597. *Deoxy-sugars. Part VI. The Constitution of β-Methyl-2-deoxy-L-ribopyranoside and of αβ-Methyl-2-deoxy-L-ribofuranoside.*

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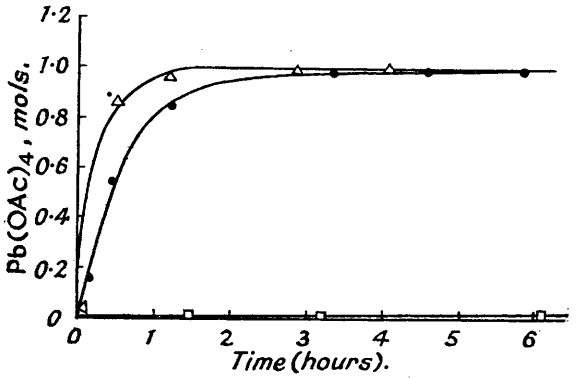
The synthesis and proof of structure of β-methyl-2-deoxy-L-ribopyranoside and of αβ-methyl-2-deoxy-L-ribofuranoside are described.

In Part V (this vol., p. 1879) we described a reinvestigation and improvement of the glycal method of preparing 2-deoxy-D-ribose from D-arabinal, and the preparation of several derivatives suitable for characterising the deoxy-sugar. In continuation of our study of 2-deoxyribose, we examined the methylglycopyranoside and methylglycofuranoside derivatives. We have prepared methyl-2-deoxyribo-pyranoside and -furanoside and established their structures.

According to the Fischer method (*Ber.*, 1893, **26**, 2400; 1895, **28**, 1145) of preparing the methyl glycosides, 2-deoxy-L-ribose was heated with 0·5% methanolic hydrogen chloride. Polarimetric observations indicated that, even after 17 hours, either the formation of the

Fig. 1.



● *β-Methyl-2-deoxy-L-ribopyranoside.* △ *α-Methyl-2-deoxy-L-ribopyranoside.*
□ *αβ-Methyl-2-deoxy-D-ribofuranoside.*

equilibrium mixture of 2-deoxy-α- and -β-methylriboside had not been completed, or degradation of the equilibrium mixture to optically inactive products was occurring during the long period of heating. The treatment of 2-deoxy-L-ribose with methanolic hydrogen chloride was therefore repeated under milder conditions (1% methanolic hydrogen chloride at 20°). Polarimetric observations indicated that after 18 hours equilibrium was reached. Neutralisation of the acid and removal of the solvent gave a syrup which crystallised spontaneously and was separated by fractional crystallisation and chromatography into pure β- (I) and *α-methyl-2-deoxyribopyranoside* (II). (The reasons for assigning the pyranose structure to these compounds are given below.) Both glycosides were extremely soluble in water and common organic solvents except ether, benzene, and light petroleum.

When 2-deoxy-L-ribose was treated at 20° for only 12 minutes with methyl alcohol containing a lower concentration (0·1%) of hydrogen chloride, syrupy *αβ-methyl-2-deoxy-L-ribofuranoside* (III) was obtained. *αβ-Methyl-2-deoxy-D-ribofuranoside* was prepared similarly.

The structures of the glycosides were established by studying the action of lead tetra-acetate, which oxidises hydroxyl groups on contiguous carbon atoms. From the formulæ of 2-deoxy-methylribopyranoside (I) or (II) and of methyl-2-deoxyribofuranoside (III), it is apparent that the former should readily reduce 1 mole of lead tetra-acetate, whereas the latter will be unaffected. This was borne out in practice with the α- and β-methyl-2-deoxy-L-ribosides (I) and (II) and αβ-methyl-2-deoxy-L-riboside (III) described above (see Fig. 1). Thus the first pair of glycosides has the pyranose structure, and the αβ-glycoside has a furanose structure. These results were confirmed by conversion of L-arabinal (which has been proved to have a pyranose structure) by methanolic hydrogen chloride into β-methyl-2-deoxy-L-ribopyranoside, identical with that already described. That the two methyl-2-deoxyribopyranosides have been correctly designated as α- and β-forms is based on the following arguments.

