Carbohydrate Research, 31 (1973) 69–80

STUDIES WITH RADIOACTIVE SUGARS

PART IV[1] THE METHANOLYSIS OF D-FRUCTOSE AND L-SORBOSE

G S BETHELL AND R. J FERRIER

Department of Chemistry, Victoria University of Wellington (New Zealand)

(Received April 2nd, 1973, accepted for publication, April 24th, 1973)

ABSTRACT

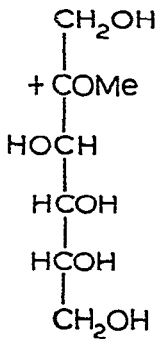
Methanolysis of radioactively labelled D-fructose gives, finally, the α-pyranoside, β-pyranoside, α-furanoside, and β-furanoside in the ratios 3 46 25 26 The corresponding ratios for the L-sorbosides are 92 1 5 2 As with the aldoses, these ketoses mainly give furanosides in kinetically controlled reactions; the pyranosides are then formed as thermodynamic products A primary objective of the work was to examine the role played in the reactions by the acyclic dimethyl acetals, with neither sugar was any such product detected, and it is estimated that their concentrations were never in excess of 0 05% in the reaction components

INTRODUCTION

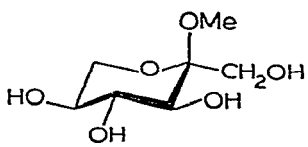
Within recent years, application of refined separatory and analytical methods to the products of the acid-catalysed methanolysis of free sugars has enabled these complex reactions to be followed with a precision not attainable by the earlier investigators[2] However, it has been established for several decades that furanosides are formed from aldoses under kinetic control, whereas pyranosides are the major, final products of the reaction, and this knowledge has been used on many occasions to obtain glycosides of specific ring-size Bishop and his colleagues[3], applying gas–liquid chromatographic methods, confirmed this generalisation They were also able to follow in detail the quantitative significance of each glycoside throughout the course of the methanolysis process, and thus provide the first detailed analysis of the reaction Their methods, however, did not reveal the acyclic dimethyl acetals proposed by Fischer[4] as likely glycoside precursors; only in later work were these detected, and then concurrently, by two groups using ^{14}C-based analytical methods Heard and Barker observed the acetals of arabinose and galactose in the methanolysis products of these sugars[5], and Ferrier and Hatton showed that the analogous compounds were formed during the reaction of xylose and glucose[6] Both investigations revealed that the acetals were never present in more than very small proportions (~2 5%), and led to the conclusion that they were not precursors of the furanosides, but were formed as kinetic products concurrently with them

The acid-catalysed methanolysis reaction has been applied to both D-fructose[7] and, to a lesser extent, L-sorbose[4,8], and the general features of the processes seem

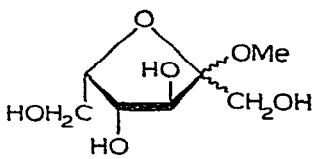
to parallel those applying with the aldoses However, it appears that no detailed investigations of the reactions have been undertaken; in particular, no assessment has been given of the contribution made to the reactions by the acyclic acetals Several features of ketose chemistry led us to suspect that these acetals might be prominent in the reaction Firstly, acyclic species are apparently more prevalent in the chemistry of ketoses than of aldoses, thus, acyclic penta-*O*-acetylhexuloses can be prepared directly[9] (presumably because of the relative difficulty with which the tertiary, anomeric hydroxyl groups can be esterified), and the free sugars[10] and simple analogues[11], although mainly cyclic in aqueous solution, show spectroscopic characteristics which indicate the presence of, in some cases, substantial proportions of acyclic forms Furthermore, trimethylsilylation of D-fructose gives some of the acyclic *keto*-pentaether[12], this being in marked contrast to findings with aldoses[13] Secondly, whereas the mercury(II)-induced methanolysis of aldose dialkyl dithioacetals usually affords methyl glycofuranosides[14], application of this reaction to D-fructose diethyl dithioacetal gives (at least at low temperatures) the dimethyl acetal in good yield[15] It would be expected that such a reaction would proceed by way of ion **1**, or a species closely related to it, and that this would react with methanol in a



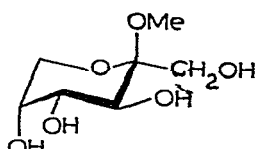
1



2



3



4

kinetically controlled process to give the product Since ion 1 could well be formed at an early stage in the acid-catalysed methanolysis of D-fructose, it seemed highly probable that D-fructose dimethyl acetal would be formed at least as a kinetic product Thirdly, thermodynamic factors also suggest that the acetal, at least in the case of D-fructose, might be found in the reaction products, in the planar zig-zag conformation, it has minimal, energetically unfavourable 1,3-interactions[16], whereas none of the cyclic species is without appreciable destabilising influences

