

CLXX.—*The Study of Lactones Derived from Simple Sugars.*

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THE investigations of one of us and his collaborators have furnished evidence that the aldoses and ketoses tend to exist normally as amylenes, whilst the less stable or  $\gamma$ -forms of sugars appear to be butylene oxides (compare J., 1926, 89, 1858, 2303).

One of the conclusions leading to this fundamental generalisation may be expressed by the statement that the lactones derived from the fully methylated normal sugars are the  $\delta$ -lactones, whilst the lactones from the  $\gamma$ -forms of these sugars are the more stable  $\gamma$ -lactones; and it has already been shown (*loc. cit.*, p. 89) that a comparison of the relative degrees of stability of the two lactones derived from a given sugar enables each of them to be classified as a  $\gamma$ - or a  $\delta$ -lactone, and thence reveals the ring structure of each parent sugar form.

The method adopted for comparing the lactones was that of observing the mutarotation-time curves for aqueous solutions, the relative slopes of the curves derived from a pair of lactones enabling each member of the pair to be classified as a  $\gamma$ - or a  $\delta$ -lactone. When, however, the specific rotations of the free acids in the same solvent are known, a direct comparison of the rate of change of each lactone into the corresponding acid can be made by means of a simple calculation, and the result exhibited in the form of a curve.

This method has the advantage of eliminating the unequal effects due to the rotations of the two methylated acids derived from a pair of lactones; and for this reason we have now determined the specific rotations of a number of acids derived from the  $\gamma$ - and  $\delta$ -forms of trimethylated pentoses and tetramethylated hexoses, and have plotted the hydration curves of the respective lactones.

In the determination of specific rotation of the acids, a lactone was dissolved in the equivalent of  $N/10$ -sodium carbonate, and the solution was heated until transformation to the sodium salt was complete. After being cooled, the solution was rapidly neutralised with  $N/10$ -sulphuric acid and its rotation was then observed at intervals. Extrapolation, where necessary, gave a value for the specific rotation of the pure acid.

The values so obtained are probably not strictly accurate, on account of the presence in the solution of a half-molecular proportion of sodium sulphate, which may modify the rotatory power

(compare Clough, J., 1914, **105**, 49; 1915, **107**, 96, 1509). They are considered sufficiently exact, however, to be applicable to the present purpose.

Other effects which cannot easily be allowed for in the observation of mutarotation values of the lactones are the effect of variation of concentration and that of variation in specific rotation of the lactone due to the presence of an increasing proportion of acid. These effects are probably only of a secondary order of magnitude.

With this reservation, then, the percentage of acid present at a given time during the hydration of a lactone is calculable from the expression  $100(R - R_l)/(R_a - R_l)$ , where  $R$  is the specific rotation of the solution at the given time and  $R_a$  and  $R_l$  are the specific rotations of the lactone in the form of acid and the lactone, respectively. (If  $r_a$  represents the true specific rotation of the acid, then  $R_a = r_a M_a/M_l$ , where  $M_a$  and  $M_l$  are respectively the molecular weights of acid and lactone.) This expression has also been employed by Levene and Simms (*J. Biol. Chem.*, 1925, **65**, 46).

Table I shows the values of the specific rotations of those lactones which have been studied and of their acids; and the accompanying diagram exhibits in each case the rate of change of lactone to acid in aqueous solution at the ordinary temperature.

TABLE I.