The specific rotation ($[\alpha]_D$ + 210°) of the methyl-2-deoxy-L-ribopyranoside (m. p. 83—84°)

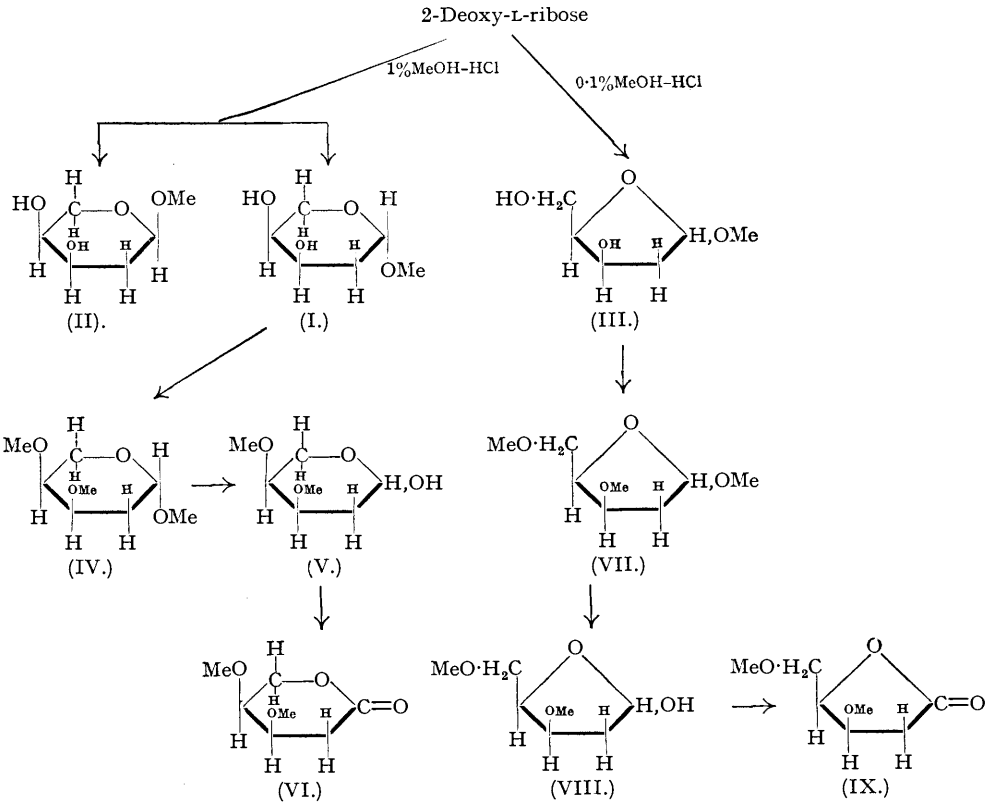
in methanol (see Experimental section) was greater in the positive direction than the specific rotation (+ 93°) of the syrupy αβ-methyl-2-deoxy-L-ribopyranoside in methanol. Consequently, the glycoside, m. p. 83—84°, was designated β- in accordance with the well-known convention (Hudson, *J. Amer. Chem. Soc.*, 1909, **31**, 66). The other crystalline methyl-2-deoxy-L-ribopyranoside must be the α-isomer, as shown by the specific rotation ($[\alpha]_D$ — 70°) in methanol.

The α–β relationship of the two methyl-2-deoxyribopyranosides is evident from a consideration of the difference in molecular rotations. The molecular rotations of the α- and β-forms ($[M]_\alpha$ and $[M]_\beta$ respectively) of the methylglycopyranosides of L-arabinose, 2-deoxy-L-ribose, D-glucose, and 2-deoxy-D-glucose are compared in Table I. There is good agreement between

TABLE I.