RESULTS AND DISCUSSION

The methods used in this study have been described in detail previously[1 6], and involve carrying out the reactions of ^{14}C-labelled sugars in dry, methanolic hydrogen chloride, removing aliquot samples, neutralising the acid, and separating the components on paper chromatograms The radioactive compounds were located by radioautography, and their relative proportions determined by use of an end-window Geiger tube. Each reaction product was characterised by co-chromatography, in two dimensions, with an authentic sample of inactive material

In experiments carried out with D-fructose and L-sorbose at ~28° with ~0.1% methanolic hydrogen chloride, reaction patterns illustrated in Figs 1 and 2 were established, *i e*, in concurrence with the analogous reactions of aldoses, furanosides are the main, initial products and these then isomerise substantially to pyranosides For sorbose, this latter conversion is almost complete, but with fructose half of the glycosides remain at equilibrium in the five-membered ring form, this result was confirmed by methanolysing methyl β-D-fructopyranoside With methyl α-L-sorbopyranoside (2), all the secondary hydroxyl groups can adopt the preferred equatorial orientation, and this ring form is favoured relative to the furanoid form (3) in which there are two destabilising 1,2-*cis*-interactions Configurational inversion at C-5 (to

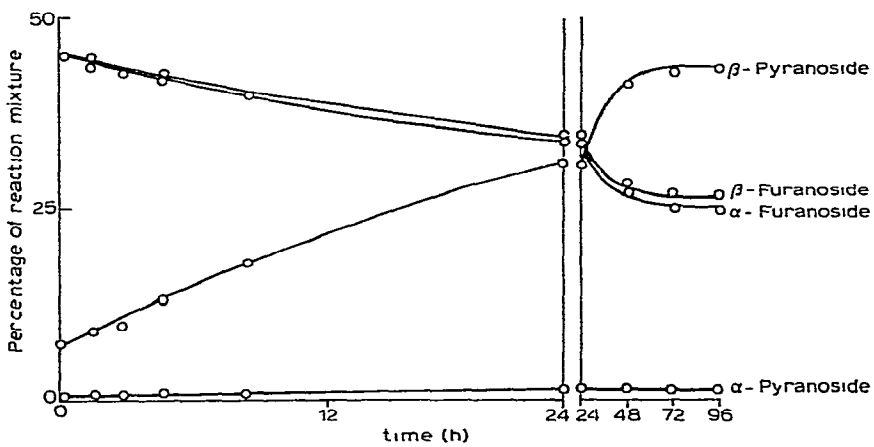


Fig. 1 Products of the reaction between D-fructose (0 5%) and methanolic hydrogen chloride (0 113%) at 27 5° (the sugar had effectively all reacted within 0 5 h).

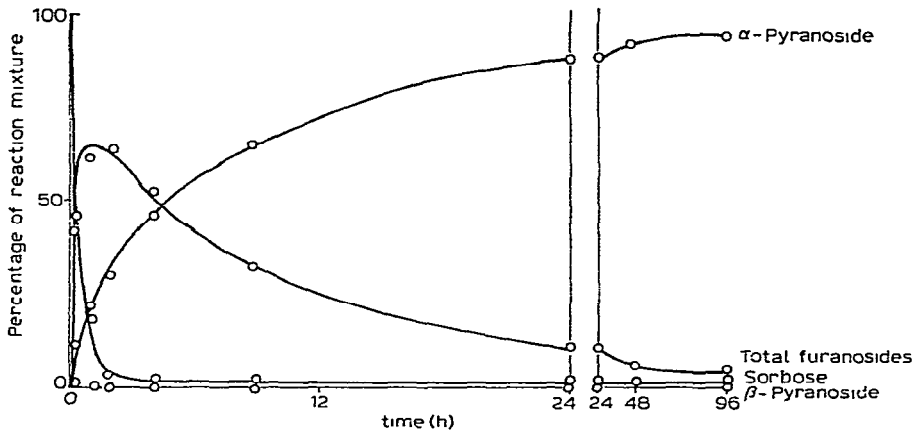


Fig 2 Components in the reaction between L-sorbose (0 5%) and methanolic hydrogen chloride (0 104%) at 28 0°

give the D-fructosides) removes one of these furanoid interactions and requires that at least one of the ring hydroxyl-groups be axial in the pyranosides, and so the furanoside–pyranoside ratio must necessarily be higher for this sugar