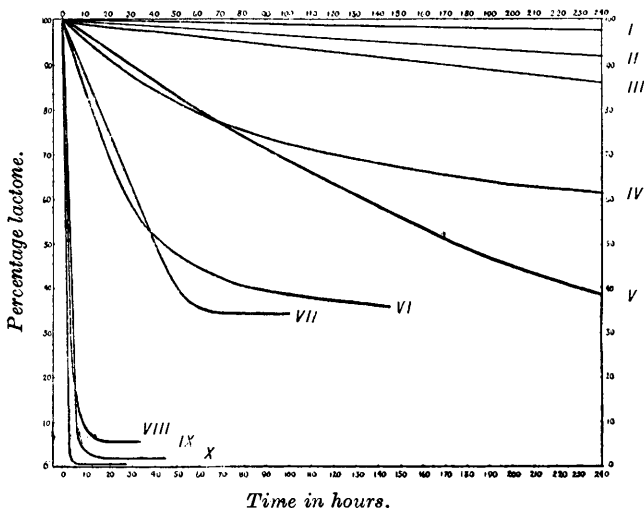
Parent sugar.	Specific rotation of lactone ( $R_l$ ).			Specific rotation of acid ( $r_a$ ).		
	$[\alpha]_{5451}$ .	$[\alpha]_D$ .	Conc.	$[\alpha]_{5451}$ .	$[\alpha]_D$ .	Conc.
<i>d</i> -2 : 3 : 5 : 6-Tetramethyl glucose .....	+ 72°	+ 63°	1.42	+ 31.8°	+ 27.7°	1.08
<i>d</i> -2 : 3 : 4 : 6- " " " " .....	+ 113	+ 98	1.56	+ 25.5	+ 22	1.09
<i>d</i> -2 : 3 : 5 : 6-Tetramethyl galactose ...	- 31	- 27	1.47	- 8.3	- 8.0	0.90
<i>d</i> -2 : 3 : 4 : 6- " " " " .....	+ 191	+ 166.5	1.89	+ 25.5	+ 22	1.23
<i>d</i> -2 : 3 : 5 : 6-Tetramethyl mannose ...	+ 73	+ 63	2.51	- 27	- 23	0.92
<i>d</i> -2 : 3 : 4 : 6- " " " " .....	+ 172	+ 150	1.88	+ 15.8	+ 13.7	1.12
<i>l</i> -2 : 3 : 5-Trimethyl xylose .....	+ 85	+ 74	1.11	+ 34.4	+ 29	1.11
<i>l</i> -2 : 3 : 4- " " " " .....	± 0	± 0	1.87	+ 29.9	+ 26	0.82
<i>l</i> -2 : 3 : 5-Trimethyl arabinose .....	- 51	- 44	1.06	- 3.4	- 2.9	0.82
<i>l</i> -2 : 3 : 4- " " " " .....	+ 206	+ 180	1.41	+ 14.6	+ 13.8	0.72

It will be observed that, in the case of each separate pair of lactones derived from a normal and a  $\gamma$ -form of the same sugar, the curve representing the rate of formation of  $\gamma$ -hydroxy-acid from  $\gamma$ -lactone is sharply distinguished from that representing the rate of formation of the  $\delta$ -hydroxy-acid from  $\delta$ -lactone, the latter being much the steeper. These results amply confirm the conclusions arrived at in the former paper (Charlton, Haworth, and Peat, J., 1926, 89). Further, the whole of the curves being taken into consideration, each of the  $\delta$ -lactone curves is steeper than any  $\gamma$ -lactone curve—a striking fact when the differences in configuration throughout the series are considered.

Between the two extreme types of curve, *viz.*, the very steep

$\delta$ -lactone curves and the very flat  $\gamma$ -lactone curves, are found two less steep  $\delta$ -lactone curves (trimethyl  $\delta$ -xylono- and tetramethyl  $\delta$ -mannono-lactones) and two less flat  $\gamma$ -lactone curves (trimethyl  $\gamma$ -arabono- and trimethyl  $\gamma$ -glucono-lactones). These modifications in the form of the hydration curves are obviously connected with the configurations of the lactones. Further physico-chemical methods are being brought to bear upon the interpretation of this phenomenon.