Methylglycopyranosides of	Isomer.	M. p.	$[\alpha]_D$ in water.	$[M]$.	$[M]_\alpha-[M]_\beta$.	Reference.
L-Arabinose	α	131°	+ 17·3°	2,840°	−37,420°	Hudson, *J. Amer. Chem. Soc.*, 1925, **47**, 270.
,,	β	169	+245·5	40,260		
2-Deoxy-L-ribose	α	99—100	− 43·4	− 6,420	−36,360	
,,	β	83— 84	+202·3	29,940		
D-Glucose	α	168	+158·9	30,830	+37,030	Riiber, *Ber.*, 1924, **57**, 1797; Patterson and Robertson, *J.*, 1929, 300.
,,	β	110	− 31·97	− 6,200		
2-Deoxy-D-glucose	α	91— 92	+138	+24,600	+33,180	Bergmann *et al.*, *Ber.*, 1922, **55**, *B*, 158; 1921, **54**, *B*, 440.
,,	β	122—123	− 48·2	− 8,580		

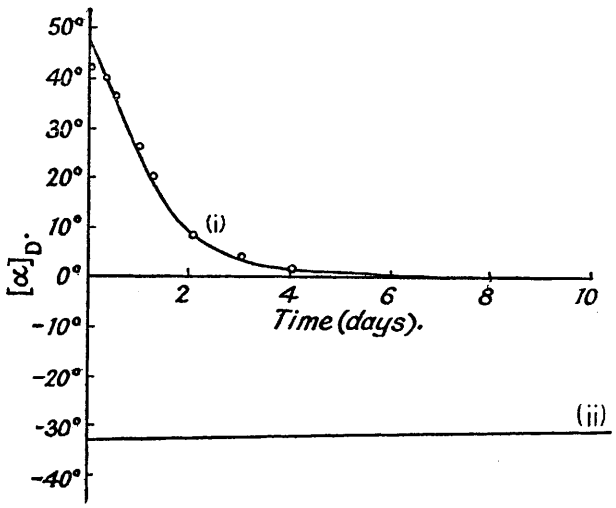
the difference in the molecular rotations of the respective α- and β-forms of methyl-2-deoxy-L-ribopyranoside and of methyl-L-arabopyranoside.



The α–β relation of the two new methyl-2-deoxy-L-ribopyranosides was further confirmed by the observations which were made (polarimetrically) that 1% methanolic hydrogen chloride separately converts each glycoside into the α–β mixture from which they were initially isolated.

Proof of the ring structure of the sugar glycosides was then sought by the classical methods of carbohydrate chemistry, involving methylation of the glycoside, hydrolysis of the fully methylated derivative, oxidation of the products to methylated lactones, study of the rates of hydrolysis of the methylated lactones in water, etc. (Carter, Robinson, and Haworth, *J.*, 1930, 2125). Methylation of β-methyl-2-deoxy-L-ribopyranoside with silver oxide and methyl iodide was achieved only with difficulty, being incomplete after eight treatments. Consequently, the glycoside was methylated by the use of the liquid-ammonia technique (Muskat, *J. Amer. Chem. Soc.*, 1934, **56**, 693, 2449; Freudenberg and Boppel, *Ber.*, 1938, **71**, 2505). Smooth methylation then occurred and 3 : 4-*dimethyl* β-*methyl*-2-*deoxy*-L-*ribopyranoside* (IV) was obtained as a colourless syrup. This compound was stable in 0·01N-hydrochloric acid at room temperature, but when it was heated at 100° for 0·25 hour the glycosidic group was completely removed and 3 : 4-*dimethyl* 2-*deoxy*-L-*ribopyranose* (V) was obtained as a colourless syrup. Oxidation of this methylated sugar with bromine in water afforded syrupy 3 : 4-*dimethyl* 2-*deoxy*-L-*ribonolactone* (VI), which with phenylhydrazine in ether gave a crystalline *phenylhydrazide*.

FIG. 2.



(*i*) 3 : 4-*Dimethyl*-2-*deoxy*-L-*ribono*-δ-*lactone*. (*ii*) 3 : 5-*Dimethyl*-2-*deoxy*-L-*ribono*-γ-*lactone*.