Another striking feature of the results is the high preponderance, in both cases, of one of the pyranosides relative to the other This can be ascribed to the strong conformational demands of the groups at the anomeric centre of the hexuloses while the hydroxymethyl group will prefer the equatorial orientation for steric reasons, the methoxyl group will prefer the axial orientation because of the manifestation of the dipolar, anomeric effect Methyl α-L-sorbopyranoside in the illustrated conformation (**2**) is therefore very much more stable than its anomer and, similarly, methyl β-D-fructopyranoside (**4**) is the favoured anomer However, with the fructopyranosides, the ratio of major anomer–minor anomer is very much smaller than for the sorbopyranosides, and this finding can be accounted for by the fact that the sorbosides differ by the interaction energies of three axial hydroxyl-groups (when each anomer is in the chair form with the methoxyl group axial), whereas the fructosides differ by the effect of only one such group From Table I, it can be seen by comparison between the equilibrated ketohexopyranosides and configurationally related aldopentopyranosides (fructosides and arabinosides; sorbosides and xylosides) that these pyranoside ratios are enhanced very substantially in favour of the thermodynamically favoured anomers by the introduction of the hydroxymethyl group at C-1 of the pentosides

For the fructose–arabinose pair, the information on the equilibrated glycosides can be further compared with related information on the free sugars in deuterium oxide (Table I) As noted previously[17], furanoid forms are relatively favoured for the glycosides in methanol and, secondly, the data suggest that a 1,2-*cis*-OH/OMe interaction in furanosides in methanol is more destabilising than the analogous

TABLE I

EQUILIBRATED PERCENTAGES OF SUGARS IN DEUTERIUM OXIDE AND METHYL GLYCOSIDES IN METHANOL

Compound	*Ring form*			
	α-Pyranoid	*β-Pyranoid*	*α-Furanoid*	*β-Furanoid*
Fructose[18]	3	57	9	31
Methyl fructoside	3	4€	25	26
Arabinose[19]	60	35 5	2 5	2
Methyl arabinoside[3b]	24	47	22	7
Methyl sorboside	91	1	5	2
Methyl xyloside[3b]	65	30	— 5	—

OH/OH interaction in water. If the anomeric ratio of fructofuranoses and fructofuranosides depends only upon interactions between anomeric carbon substituents and neighbouring carbon groups (possibly a weak assumption), it can be deduced that the OH/OMe interaction in methyl β-D-fructofuranoside equals the OH/CH_2OH interaction (considered to be the most unfavoured interaction in a furanoid ring[20]) in the anomer, whereas with the free sugar this latter interaction exceeds that of the α-diol

No dimethyl acetals were revealed during these first experiments, and so the early parts of the reactions were examined in detail by repeating the methanolyses with smaller amounts of acid, with a view to revealing possible kinetic products The reaction courses are illustrated in Figs 3 and 4, no acetals were detected on the radioautograms, and counting of radioactivity (on the areas of the papers on which they would have been located) indicated that they were not present in any of the samples examined to an extent of greater than 0 05% Thus, if the dimethyl acetals are formed

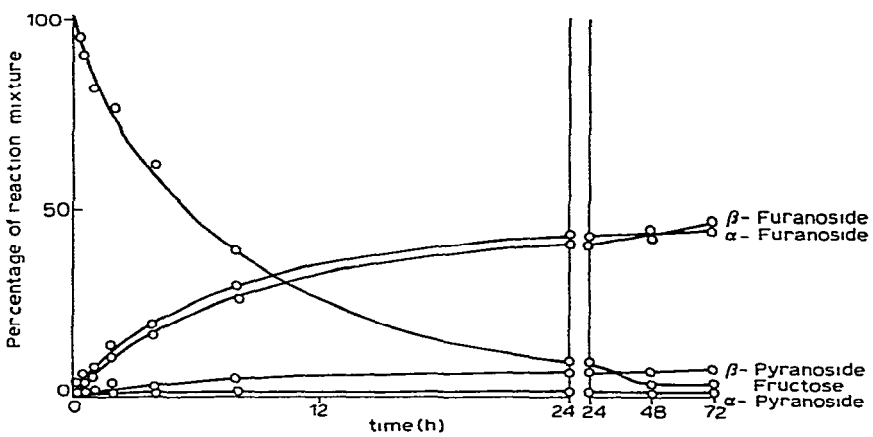


Fig 3 Components in the reaction between D-fructose (0 5%) and methanolic hydrogen chloride (0 0011%) at 26 2°