FIG. 1.  
*Comparative rates of hydrolysis of the lactones.*



- |  |  |
|--|--|
| I Tetramethyl $\gamma$ -mannonolactone.    | II Tetramethyl $\gamma$ -galactonolactone. |
| III Trimethyl $\gamma$ -xylonolactone.     | IV Trimethyl $\gamma$ -arabonolactone.     |
| V Tetramethyl $\gamma$ -gluconolactone.    | VI Tetramethyl $\delta$ -mannonolactone.   |
| VII Trimethyl $\delta$ -xylonolactone.     | VIII Tetramethyl $\delta$ -gluconolactone. |
| IX Tetramethyl $\delta$ -galactonolactone. | X Trimethyl $\delta$ -arabonolactone.      |

Since the equilibrium values of all the lactones cannot be observed with much accuracy owing to the extreme length of time required in some instances, it is interesting to compare the times in which a quarter (say) of the lactone is changed to acid in the various cases. These are shown in Table II.

TABLE II.

	$\gamma$ -Lactones. 25% Acid developed in (hrs.).	$\delta$ -Lactones. 25% Acid developed in (hrs.).
Tetramethyl glucono- .....	75	<1
Tetramethyl galactono- .....	600	1
Tetramethyl mannono- .....	(this stage is not reached)	17
Trimethyl xylono-.....	430	22
Trimethyl arabono- .....	60	<1

The results do not support the generalisation arrived at by Levene and Simms (*loc. cit.*), that the rates of lactone formation among normal hexose acids are practically identical. The speeds of the lactone  $\rightarrow$  acid and acid  $\rightarrow$  lactone reactions are considerably affected by the configuration of the sugar.

Table III shows the approximate proportions of acid and lactone at equilibrium, where these have been measured or calculated from the curves. The ratios of these values give the relative speed constants for the acid  $\rightarrow$  lactone change.

TABLE III.

	$\gamma$ -Lactones.			$\delta$ -Lactones.		
	Acid : lactone at equil.			Acid : lactone at equil.		
			Attained in (hrs.).			Attained in (hrs.).
Tetramethyl glucono- .....	87	13	520	95	5	5
Tetramethyl galactono- ...	—	—	—	98.5	1.5	18
Tetramethyl mannono- ...	11	89	>900	64	36	140
Trimethyl xylono- .....	31	69	>500	65	35	70
Trimethyl arabono- .....	45	55	>500	99.5	0.5	4

In many cases (see experimental section), we have re-determined the mutarotation curves of the lactones, using material which is seen, in some instances, to be substantially purer than that hitherto obtained. Thus, three lactones (trimethyl  $\delta$ -arabono-, tetramethyl  $\delta$ -mannono-, and tetramethyl  $\gamma$ -glucono-), which were previously known only as syrups, have been obtained in the crystalline condition. In all, six of the ten lactones examined are crystalline. In two of these cases, the specific rotation shows marked enhancement of the former values.

The initial material in the preparation of tetramethyl  $\delta$ -mannono-lactone was pure  $\alpha$ -methylmannoside, which was methylated to tetramethyl  $\alpha$ -methylmannoside, obtained in a pure crystalline condition. Hydrolysis yielded 2 : 3 : 4 : 6-tetramethyl mannose, having  $[\alpha]_D^{18} + 26^\circ$  in methyl alcohol ( $c = 5.15$ ), rising at equilibrium to  $+31^\circ$ . Irvine and Moodie's product (J., 1905, **87**, 1462) had  $[\alpha]_D^{20} + 14.6^\circ$  in methyl alcohol ( $c = 5$ ), rising to  $+17.2^\circ$  at equilibrium.

Oxidation of tetramethyl mannose gave the crude syrupy lactone, which, after transformation to the *phenylhydrazide*, followed by crystallisation and recovery, gave 2 : 3 : 4 : 6-tetramethyl mannono-lactone in colourless, prismatic needles (m. p. 23—25°), having  $[\alpha]_D^{18} + 150^\circ$  in water ( $c = 1.88$ ); and  $[\alpha]_D^{28} + 130.5^\circ$ , falling to  $[\alpha]_D^{20} + 34^\circ$  in 14 days, in 60% methyl alcohol ( $c = 1.489$ ). Irvine and Miss B. M. Paterson (J., 1914, **105**, 915) describe a liquid product having  $[\alpha]_D^{20} + 78.8^\circ$ , falling to  $+38.5^\circ$  in 10 days, in 60%

methyl alcohol ( $c = 1.384$ ), as the above lactone, but quote an inconclusive analytical result for carbon and do not record a value for methoxyl. Their product was obviously impure. The same remark can be applied to the syrup obtained by Levene and Meyer (*J. Biol. Chem.*, 1924, **60**, 167), which had  $[\alpha]_D +105^\circ$  in water ( $c = 2.85$ ) and gave poor analytical values.