A similar series of reactions was carried out on αβ-methyl-2-deoxy-L-ribofuranoside (III). Methylation in liquid ammonia with sodium and methyl iodide gave 3 : 5-*dimethyl* αβ-*methyl*-2-*deoxy*-L-*ribofuranoside* (VII), although greater difficulty was experienced than in the case of the pyranose isomer. Hydrolysis of the glycosidic group by 0·01 N-hydrochloric acid at 100° yielded 3 : 5-*dimethyl* 2-*deoxy*-L-*ribofuranose* (VIII) as a colourless liquid. Oxidation of this in the normal way with bromine water gave 3 : 5-*dimethyl* 2-*deoxy*-L-*ribonolactone* (IX). The rates of hydrolysis of the lactones (VI) and (IX) were measured polarimetrically at room temperature. The hydrolysis of 3 : 4-dimethyl 2-deoxy-L-ribonolactone (VI) was complete in approximately 96 hours, whereas 3 : 5-dimethyl 2-deoxy-L-ribonolactone (IX) was hydrolysed exceedingly slowly (see Fig. 2), showing that the original glycosides (I) and (III), from which they were derived, must have had the pyranoside and furanoside structure, respectively.

The complementary reaction of the rate of lactonization of δ- and γ-hydroxy-aldonic acids does not appear to have been as closely studied as the rate of hydrolysis of the lactones. From the information available concerning various methylated aldonic acids, δ- and γ-hydroxy-aldonic acids are not sharply divisible into two classes on this basis. In the cases of 2 : 3 : 4-trimethyl L-arabonic acid (Drew, Goodyear, and Haworth, *J.*, 1927, 1237) and 2 : 3 : 5-trimethyl L-arabonic acid (Pryde and Humphreys, *J.*, 1927, 559) lactonization is complete in 48 and 24 hours, respectively; 2 : 3 : 4 : 6-tetramethyl D-gluconic acid (Drew *et al.*, *loc. cit.*) and 2 : 3 : 5 : 6-tetramethyl D-gluconic acid (*loc. cit.*) require 6 and 4 days, respectively.

In contrast, the work of Isbell (*J. Res. Nat. Bur. Stand.*, 1942, **28**, 95) may be quoted which was concerned with the changes that occur when D-gluconic acid is dissolved in water. The interpretation which he gives to his experiments is that initially δ- and γ-lactones are formed simultaneously, but that the δ-lactone is produced more rapidly and reaches a maximum con-

centration in 4—5 hours, after which its concentration decreases as the aldonic acid is slowly converted into γ-lactone. We studied the rate of lactonization of 3 : 4- and 3 : 5-dimethyl 2-deoxy-L-ribonic acid (see Experimental section). The lactonization of 3 : 4-dimethyl 2-deoxy-L-ribonic acid ($[\alpha]_D^{18}$ + 3·5° ⟶ 9·6°) was complete in 2·5 days, but that of 3 : 5-dimethyl 2-deoxy-L-ribonic acid ($[\alpha]_D^{20}$ — 1·32° ⟶ — 20°) was not complete after 22 days. The behaviour of the two acids is thus very dissimilar but, because of the conflicting evidence recorded above, the results in themselves cannot be made the basis of allocation of the two methylated deoxyribonolactones to the δ- and γ-class of lactones.

Experimental.

α- and β-Methyl-2-deoxy-L-ribopyranoside.—2-Deoxy-L-ribose (3·27 g.) was dissolved in 1% methanolic hydrogen chloride solution (60 c.c.) at room temperature. After 18 hours the solution {$[\alpha]_D^{20}$ + 103° (calculated in terms of the weight of 2-deoxy-L-ribose); $[\alpha]_D^{20}$ + 93·2° (corrected value)} was neutralised with silver carbonate and filtered, and the solvent removed from the filtrate by evaporation *in vacuo* at 40°. Spontaneous crystallisation of the resulting syrup gave a solid (1·5 g.; m. p. 66—70°) which was purified by recrystallisation from ether or benzene (0·9 g.; m. p. 18—82°). Repeated recrystallisation of a small portion of this solid gave pure *β-methyl-2-deoxy-L-ribopyranoside*, m. p. 83—84°, $[\alpha]_D^{20}$ + 202·3° (*c*, 0·88 in water), +210° (*c*, 0·78 in methanol), +193° (*c*, 0·64 in chloroform) (Found: C, 48·5; H, 8·2. $C_6H_{12}O_4$ requires C, 48·6; H, 8·1%).