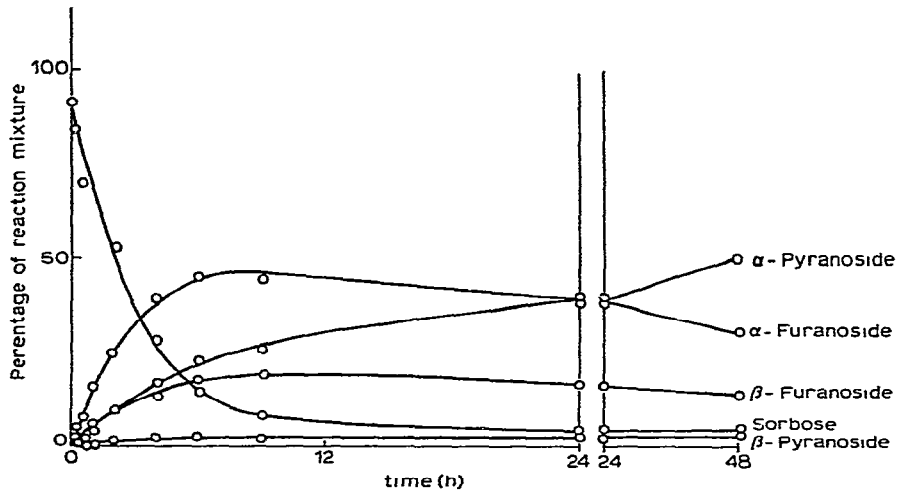


Fig. 4 Components in the reaction between L-sorbose (0 5%) and methanolic hydrogen chloride (0.013%) at 28°.

as kinetically controlled products, they must cyclise to give furanosides extremely rapidly The furanosides are again shown to be early products but, as with some aldoses, they are not initially formed in their equilibrated ratio For both ketoses, as with the xylosides[6 3b] and glucosides[3c], the thermodynamically less-stable furanoside is found initially in higher than its final proportions (Figs 5 and 6) This could arise because of factors which operate during kinetically controlled, ring-closure steps, but it is difficult to speculate since it is not known whether the compounds in question arise from acyclic species or from furanoses

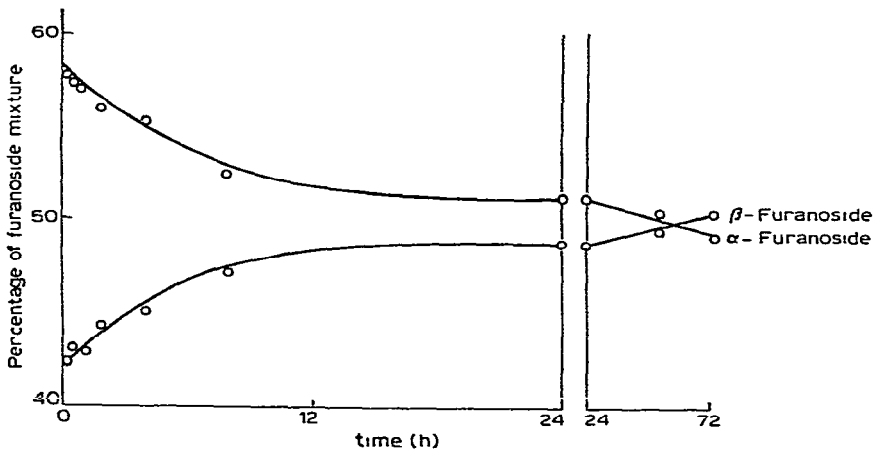


Fig. 5. Proportions of furanosides produced in the reaction between D-fructose (0 5%)and methanolic hydrogen chloride (0.0011%) at 26.2°.

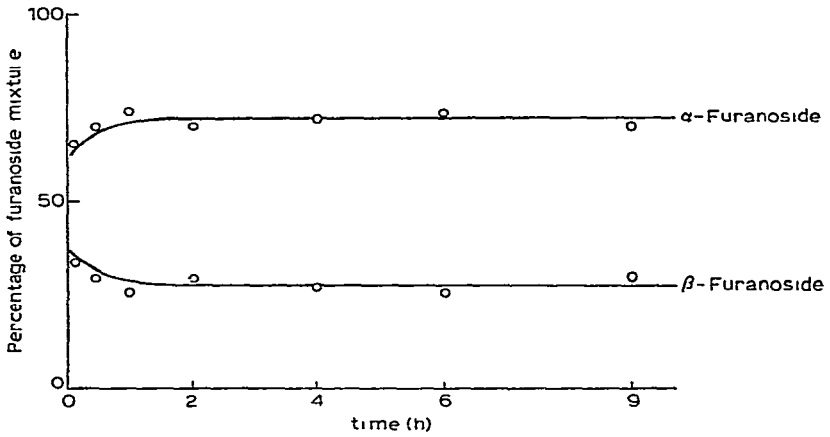


Fig 6 Proportions of furanosides produced in the reaction between L-sorbose (0 5%) and methanolic hydrogen chloride (0 013%) at 28°