We have repeated the preparation of the 2 : 3 : 5 : 6-tetramethyl mannonolactone described by Levene and Simms (*loc. cit.*), who record an inconclusive analysis; and have found that another product accompanies the lactone under the experimental conditions employed by these authors. The homogeneity of this lactone is therefore under suspicion, and test experiments are in progress to decide the point. In the meantime, the figures recorded in this paper should be regarded as provisional in the case of this lactone and also of the trimethyl  $\gamma$ -xylonolactone. It seems doubtful whether a pure specimen of a completely methylated lactone is readily obtainable by direct methylation of the lactone of a hexonic or pentonic acid. Pure specimens we have handled have been prepared by oxidation of a methylated sugar.

In the case of arabinose, the observations were conducted on the crystalline 2 : 3 : 4-trimethyl  $\delta$ -arabonolactone (m. p.  $45^\circ$ ) isolated as described by Drew and Haworth (this vol., p. 778).

2 : 3 : 5 : 6-Tetramethyl  $\gamma$ -gluconolactone was similarly obtained as a crystalline solid (m. p.  $26-27^\circ$ ), having  $[\alpha]_D^{21^\circ} +62.5^\circ$  in water ( $c = 1.415$ ), a value which substantially agrees with that recorded by Charlton, Haworth, and Peat (*loc. cit.*), *viz.*,  $[\alpha]_D +61.5^\circ$ .

In a further paper (*J. Biol. Chem.*, 1926, **68**, 737), Levene and Simms record for tetramethyl  $\delta$ -gluconolactone a specific rotation of  $[\alpha]_D^{22^\circ} +108^\circ$  in water, and for the corresponding equilibrium solution a specific rotation of  $[\alpha]_D^{22^\circ} +46^\circ$ ; whereas Charlton, Haworth, and Peat (*loc. cit.*) record values of  $[\alpha]_D +101^\circ$  and  $[\alpha]_D +25.6^\circ$ , respectively. We have now examined two separately prepared specimens of this lactone, and have obtained specific rotations of  $[\alpha]_D^{19^\circ} +98^\circ$  for the lactone in water and  $[\alpha]_D^{19^\circ} +28^\circ$  for the equilibrium solution. The specific rotation of the acid in water was observed to be  $[\alpha]_D^{19^\circ} +22^\circ$  ( $c = 1.09$ ) and  $[\alpha]_D^{20^\circ} +28^\circ$  ( $c = 0.9$ ) for the two samples, as against Levene and Simms's value of  $[\alpha]_D +40.5^\circ$ . It is therefore considered that the figure obtained by Levene and Simms is of doubtful accuracy.

#### EXPERIMENTAL.

*Tetramethyl  $\gamma$ -Gluconolactone.*—Tetramethyl  $\gamma$ -glucose, oxidised at  $75^\circ$  by means of bromine, gave the *lactone* as an oil ( $n_D^{20}$  1.4501)

which solidified in colourless needles, m. p. 26—27° (Found : C, 51.0; H, 7.6.  $C_{10}H_{18}O_6$  requires C, 51.3; H, 7.7%).