Concentration of the mother-liquors from the crude β-methyl-2-deoxy-L-ribopyranoside yielded further crystalline material (0·5 g., m. p. 68—75°), which was dissolved in 1 : 1 (vol.) benzene–chloroform (40 c.c.) and run on a 15-cm. alumina column wetted with the same solvent mixture. Elution with 3 : 1 (vol.) benzene–chloroform gave a crude α-methyl-pyranoside (0·14 g.) in the first fractions, which after repeated recrystallisation from benzene gave pure *α-methyl-2-deoxy-L-ribopyranoside*, m. p. 99—100°, $[\alpha]_D^{20}$ — 43·4° (*c*, 0·97 in water), —70° (*c*, 0·80 in methanol), —176° (*c*, 0·81 in chloroform) (Found: C, 48·6; H, 8·1. $C_6H_{12}O_4$ requires C, 48·6; H, 8·1%).

Oxidation of α- and β-Methyl-2-deoxy-L-ribopyranoside with Lead Tetra-acetate.—β-Methyl-2-deoxy-L-ribopyranoside (0·0259 g.) was dissolved in glacial acetic acid (50 c.c.) containing excess of lead tetra-acetate (0·69 g.). One mol. of β-methyl-2-deoxy-L-ribopyranoside consumed lead tetra-acetate in the following way:

Time (hours)	0·175	0·55	1·238	3·117	4·667	5·667
Mol. consumed	0·165	0·538	0·847	0·97	1·01	1·05

Similarly, β-methyl-2-deoxy-L-ribopyranoside (0·0299 g.) was dissolved in glacial acetic acid (50 c.c.) containing excess of lead tetra-acetate (0·69 g.). One mol. of this pyranoside consumed lead tetra-acetate as follows:

Time (hours)	0·067	0·596	1·266	2·626	3·90
Mol. consumed	0·0536	0·910	0·983	1·00	1·00

Treatment of L-Arabinal with Methanolic Hydrogen Chloride.—L-Arabinal (2 g.) was dissolved in 1% methanolic hydrogen chloride at room temperature. After 2—3 days the solution was neutralized with silver carbonate and filtered. Evaporation of the solvent from the filtrate gave a syrup. This was dissolved in benzene (20 c.c.) and then adsorbed on an alumina column. Elution of the column with a large amount of benzene gave β-methyl-2-deoxy-L-ribopyranoside (0·2 g.), m. p. alone or in admixture with an authentic specimen 80—83°. (Our thanks are due to Mr. B. Howe, B.Sc., for assistance with this experiment.)

Treatment of α- and β-Methyl-2-deoxy-L-ribopyranoside with Methanolic Hydrogen Chloride.—(*a*) α-Methyl-2-deoxy-L-ribopyranoside (0·0091 g.) was dissolved in 1% methanolic hydrogen chloride (1·49 c.c.) at room temperature. Polarimetric observations were as follows:

Time (hours)	0·30	0·635	0·88	1·22	1·50	2·50	4·50
$[\alpha]_D^{20}$ (*c*, 0·61)	+27·4°	+51·6°	+77°	+88·2°	+91·5°	+94·4°	+94·4°

(*b*) β-Methyl-2-deoxy-L-ribopyranoside (0·0101 g.) was dissolved in 1% methanolic hydrogen chloride (1·5 c.c.) at room temperature. Polarimetric observations were as follows:

Time (hours)	0·083	0·15	2·75	4·5
$[\alpha]_D^{20}$ (*c*, 0·67)	+162°	+160°	+108°	+102°