Experimental

D-Fructose-*U*-^{14}C and L-sorbose-*U*-^{14}C were obtained from the Radiochemical Centre, Amersham, England, at specific activities of 2–4 mCi/mmole

Inactive glycosides and dimethyl acetals, having the physical constants indicated in Table II, were prepared either by the published methods referred to in this Table or as indicated below Chromatographic mobilities (in butanone saturated with water) are also noted, as are the reductions[21] of periodate ion for the fructose derivatives.

Methyl L-*sorbofuranosides* — L-Sorbose (10 g) was dissolved in methanol (1 litre) containing hydrogen chloride (0.0127%), and the solution was left at room temperature for 8 h, after which time the acid was neutralised with sodium hydrogen carbonate. Removal of the solids and solvent gave a syrup, a portion (5 g) of which was fractionated on a column of cellulose powder, using butanone saturated with water as eluting solvent. The first fraction contained a mixture of furanosides (1.87 g, $R_{SORBOSE}$ 4 3), subsequent fractions contained the α-pyranoside and the free sugar A portion (0 87 g) of the furanoside fraction was treated with benzoyl chloride in pyridine at 0° under standard conditions, and gave two products which were fractionated by preparative t l c The more-mobile product was methyl β-L-sorbofuranoside tetrabenzoate (0 25 g), m p 110–112° (from methanol), $[\alpha]_D$ +17° (*c* 1.0, chloroform) (Found C, 69 1, H, 5 0 $C_{35}H_{30}O_{10}$ calc · C, 68 8; H, 4 9%), and the less-mobile compound was syrupy methyl α-L-sorbofuranoside tetrabenzoate (0 6 g), $[\alpha]_D$ −115° (*c* 0 75, chloroform) (Found C, 67.7; H, 5.0%). The n m r. spectra of the isomers were consistent with the assigned structures. each showed the presence of one methyl group and four ester groups, two of which were primary (primary ester protons resonating at δ 4 3–5 1, whereas secondary, ring-ester protons resonated at δ 5 8–6 3).

TABLE II

PROPERTIES OF METHYL GLYCOSIDES AND DIMETHYL ACETALS

Compound	*Mobility*[a]	*Periodate reduction (moles/mole)*	*Observed*		*Literature*		*Ref*
			M p (degrees)	$(\alpha)_D$ *(degrees)*	*M p (degrees)*	$(\alpha)_D$ *(degrees)*	
Methyl α-D-fructopyranoside[b]	3.78	2 0	—	+74 (EtOH)	102	+93 (EtOH)	22
Methyl β-D-fructopyranoside	2 07	2 2	118–119	−183 (H_2O)	119–120	−172 (H_2O)	23
Methyl α-D-fructofuranoside	4 91	1 0	—	+87 (H_2O)	69	+93 (H_2O)	24
Methyl β-D-fructofuranoside	2 51	1 0	—	−49 (H_2O)	—	−47 (H_2O)	6[e]
D-Fructose dimethyl acetal[c]	5 15	2 9	130–131	−42 (H_2O)	107–108	−46 (H_2O)	24
Methyl α-L-sorbopyranoside	2 60	—	118–119	−87 (H_2O)	120–122	−88 (H_2O)	4
Methyl β-L-sorbopyranoside	6 00	—	—	+32 (H_2O)	106	+39 (H_2O)	25
Methyl α-L-sorbofuranoside	4 50	—	—	−85 (EtOH)	—	—	See below
Methyl β L-sorbofuranoside	4 10	—	—	+60 (EtOH)	—	—	
L-Sorbose dimethyl acetal	5 64	—	—	−42 (EtOH)	—	—	

[a]Chromatographic mobilities measured on paper chromatograms eluted with butanone saturated with water, and expressed relative to the respective free-sugar [b]Characterised as the tetra-acetate, m p. 111–112°, $(\alpha)_D$ +44° (*c* 1, chloroform), lit [26] m p 112°, $(\alpha)_D$ +45° (chloroform) [c]Found C, 42 6, H,8 ? $C_8H_{18}O_7$ calc C, 42 5, H, 8 0% The compound was characterised as the penta-acetate, m p 108–109°, $(\alpha)_D$ 0° (*c* 1, chloroform), lit [15] m.p 109°, $(\alpha)_D$ 0° (chloroform)