In water ( $c = 1.415$ ), the following rotations were observed :

Time (hrs.).	$[\alpha]_{5461}^{20^\circ}$ .	% Lactone present.	Time (hrs.).	$[\alpha]_{5461}^{20^\circ}$ .	% Lactone present.
0	+72°	100	240	+48.8°	38.7
73.7	62.3	76	360	42.4	21.8
121.2	58.3	63.7	408	40.7	17.4
144	55.9	57.4	501	38.8	12.4
192	51.6	46			(constant)

For the lactone :  $[\alpha]_{5461}^{21^\circ} + 72^\circ$ ,  $[\alpha]_{5780}^{21^\circ} + 65^\circ$ ,  $[\alpha]_D^{21^\circ} + 62.5^\circ$ . For the acid (calculated as lactone) :  $[\alpha]_{5461}^{20^\circ} + 34^\circ$ ,  $[\alpha]_D^{20^\circ} + 30^\circ$  (in water,  $c = 1.08$ ), rising after 4 days to  $[\alpha]_{5461}^{19^\circ} + 41^\circ$ .

*Tetramethyl  $\delta$ -Gluconolactone.*—In water ( $c = 1.564$ ), the lactone gave the rotations :

Time (hrs.).	$[\alpha]_{5461}^{19^\circ}$ .	% Lactone present.	Time (hrs.).	$[\alpha]_{5461}^{19^\circ}$ .	% Lactone present.
0	+112.5°	100	0.58	+95°	79.4
0.12	109	95.9	0.68	91.5	75.3
0.25	105	91.2	1.33	73	53.6
0.33	101.5	86.5	1.82	59	37.1
0.45	100	85.3	16.75	32	5.4
					(constant)

For the acid (calculated as lactone) :  $[\alpha]_{5461}^{19^\circ} + 27.4^\circ$  in water ( $c = 1.095$ ), rising after 6 days to  $[\alpha]_{5461}^{19^\circ} + 33.8^\circ$ .

*Tetramethyl  $\gamma$ -Galactonolactone.*—For this lactone, Haworth, Ruell, and Westgarth (*loc. cit.*) give  $[\alpha]_D - 27^\circ$  for the initial value in water ( $c = 1.47$ ), changing after 12 days to  $[\alpha]_D - 25^\circ$ . Thus, 89.7% of lactone is still present after 12 days, the acid (calculated as lactone) having  $[\alpha]_D^{19^\circ} - 8.6^\circ$  in water ( $c = 0.896$ ). It seems improbable, therefore, that equilibrium had been attained in the period indicated. Further experiments in this connexion are in progress.

*Tetramethyl  $\delta$ -Galactonolactone.*—The following values were observed for the lactone in water ( $c = 1.891$ ) :

Time (hrs.).	$[\alpha]_D^{21^\circ}$ .	% Lactone present.	Time (hrs.).	$[\alpha]_D^{21^\circ}$ .	% Lactone present.
0	+166.5°	100	3.0	+69.5°	32.0
1.5	114.5	63.5	4.25	47.8	16.8
2.5	84.7	42.7	21.0	26.2	1.7
					(constant)

For the acid (calculated as lactone) :  $[\alpha]_D^{21^\circ} + 24^\circ$  in water ( $c = 1.228$ ), rising after 48 hours to  $[\alpha]_D^{21^\circ} + 26.3^\circ$  (compare Haworth, Ruell, and Westgarth, J., 1924, **125**, 2473; Pryde, Hirst, and Humphreys, J., 1925, **127**, 355).

*Tetramethyl  $\gamma$ -Mannonolactone.*—A sample of the lactone (m. p.

106—107°), prepared by Levene and Simms's process (*loc. cit.*), gave an initial rotation of  $[\alpha]_D^{19} + 63^\circ$  in water ( $c = 2.51$ ), falling during 9 days to  $[\alpha]_D^{20} + 61^\circ$ . Catalysis with hydrochloric acid gave an equilibrium rotation of  $[\alpha]_D^{20} + 53^\circ$ . For the acid, in water ( $c = 0.923$ ):  $[\alpha]_D^{21} - 23^\circ$ , becoming  $[\alpha]_D^{21} - 17^\circ$  after 5 days. It is clear, therefore, that the mutarotation of the lactone is extremely slow. Further work is in progress to test the purity of the lactone and to determine the equilibrium composition of the aqueous solution.