3 : 4-*Dimethyl β-Methyl-2-deoxy-L-ribopyranoside.*—β-Methyl-2-deoxy-L-ribopyranoside (1·73 g.) was dissolved in liquid ammonia (200 c.c.) contained in a 1-l. flask cooled by means of solid carbon dioxide. Sodium (1·62 g., three times the theoretical quantity) was added cautiously, and the blue solution was stirred vigorously at intervals. After 1 hour, methyl iodide (14 c.c., three times the theoretical quantity based on the weight of sodium used) was added cautiously. After evaporation of the liquid ammonia by setting the mixture aside overnight, ether was added to the slightly yellow residual syrup. Anhydrous magnesium sulphate was added, and the solid was repeatedly extracted with ether by heating under reflux. The ethereal extracts were combined and washed with sodium thiosulphate solution to remove dissolved iodine, and then with water. The ethereal layer was separated and dried ($MgSO_4$). Evaporation left a syrup consisting mainly of 3 : 4-dimethyl β-methyl-2-deoxy-L-ribopyranoside (Found: OMe, 50·8. $C_8H_{16}O_4$ requires OMe, 52·8%). A repetition of the above operations finally gave syrupy 3 : 4-*dimethyl β-methyl-2-deoxy-L-ribopyranoside* (0·66 g.), b. p. 85—95° (bath temp.)/12 mm., n_D^{20} 1·4440, $[\alpha]_D^{20}$ + 224° (*c*, 0·97 in water) (Found: C, 54·4; H, 9·4; OMe, 52·0. $C_8H_{16}O_4$ requires C, 54·6; H, 9·1; OMe, 52·8%).

3 : 4-*Dimethyl* 2-*Deoxy*-L-*ribopyranose*.—3 : 4-Dimethyl β-methyl-2-deoxy-L-ribopyranoside (3·25 g.) was heated at 100° for 15 minutes with 0·01N-hydrochloric acid (60 c.c.), the product then being completely hydrolysed ($[\alpha]_D$ + 52·6°, uncorr.). The solution was neutralised with silver carbonate and worked up in the usual manner. Crude 3 : 4-*dimethyl* 2-*deoxy*-L-*ribopyranose* (2·65 g.) was obtained as a slightly brown syrup which was distilled, giving a colourless syrup (2·226 g.), b. p. 90—100°/0·3 mm., n_D^{20} 1·4590, $[\alpha]_D^{24}$ + 73·8° (*c*, 0·75 in water), which failed to yield a crystalline anilide (Found: C, 52·2; H, 8·9; OMe, 38·23. $C_7H_{14}O_4$ requires C, 51·8; H, 8·7; OMe, 38·27%).

3 : 4-*Dimethyl* 2-*Deoxy*-L-*ribonolactone*.—3 : 4-Dimethyl 2-deoxy-L-ribopyranose (1·643 g.) was treated with water (8·5 c.c.) and bromine (3·4 c.c.). A sharp rise in temperature was noted. After 4—5 days the solution did not reduce Fehling's solution, and the excess of free bromine was removed by aëration. The solution was neutralised with silver carbonate, and the silver bromide and excess of silver carbonate were filtered off. Passage of hydrogen sulphide into the filtrate eliminated silver ions. After filtration the solution was concentrated *in vacuo* at 40° to a thick syrup (1·477 g.) which was lactonized by heating at 80°/*ca.* 12 mm. for 10 minutes or at 40° for 45 minutes. The product was distilled, to yield 3 : 4-*dimethyl* 2-*deoxy*-L-*ribonolactone* (0·903 g.) as a colourless liquid, b. p. 106—112°/0·2 mm., n_D^{15} 1·4595 (Found: C, 52·2; H, 7·5; OMe, 38·7; equiv., 157. $C_7H_{12}O_4$ requires C, 52·5; H, 7·5; OMe, 38·7%; equiv., 160).

When 3 : 4-dimethyl 2-deoxy-L-ribonolactone (0·08958 g.) was dissolved in 0·123M-sodium chloride solution (9·0 c.c.), the following values of [α] were obtained (uncorrected for change in molecular weight during hydrolysis) :

Time (days)	0·00348	0·032	0·166	0·25	0·42	0·96	1·04	1·16
$[\alpha]_D^{15}$	+43·6°	+45·2°	+41·7°	+42·2°	+39·2°	+24·1°	+20·1°	+20·1°
Time (days)	1·38	2·0	2·29	3·0	4·0	5·0	6·0	
$[\alpha]_D^{15}$	+14·1°	+8·0°	+5·0°	+3·0°	0°	0°	0°	