Debenzoylation of the minor tetrabenzoate (0 24 g) was accomplished by using sodium methoxide in methanol, the sodium being removed after completion of the reaction by the use of cationic resin in the presence of a little pyridine The solvent was removed, and an aqueous solution of the residual syrup was twice extracted with light petroleum and then concentrated to dryness to give methyl β-L-sorbofuranoside (73 mg, 95%), $[\alpha]_D$ +60° (*c* 0.7, ethanol) Similarly, the major benzoate (0.6 g) gave methyl α-L-sorbofuranoside (0 17 g, 89%), $[\alpha]_D$ −85° (*c* 1 7, ethanol) These furanosides have, apparently, not been isolated before (see, however, Ref 27), although their acetates have been described[28], as with the benzoates, only the β-ester is crystalline

L-*Sorbose dimethyl acetal* — L-Sorbose diethyl dithioacetal (0 5 g) was dissolved in dry methanol (6 ml) and, at −80°, mercury(II) oxide (1 g) was added followed by a saturated, methanolic solution of mercury(II) chloride (1 05 g, 2 2 mol) The mixture was shaken at −80° for 48 h, and t l c then indicated that the starting material had been converted into both furanosides together with a major product ($R_{SORBOSE}$ 5 64) which was separable from the four glycosides In addition, a small amount of sorbose was produced After separation on a column of cellulose, the acetal was obtained from the main product in 25% yield, $[\alpha]_D$ −42° (*c* 0 9, ethanol) The n m r spectrum in pyridine showed two equal methoxyl resonances (δ 3 29, 3 38) similar to those (δ 3 35, 3 43) in the spectrum of the fructose analogue The mass spectrum of the derived acetate showed a small molecular ion (*m/e* 436) and major peaks at *m/e* 405, 363, 345, 331, 303, and 289, consistent with the following ions $(M-OMe)^+$, $(M-OMe-CH_2CO)^+$, $(M-OMe-AcOH)^+$, $(M-OMe-HOMe-CH_2CO)^+$, $(M-OMe-CH_2CO-AcOH)^+$, and (M−C-1, C-2, and substituents)$^+$

Radiochemical methods — The methods employed were those described previously[1 6], however, no chemically inert, radioactive reference compound was used, nor were corrections made for possible preferential absorption of compounds on the solids employed for neutralisation of the acid catalyst, nor for distances travelled on chromatograms After elution from chromatograms, radioactive products of methanolysis were mixed with small samples of appropriate, inactive glycosides and co-chromatographed on square papers developed in one direction with butanone saturated with water and in the other (90°) with 1-butanol–ethanol–water (4 1 5, upper phase) The active samples were located by radioautography, and the inactive materials with a silver nitrate spray reagent (for sorbose compounds) and with ethanol containing 20% conc hydrochloric acid (for fructose compounds)

Methanolysis of D-*fructose* (*the complete reaction*) — D-Fructose (5 mg) and D-fructose-^{14}C (10 μCi) were dissolved in dry methanol, and the solution was diluted to 1 0 ml by the addition of methanolic hydrogen chloride so that the final concentration of acid was 0 113% The flask was placed in a thermostated bath at 27 5 ±0 1° and aliquot samples were withdrawn at intervals. The acid was neutralised by the addition of a few grains of Deacidite FF(HO^-) resin, and the solutions were subjected to paper chromatography (24 h, using butanone saturated with water) The results of radioactivity counting of the developed chromatogram are given in Table III and are

represented diagramatically in Fig. 1, the final proportions of α-pyranoside, β-pyranoside, α-furanoside, and β-furanoside were 3, 46, 25, and 26% in this experiment In a duplicate experiment carried out under identical conditions, except that the reaction was allowed to proceed for 6 days, the corresponding percentages were 3, 48, 23, and 26; when radioactive methyl β-D-fructopyranoside (obtained by elution from a chromatogram) was treated for 6 days at 22° in methanolic hydrogen chloride (0.113%), the figures were 2, 50, 23, and 25%. It is concluded that the initial figures represent, to within experimental error, the concentrations of an equilibrated set of methyl fructosides under these conditions

