, 6·0; OEt, 19·1; CO_2, 17·6. $C_9H_{14}O_7$ requires C, 46·15; H, 6·05; OEt, 19·25; CO_2, 18·7%).

The mother-liquors from the above crystallisations yielded a crystalline mixture of α- and β-forms which were separated as the diacetyl derivatives as follows :

2 : 3-*Diacetyl-α-ethylglucofuranoside* 5 : 6-*Monocarbonate and the Corresponding* β-*Isomeride.*—When as much as possible of the β-ethylglucofuranoside 5 : 6-monocarbonate had been separated from the mixture, obtained by the action of acid ethyl alcohol on glucose-acetone carbonate, the mother-liquors were evaporated to a syrup, and from this further crystals gradually separated. These were recrystallised from ethyl acetate or alcohol and ether until a constant m. p. 120—122° was reached and the rotation observed was $[\alpha]^{20\cdot5°}_{5780}$ + 41°. This substance was obviously a mixture of α- and β-forms of ethylglucofuranoside 5 : 6-monocarbonate and possibly a little impurity. The mixture was acetylated by dissolving it in pyridine containing acetic anhydride, and the solution was heated for 2 hours on a water-bath and then diluted with water. A crystalline solid separated immediately; this was collected and recrystallised from ethyl alcohol, aqueous alcohol, or water, forming large spangles, m. p. 159—160° (with slight decomposition and previous sintering at 155°). This was found to be 2 : 3-*diacetyl-α-ethylglucofuranoside* 5 : 6-*monocarbonate*, $[\alpha]^{21°}_{5780}$ + 143°, $[\alpha]^{21°}_{5461}$ + 157° in acetone (*c*, 1·71) (Found : C, 48·8; H, 5·9. $C_{13}H_{18}O_9$ requires C, 49·0; H, 5·7%).

The corresponding β-isomeride was obtained in the same manner, but it crystallised at first with difficulty (yield, 85% of the theoretical). 2 : 3-*Diacetyl-β-ethylglucofuranoside* 5 : 6-*monocarbonate* was considerably more soluble than the α-isomeride, and crystallised from aqueous alcohol in colourless needles, m. p. 79—81°; $[\alpha]^{23°}_{5780}$ — 39°, $[\alpha]^{23°}_{5461}$ — 42° in acetone (*c*, 0·93) (Found : C, 49·1; H, 5·6; OEt, 13·55. $C_{13}H_{18}O_9$ requires C, 49·0; H, 5·7; OEt, 14·15%).

α-*Ethylglucofuranoside* (VIII).—A solution of the above-mentioned 2 : 3-diacetyl-α-ethylglucofuranoside 5 : 6-monocarbonate in acetone was diluted with water and heated on a water-bath with an excess of barium hydroxide solution. The excess of barium hydroxide was neutralised by carbon dioxide and after evaporation of the solution under diminished pressure the residue was extracted with boiling alcohol. The filtered extract was again evaporated, and extracted with ethyl acetate. On evaporating this to dryness and again extracting the residue with ethyl acetate, an almost ash-free product was obtained which crystallised from ethyl acetate, containing a little ethyl alcohol, in colourless needles, m. p. 82—83°; $[\alpha]^{23°}_{5780}$ +106°, $[\alpha]^{23°}_{5461}$ + 116°, $[\alpha]^{23°}_{D}$ + 98° in water (*c*, 1·58) (Found : C, 46·1; H, 8·0; OEt, 20·05. $C_8H_{16}O_6$ requires C, 46·1; H, 7·75; OEt, 21·6%). The α-*ethylglucofuranoside* was stable in contact with Fehling's solution or cold dilute permanganate for a period of several

hours, but was completely hydrolysed in ½ hour on being heated with N/100-hydrochloric acid.