3 : 4-Dimethyl 2-deoxy-L-ribonolactone (0·1149 g.) was dissolved in 5·0 c.c. of approx. 0·26N-sodium hydroxide. After 1·5 hours at 40° the solution was exactly neutralised with hydrochloric acid (5·0 c.c.). Polarimetric observations, carried out immediately gave the following values (uncorrected for change in molecular wieght during lactionisation) :

Time (days)	0·00348	0·084	0·19	0·25	2·0	2·78	3·78
$[\alpha]_D^{15}$	+3·5°	+2·6°	+2·6°	+6·5°	+8·7°	+9·6°	+9·2°

3 : 4-*Dimethyl* 2-*Deoxy*-L-*ribonolactone Phenylhydrazide*.—3 : 4-Dimethyl 2-deoxy-L-ribonolactone (0·31 g.) was dissolved in ether (6·2 c.c.) containing the exact equivalent of freshly distilled phenylhydrazine (0·2095 g.). The *phenylhydrazide* crystallised in a few days and was recrystallised from benzene; m. p. 67—72° (Found: N, 10·5. $C_{13}H_{20}O_4N_2$ requires N, 10·4%).

αβ-*Methyl*-2-*deoxy*-D-*ribofuranoside*.—2-Deoxy-D-ribose (0·26 g.) was treated with 0·1% methanolic hydrogen chloride (5·0 c.c.) at 23°; after 12 minutes the specific rotation of the solution reached a maximum value [+ 39·4° (calculated in terms of the weight of 2-deoxy-D-ribose), +35·6° (corrected value)], and the solution was neutralized with silver carbonate. Subsequent operations were carried out as already described. The resultant syrup was rapidly distilled, and gave αβ-*methyl*-2-*deoxy*-D-*ribofuranoside*, as a viscous, clear, colourless distillate (0·18 g.), b. p. 115—125° (bath temp.)/0·45 mm., n_D^{23} 1·4673, $[\alpha]_D^{23}$ + 38·4° (*c*, 0·6 in acetic acid), which did not give a Fehling's test (Found: OMe, 21·4. $C_6H_{12}O_4$ requires OMe, 21·0%).

When αβ-methyl-2-deoxy-D-ribofuranoside (0·0377 g.) was dissolved in glacial acetic acid (50 c.c.) containing excess of lead tetra-acetate (0·72 g.), one mol. consumed lead tetra-acetate as follows :

Time (hours)	1·42	3·17	6·42
Mol. consumed	0·00	0·028	0·028

αβ-*Methyl*-2-*deoxy*-L-*ribofuranoside*.—2-Deoxy-L-ribose (2·38 g.) was treated with 0·1% methanolic hydrogen chloride (40 c.c.) at 15°; after 15 minutes the specific rotation of the solution reached a minimum value [− 37° (calculated in terms of the weight of 2-deoxy-L-ribose), −33·5° (corrected value)], and the solution was neutralised with silver carbonate. Subsequent operations were carried out as above. The resultant syrupy αβ-*methyl*-2-*deoxy*-L-*ribofuranoside* did not give Fehling's test and had n_D 1·4668. It could be distilled rapidly to give a colourless viscous liquid, b. p. 120—140° (bath temp.)/0·14 mm., $[\alpha]_D^{20}$ − 27·6° (*c*, 1·05 in water), but polymerised when slowly distilled (Found: C, 48·4; H, 8·3; OMe 20·5. $C_6H_{12}O_4$ requires C, 48·6; H, 8·1; OMe, 21·0%).

3 : 5-*Dimethyl* αβ-*Methyl*-2-*deoxy*-L-*ribofuranoside*.—2-Deoxy-αβ-methyl-L-ribofuranoside (2·70 g.) was dissolved in liquid ammonia (200 c.c.) and cooled with solid carbon dioxide. Sodium (2·2 g., 180% of the theoretical quantity) was added cautiously, with stirring. After 1 hour, methyl iodide (10 c.c.) was added cautiously. The subsequent operations were carried out in the manner already described for 3 : 4-dimethyl β-methyl-2-deoxy-L-ribopyranose. The mobile yellow syrup which was obtained was re-treated three times by the same procedure. This crude material obtained (1·6 g.) was distilled, to give fractions (i) 3 : 5-*dimethyl* αβ-*methyl*-2-*deoxy*-L-*ribofuranoside* (0·81 g.), b. p. 96—101° (bath temp.)/12—15 mm., $[\alpha]_D^{20}$ + 5·1° (*c*, 0·97 in water), +5·9° (*c*, 1·16 in water), n_D^{20} 1·4335 (Found: C, 55·1; H, 9·5. $C_8H_{16}O_4$ requires C, 54·6; H, 9·1%), and (ii) (0·13 g.), b. p. 101—103° (bath temp.)/12—15 mm., n_D^{20} 1·4357.