TABLE III

ACTIVITIES (COUNTS/MIN)[a] OF THE RESOLVED COMPONENTS FROM THE METHANOLYSIS OF D-FRUCTOSE[b] AT 27 5°

Compound	*Time (h)*								
	0 5	*1 5*	*3*	*5*	*9*	*24*	*48*	*72*	*96*
D-Fructose	720	<500	<500	<500	<500	<500	<500	<500	<500
α-Pyranoside	235	290	300	350	570	820	930	1060	1170
β-Pyranoside	3370	4110	4320	5850	9510	14530	17100	17650	18600
α-Furanoside	17920	19190	17870	18740	20350	15300	11350	10160	10300
β-Furanoside	17930	19350	18010	18990	21150	15590	11730	10860	10600

[a]Counts are corrected for paralysis and for background count [b]D-Fructose, 0 5%, hydrogen chloride, 0 113%)

Methanolysis of L-*sorbose* (*the complete reaction*) — L-Sorbose (7 5 mg) and L-sorbose-^{14}C (15 μCi) were treated, as described above, with methanolic hydrogen chloride (1 5 ml, 0 104%) at 28.0 ±0.1°. Aliquot samples (75 μl) were analysed, as previously indicated, after neutralisation of the acid with solid sodium hydrogen carbonate The results are given in Table IV and are represented in Fig 2. In this

TABLE IV

ACTIVITIES (COUNTS/MIN)[a] OF THE RESOLVED COMPONENTS FROM THE METHANOLYSIS OF L-SORBOSE[b] AT 28 0°

Compound	*Time (h)*								
	0.25	*0 5*	*1*	*2*	*4*	*9*	*24*	*48*	*96*
L-Sorbose	22530	9430	7900	1750	1590	1665	790	750	1130
α-Pyranoside	5960	11210	16790	21570	22550	50330	39090	57680	69500
β-Pyranoside	230	340	330	310	320	540	640	320	550
α- + β-Furanosides	21620	32670	32760	39080	25690	25400	5920	4720	4870

[a]Counts are corrected for paralysis and for background count [b]L-Sorbose, 0 5%; hydrogen chloride 0 104%).

experiment, the anomeric furanosides were poorly resolved and were therefore determined together.

Methanolysis of D-*fructose (early stages of the reaction).* — D-Fructose (7 5 mg) and D-fructose-^{14}C (15 μCi) were treated, as described above, with methanolic hydrogen chloride (1 5 ml, 0 0011%) at 26 2 $\pm$0.1° Aliquot samples (100 μl) were analysed after neutralisation with Deacidite FF(HO$^-$) resin, and the results are given in Table V and are represented in Fig 3. The furanosides are treated separately in Fig 5

TABLE V

ACTIVITIES (COUNTS/MIN)[a] OF THE RESOLVED COMPONENTS FROM THE METHANOLYSIS OF D-FRUCTOSE[b] AT 26 2°

Compound	*Time (h)*								
	0 25	*0 5*	*1*	*2*	*4*	*8*	*24*	*48*	*72*
D-Fructose	57410	57320	48070	44820	44630	28450	7130	1640	815
α-Pyranoside	80	100	140	200	340	460	600	480	400
β-Pyranoside	250	330	420	670	1500	3600	4970	4690	4200
α-Furanoside	1140	2660	4410	7640	14580	21200	33580	31360	27160
β-Furanoside	840	1990	3300	6080	11990	19080	32030	30710	27720

[a]Counts are corrected for paralysis and for background count. [b]D-Fructose, 0.5%, hydrogen chloride, 0 0011%)

Methanolysis of L-*sorbose (early stages of the reaction)* — L-Sorbose (7.5 mg) and L-sorbose-^{14}C (15 μCi) were treated, as described above, with methanolic hydrogen chloride (1 5 ml, 0 013%) at 28 0 $\pm$0 1°. Aliquot samples (75 μl) were analysed after neutralisation with solid sodium hydrogen carbonate The results are given in Table VI and are represented in Fig. 4 The furanosides are treated separately in Fig 6.