2 : 3 : 4 : 6-Tetramethyl  $\delta$ -Mannonolactone.—Pure  $\alpha$ -methylmannoside was methylated by means of sodium hydroxide and methyl sulphate, and then by means of silver oxide and methyl iodide. The product (b. p.  $105^\circ/0.03$  mm.;  $n_D^{16} 1.4494$ ) solidified in crystals of tetramethyl  $\alpha$ -methylmannoside, m. p.  $38-40^\circ$ . The mannoside was hydrolysed by 5% hydrochloric acid to 2 : 3 : 4 : 6-tetramethyl mannose, obtained as a colourless syrup (b. p.  $114.5^\circ/0.035$  mm.;  $n_D^{16} 1.4597$ ). The overall yield of pure product was 50% (Found: OMe, 50.5.  $C_{10}H_{20}O_6$  requires OMe, 52.5%). The sugar had  $[\alpha]_D^{18} + 26^\circ$  in methyl alcohol ( $c = 5.15$ ), rising to  $+31^\circ$  at equilibrium.

The tetramethyl mannose, on oxidation at  $45^\circ$  with bromine, yielded the crude lactone as a colourless syrup (b. p.  $117^\circ/0.04$  mm.;  $n_D^{17} 1.4643$ ;  $[\alpha]_{5461}^{19} + 156^\circ$  in water). Since the analytical figures (C, 50.7; H, 7.8; OMe, 48.8, 49.3%) indicated the presence of appreciable impurity, the whole was converted into the *phenylhydrazide*, white, nacreous flakes from benzene; m. p.  $184-185^\circ$  (Found: C, 56.0; H, 7.6; N, 8.4; OMe, 35.0.  $C_{16}H_{26}O_6N_2$  requires C, 56.1; H, 7.6; N, 8.2; OMe, 36.3%). The recrystallised phenylhydrazide was hydrolysed by means of 1% hydrochloric acid, and the lactone recovered as a syrup (b. p.  $104^\circ/0.02$  mm.;  $n_D^{18} 1.4650$ ), which solidified in colourless, prismatic needles, m. p.  $23-25^\circ$  after being drained on porous tile in a vacuum (Found: C, 51.2; H, 7.8; OMe, 50.5.  $C_{10}H_{18}O_6$  requires C, 51.3; H, 7.7; OMe, 53.0%).

In water ( $c = 1.88$ ) the following rotations were observed :

Time (hrs.).	$[\alpha]_{5461}^{19}$ .	% Lactone present.	Time (hrs.).	$[\alpha]_{5461}^{19}$ .	% Lactone present.
0	$+172^\circ$	100	34.3	$+102^\circ$	54.8
0.3	171	99.4	57.1	88	45.8
5.8	157.5	90.6	71.1	82.5	42.3
9.3	148	84.5	146.3	73.4	36.0

(constant)

For the lactone:  $[\alpha]_{5461}^{18} + 172.3^\circ$ ,  $[\alpha]_{5789}^{18} + 153^\circ$ ,  $[\alpha]_D^{18} + 150^\circ$ .  
For the acid (calculated as lactone):  $[\alpha]_{5461}^{14} + 17^\circ$ ,  $[\alpha]_D^{14} + 14.8$   
in water ( $c = 1.12$ ), rising after 88 hours to  $[\alpha]_{5461}^{18} + 60.7^\circ$ .

*Trimethyl  $\gamma$ -Xylonolactone.*—The records of Haworth and Westgarth (J., 1926, 886) give the following mutarotation figures for the lactone in water ( $c = 1.106$ ): \*

Time (hrs.) .....	0	64	168	504
$[\alpha]_D$ .....	+74°	+71.8°	+69.6°	+61.4°
% Lactone present .....	100	94.6	89.4	70.0

For the acid (calculated as lactone), we observed  $[\alpha]_D^{16^{\circ}} + 31.7^{\circ}$  in water ( $c = 0.944$ ), rising after 17 hours to  $[\alpha]_D^{16^{\circ}} + 33.5^{\circ}$  (equilibrium not attained).