β-*Ethylglucofuranoside* (VI).—The above β-ethylglucofuranoside 5 : 6-monocarbonate was dissolved in N/4-sodium hydroxide solution (exactly 2 mols. of NaOH). The initial rotation (— 82·5°) did not change after the solution had been kept in the cold for several hours. The solution was now evaporated to dryness under diminished pressure at 35°, and the residue extracted several times with ethyl acetate. Evaporation of this solution led to a viscid residue which crystallised when kept in a vacuum desiccator containing phosphoric oxide. It was very hygroscopic. The recrystallisation was effected by dissolving the crystals in dry ethyl acetate containing a trace of ethyl alcohol and then adding dry ether until a slight turbidity appeared. The solution was now kept for some days at — 10°; large clusters of crystals had then accumulated (yield, 85—90%). These were washed twice with dry ethyl acetate, drained on porous tile, and kept over phosphoric oxide in a vacuum. β-*Ethylglucofuranoside* had the following properties: $[\alpha]_D^{26\cdot5^\circ}$ — 86°, $[\alpha]_{57\cdot0}^{26\cdot5^\circ}$ — 93°, $[\alpha]_{5\cdot61}^{26\cdot5^\circ}$ — 101° (*c*, 0·9 in water) (Found: C, 46·2; H, 7·55; OEt, 21·2%). The pure substance was stable to and recoverable unchanged from hot alkali (15%), but easily hydrolysed by N/100-hydrochloric acid at 90°, the hydrolysis being accompanied by the following rotation changes: $[\alpha]_{5780}$ — 91° (initial), — 26° (5 mins.), — 9° (8 mins.), + 17° (12 mins.), + 28° (16 mins.), + 38° (20 mins.), + 43° (25 mins.), + 46° (30 mins.), + 49° (40 mins.). The last value, calculated as for glucose, corresponds to $[\alpha]_{5780}$ + 55°. A comparison was made with Fischer's γ-methylglucoside, which, under these conditions, was hydrolysed at a similar rate. β-Ethylglucofuranoside was not affected by dilute permanganate over a period of several hours, or by Fehling's solution.

β-*Methylglucofuranoside 5 : 6-Monocarbonate* (III).—Glucose-acetone carbonate (1 g.) was dissolved in methyl alcohol (25 c.c.) containing concentrated sulphuric acid (0·3 c.c.). The solution was kept at 45° and the reaction, which was followed polarimetrically, appeared to be complete after 5 hours. The solution was now neutralised with barium carbonate, filtered, and evaporated to dryness under diminished pressure, and the residue extracted with dry methyl alcohol. A small amount of barium methyl sulphate was removed, and the remaining product recrystallised by addition of dry ether to the methyl-alcoholic solution. β-*Methylglucofuranoside 5 : 6-monocarbonate*, m. p. 143—145° (with efferv.), was extremely soluble in ethyl alcohol or water and less so in chloroform, benzene, or ether. $[\alpha]_{5780}^{22^\circ}$ — 66°, $[\alpha]_{5461}^{22^\circ}$ — 75° (*c*, 0·7 in water)

(Found: C, 43·8; H, 5·5; OMe, 14·15; CO_2, 19·3. $C_8H_{12}O_7$ requires C, 43·6; H, 5·5; OMe, 14·1; CO_2, 20·0%).

Glucofuranose 5 : 6-*Monocarbonate* (VII).—(a) *From* β-*ethylglucofuranoside* 5 : 6-*monocarbonate*. 1 G. of this substance was dissolved in 100 c.c. of *N*/50-hydrochloric acid, and the solution kept at 80° during 50 minutes. When the rotation had become constant, the solution was neutralised with silver carbonate and evaporated to small bulk under diminished pressure at 30° and the residue was extracted with boiling ethyl alcohol. This solution was filtered and evaporated to small bulk under diminished pressure; crystals then separated, m. p. 182—183° with efferv. (sintering at about 170°).

(b) *From* β-*methylglucofuranoside* 5 : 6-*monocarbonate*. This material (1 g.) was dissolved in *N*/100-sulphuric acid (38 c.c.). The solution was kept at 91—93° during 2 hours; the rotation had then become constant. The solution was neutralised with barium carbonate, filtered, and evaporated to dryness, and the residue recrystallised from ethyl alcohol; it formed large colourless crystals, m. p. 182—183°.