3 : 5-*Dimethyl* 2-*Deoxy*-L-*ribofuranose*.—3 : 5-Dimethyl αβ-methyl-2-deoxy-L-ribofuranoside (0·66 g.) was heated with 0·01N-hydrochloric acid at 100°. The specific rotation of the solution, initially + 4·2°, changed to −50·2° (corrected value for loss of glycosidic group) after 20 minutes, and did not change further after an additional 20 minutes' heating. The solution was neutralized with silver carbonate, and subsequent operations were carried out in the usual manner. After removal of solvent the 3 : 5-*dimethyl* 2-*deoxy*-L-*ribofuranose* produced (0·429 g.) was kept in an atmosphere of nitrogen. It was a colourless

liquid, n_D^{20} 1·4506, $[\alpha]_D^{22}$ − 42·5° (*c*, 0·8 in water), giving positive Fehling's and Schiff's tests, decolourising bromine water, and reducing neutral potassium permanganate solution (Found: C, 51·5; H, 8·55; OMe, 38·8. $C_7H_{14}O_4$ requires C, 51·8; H, 8·7; OMe, 38·2%).

3 : 5-*Dimethyl* 2-*Deoxy*-L-*ribonolactone*.—3 : 5-Dimethyl 2-deoxy-L-ribofuranose (0·292 g.) was treated with water (1·5 c.c.) and bromine (0·6 c.c.); when the mixture was shaken, part of the bromine was absorbed with the evolution of heat. After 4 days the mixture no longer gave Fehling's test. The excess of bromine was removed by aëration, and the solution neutralised with silver carbonate. The filtrate from the insoluble silver salts was treated with hydrogen sulphide and filtered to remove silver sulphide. Evaporation of the aqueous solution at 50° *in vacuo* gave 0·20 g. of a syrup, of which 0·094 g. was distilled, to give 3 : 5-*dimethyl* 2-*deoxy*-L-*ribonolactone* (0·045 g.) as a clear, mobile, colourless liquid, b. p. 100—110° (bath temp.)/0·3 mm., n_D^{20} 1·4445, $[\alpha]_D^{20}$ − 33·3° (*c*, 0·63 in water) (Found: C, 53·1; H, 7·7; OMe, 38·1; equiv., 154. $C_7H_{12}O_4$ requires C, 52·5; H, 7·5; OMe, 38·7%; equiv., 160), which did not give a Fehling's test and did not decolourise bromine water.

A portion of the distillate (0·00813 g.) was treated with excess of 0·5N-sodium hydroxide (0·18 c.c.) at 40° for 1·5 hours; the excess of sodium hydroxide was then exactly neutralised with hydrochloric acid (0·1765 c.c.); polarimetric readings were (*c*, 2·28 in 0·25M-sodium chloride) as follows:

Time (days)	(initial)	0·81	1·125	2·125	3·0	5·81	8·81
$[\alpha]_D^{20}$	−1·32°	−5·26°	−6·14°	−6·56°	−9·63°	−8·74°	−10·2°

Time (days)	10·13	13·1	14·0	18·1	20·1	22·1
$[\alpha]_D^{20}$	−12·23°	−14·4°	−16·2°	−18·4°	−22·8°	−20·6°

($[\alpha]_D^{20}$ are based on the weight of lactone used.)

The analyses were carried out, some by Drs. Weiler and Strauss (Oxford) and some by Dr. W. T. Chambers. One of us (W. G. O.) is indebted to the Board of the British Rubber Producers' Research Association for financial assistance which enabled him to take part in this investigation. We also thank the Birmingham branch of the British Empire Cancer Campaign for financial assistance.

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