*Trimethyl  $\delta$ -Xylonolactone.*—Pure trimethyl methylxyloside (m. p. 46—48°) was hydrolysed by means of 3% hydrobromic acid, and the resulting sugar oxidised at 75° with bromine. The lactone (b. p. 101°/0.04 mm.) at once solidified. It crystallised from petroleum in long, colourless needles, m. p. 56° [Found: C, 50.75; H, 7.2; OMe, 48.9;  $M$ , ebullioscopic in benzene, 200 ( $c = 0.93$ ).  $C_8H_{14}O_5$  requires C, 50.5; H, 7.4; OMe, 48.9%;  $M$ , 190] (compare Haworth and Westgarth, *loc. cit.*). In water ( $c = 1.871$ ) the lactone gave:

Time (hrs.)	$[\alpha]_{5461}^{20^{\circ}}$	% Lactone present.	Time (hrs.)	$[\alpha]_{5461}^{20^{\circ}}$	% Lactone present.
0	$\pm 0^{\circ}$	100	32.75	+13.3°	59.1
6.75	+ 2.4	92.7	46.75	17.4	46.8
22.25	8.8	73.1	70.75	21.4	34.6
					(constant)

For the acid (calculated as lactone):  $[\alpha]_{5461}^{15^{\circ}} + 32.7^{\circ}$  in water ( $c = 0.977$ ), falling after 8 hours to  $[\alpha]_{5461}^{15^{\circ}} + 21.5^{\circ}$ .

*2 : 3 : 5-Trimethyl  $\gamma$ -Arabonolactone.*—The following values are taken from the record of Haworth and Nicholson (J., 1926, 1902).

Time (hrs.)	$[\alpha]_D$	% Lactone present.	Time (hrs.)	$[\alpha]_D$	% Lactone present.
0	-44.4°	100	168	-30.0°	65.0
2	43.8	98.5	288	27.0	57.8
24	40.0	89.3	480	25.2	53.4
120	32.1	70.1			

For the acid (calculated as lactone), we observed  $[\alpha]_D^{15^{\circ}} - 3^{\circ}$ , rising after 40 hours to  $[\alpha]_D^{15^{\circ}} - 15^{\circ}$  (equilibrium not attained).

*2 : 3 : 4-Trimethyl  $\delta$ -Arabonolactone.*—This was prepared as described by Drew and Haworth (this vol., p. 778). The crystals (m. p. 45°), which were drained on porous tile in a vacuum, could not be recrystallised owing to the remarkable tendency of the

\* This lactone has now been prepared from a different source and identified through the crystalline phenylhydrazide. This specimen gives rather higher mutarotation figures. The result is to increase slightly the declination of the curve for this lactone in Fig. 1, but its relative position in the sequence of the curves is not affected.



substance to absorb water (Found: C, 50.7; H, 7.3; OMe, 45.5. Calc. for  $C_8H_{14}O_5$ : C, 50.5; H, 7.4; OMe, 48.9%).

For the lactone in water ( $c = 1.411$ ), the following values were observed:

Time (hrs.).	$[\alpha]_{5461}^{20^\circ}$	% Lactone present.	Time (hrs.).	$[\alpha]_{5461}^{20^\circ}$	% Lactone present.
0	+206°	100	2.0	+70°	28.4
0.07	199	96.3	2.5	45	15.3
0.5	161	76.3	3.2	21	2.6
1.4	104	46.3	3.8	17	0.5

(constant)

For the lactone:  $[\alpha]_{5461}^{21^\circ} +206.3^\circ$ ,  $[\alpha]_{5780}^{21^\circ} +183.5^\circ$ ,  $[\alpha]_{5461}^{21^\circ} +179.5^\circ$  in water ( $c = 1.411$ ). For the acid (calculated as lactone):  $[\alpha]_{5461}^{19^\circ} +16^\circ$  in water ( $c = 0.72$ ), rising after 2 days to  $[\alpha]_{5461}^{21^\circ} +18^\circ$  (compare Pryde, Hirst, and Humphreys, J., 1925, **127**, 355).

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