Glucofuranose 5 : 6-monocarbonate was sparingly soluble in ethyl alcohol, but more soluble in acetone or water. It reduced Fehling's solution actively, decolorised potassium permanganate solution in the cold, but did not restore the colour to Schiff's reagent. $[\alpha]_{5780}^{20°}$ + 18° (*c*, 0·8 in water); probably this represents the equilibrium value, since mutarotation had apparently been instantaneous; no change of reading could be observed from that shown 2 minutes after dissolution in water.

(c) *From glucose-acetone carbonate*. This material (1·9 g.) was dissolved in ethyl alcohol (50 c.c.) containing concentrated hydrochloric acid (2·5 c.c.), and the solution was heated at 70—75° during 40 minutes. It was then evaporated at 45° under diminished pressure, 100 c.c. of water being gradually added so that the volume did not diminish below 50 c.c. The resulting solution showed $[\alpha]_{5780}$ + 15°, and after neutralisation with silver carbonate it was concentrated under diminished pressure, treated with charcoal, and evaporated to dryness. The residue was extracted with hot methyl alcohol, and from this solution glucofuranose carbonate (1·2 g.) crystallised on cooling (yield, 75% of the theoretical). This specimen of *glucofuranose* 5 : 6-*monocarbonate* had the same properties as those indicated for each of the above two preparations (Found: C, 41·0; H, 4·9. $C_7H_{10}O_7$ requires C, 40·8; H, 4·9%).

Phenylosazone of Glucofuranose 5 : 6-*Monocarbonate*.—To glucofuranose monocarbonate, dissolved in warm water, was added phenylhydrazine (3 mols.) in a slight excess of acetic acid; a little

sodium acetate was also introduced to reduce acidity. After the solution had been kept at 100° for 30—40 minutes and then cooled, a yellow crystalline solid separated which corresponded to about half the weight of the glucofuranose monocarbonate used. It appeared to be equally soluble in hot and cold alcohol, but crystallised readily from aqueous alcohol in felted masses of yellow needles, m. p. 202—203° (variable with the rate of heating) (Found: C, 59·35; H, 5·4; N, 14·3. $C_{19}H_{20}O_5N_4$ requires C, 59·35; H, 5·25; N, 14·6%). The properties were in agreement with those expected for the phenylosazone of glucofuranose monocarbonate. It is almost insoluble in water, but gave a precipitate of barium carbonate when heated with aqueous barium hydroxide. The *phenylosazone* showed mutarotation in pyridine solution, $[\alpha]^{21°}_{5780}$ changing from — 103° to — 48° after 4 days. At this stage the solution had darkened and further readings could not be recorded. Treatment of the osazone with a boiling solution of barium hydroxide, followed by rapid filtration of the barium carbonate, led to the crystallisation from the solution of glucose phenylosazone (m. p. 205—206°), identical with that prepared from ordinary glucose.

Anilide of Glucofuranose 5:6-*Monocarbonate.*—The monocarbonate was dissolved in a little hot alcohol, and freshly distilled aniline (3 mols.) was introduced. The solution, after being heated for 3 hours, was allowed to evaporate; the residue crystallised. This was obtained almost pure by washing with alcohol. The *anilide* was insoluble in most organic solvents, slightly soluble in ethyl acetate, and more soluble in ethyl alcohol. From either of the latter it could be crystallised in needles, sintering at 175° and decomposing at 180° (Found: C, 55·75; H, 5·5. $C_{13}H_{15}O_6N$ requires C, 55·5; H, 5·4%). Owing to the length of time required to dissolve the anilide it was impossible to observe mutarotation. The specific rotation appeared to be nearly zero. The anilide of glucofuranose 5 : 6-monocarbonate was converted into glucose-anilide by a similar method to that adopted in the case of the osazone. The unsubstituted glucose-anilide obtained by eliminating the carbonate group from the above compound was identical with that prepared from ordinary glucose.

The authors are grateful to the Department of Scientific and Industrial Research for a Senior Research Award to one of them (C. R. P.), and also to the Government Grant Committee of the Royal Society for a contribution towards the cost of materials.

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[*Received, November 18th*, 1929.]