TABLE VI

ACTIVITIES (COUNTS/MIN)[a] OF THE RESOLVED COMPONENTS FROM THE METHANOLYSIS OF L-SORBOSE[b] AT 28 0°

Compound	*Time (h)*								
	0.25	*0 5*	*1*	*2*	*4*	*6*	*9*	*24*	*48*
L-Sorbose	38250	42410	37830	28660	15610	8810	5210	3020	3360
α-Pyranoside	900	1380	2900	5860	9560	13610	15120	26250	35740
β-Pyranoside	35	40	100	70	120	130	150	320	340
α-Furanoside	1790	4180	8580	13930	21180	27190	25420	26910	22770
β-Furanoside	970	1740	2990	5810	7740	10030	11130	10500	10130

[a]Counts are corrected for paralysis and for background count [b]L-Sorbose, 0 5%, hydrogen chloride, 0 013%)

ACKNOWLEDGMENTS

The authors thank Professors J F Duncan and W G. Overend for their assistance One of them (G S B) acknowledges with thanks the award of an S R C studentship in England and its continuance in New Zealand, and also of travel grants from the British Council and Victoria University of Wellington

REFERENCES

1 Part III R J FERRIER, L R HATTON, AND W G OVEREND, *Carbohyd Res*, 8 (1968) 56
2 J CONCHIE, G A. LEVVY, AND C A MARSH, *Advan Carbohyd Chem*, 12 (1957) 157
3 C T BISHOP AND F P COOPER, *Can J Chem*, (*a*) 40 (1962) 224, (*b*) 41 (1963) 2743, (*c*) V SMIRNYAGIN AND C T BISHOP, 46 (1968) 3085
4 E FISCHER, *Ber*, 28 (1895) 1145
5 D D HEARD AND R BARKER, *J Org Chem*, 33 (1968) 740
6 R J FERRIER AND L R HATTON, *Carbohyd Res*, 6 (1968) 75
7 (*a*) E FISCHER, *Ber*, 28 (1898) 1160, (*b*) P A LEVENE, A L RAYMOND, AND R T DILLON, *J Biol Chem*, 95 (1932) 699, (*c*) C B PURVES AND C S HUDSON, *J Amer Chem Soc*, 56 (1934) 708, (*d*) H H SCHLUBACH AND H E BARTELS, *Ann*, 541 (1939) 76, (*e*) I AUGESTAD, E BERNER, AND E WEIGNER, *Chem Ind (London)*, (1953) 376, (*f*) E BAYER AND R WIDDER, *Ann*, 686 (1965) 181, (*g*) G W O'DONNELL AND G N RICHARDS, *Austr J Chem*, 25 (1972) 907
8 R. L WHISTLER AND R M HIXON, *J Amer Chem Soc*, 59 (1937) 2047
9 F B CRAMER AND E PACSU, *J Amer Chem Soc*, 59 (1937) 1148, H ZINNER AND U SCHNEIDER, *Chem Ber*, 96 (1963) 2159
10 G R. GRAY AND R BARKER, *Biochemistry*, 9 (1970) 2454, C A SWENSON AND R BARKER, *ibid*, 10 (1971) 3151, G AVIGAD, S ENGLARD, AND I LISTOWSKY, *Carbohyd Res*, 14 (1970) 365
11 K JAMES AND S J ANGYAL, *Aust J Chem*, 25 (1972) 1967, J E WHITING AND J T EDWARD, *Can J Chem*, 49 (1971) 3799
12 H C CURTIUS, M MUELLER, AND J A VOELLMIN, *J Chromatogr*, 37 (1968) 216
13 C T. BISHOP, *Advan Carbohyd Chem*, 19 (1964) 95
14 J W GREEN, *Advan Carbohyd Chem*, 21 (1966) 95
15 E PACSU, *J Amer Chem Soc*, 61 (1939) 1671
16 D HORTON AND P L DURETTE, *Advan Carbohyd Chem Biochem*, 26 (1971) 49
17 S J ANGYAL, *Angew Chem Int Ed Engl*, 8 (1969) 157
18 D DODDRELL AND A ALLERHAND, *J Amer Chem Soc*, 93 (1971) 2779
19 S J ANGYAL AND V A PICKLES, *Aust J Chem*, 25 (1972) 1695
20 S J ANGYAL AND V A PICKLES, *Aust J Chem*, 25 (1972) 1711
21 G O ASPINALL AND R J FERRIER, *Chem Ind (London)*, (1957) 1216
22 H H SCHLUBACH AND G A SCHROTER, *Ber*, 63 (1930) 364
23 C S HUDSON AND D H BRAUNS, *J Amer Chem Soc*, 38 (1916) 1216
24 E PACSU, *J Amer Chem Soc*, 61 (1939) 1671.
25 H H SCHLUBACH AND G GRAEFE, *Ann*, 532 (1937) 211
26 H H SCHLUBACH AND G A. SCHROTER, *Ber*, 61 (1928) 1216
27 J K N JONES AND W W REID, *Can J Chem*, 33 (1955) 1682
28 T MAEDA, K. TORI, S SATOH, AND K. TOKUYAMA, *Bull Chem Soc Jap*, 41 (1968) 2495