

62. *Optical Rotatory Dispersion in the Carbohydrate Group. Part V.*
Tetramethyl γ -Gluconolactone.

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IN marked contrast with tetramethyl γ -mannonolactone (I), the epimeric γ -gluconolactone (II) exhibits only small variation in specific rotation when measurements in different solvents are compared (Haworth, Hirst, and Smith, J., 1930, 2659). These two substances differ structurally only in the configurations of the second carbon atoms, and since (I) has been found to display anomalous rotatory dispersion in organic solvents (Part IV, J., 1934, 1825), it was of particular interest to investigate for comparison the optical rotatory dispersion of (II).

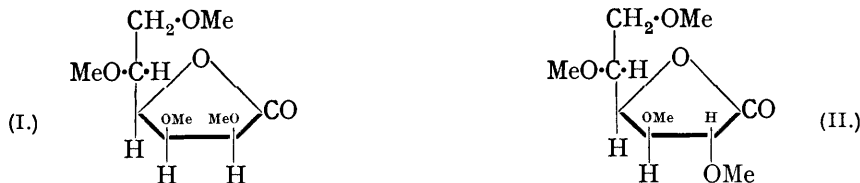
The rotation of (I) in organic solvents can be represented by a Drude equation with two terms of opposite sign (see Table I), the frequency constants of which are identifiable with absorbing centres due (*a*) to the carbonyl group (induced dissymmetry) and (*b*) to the C-C, C-O-, and C-H valencies present in the molecule (bands in the Schumann region). The term ($\lambda_0^2 = 0.06$) representing the induced dissymmetry was in this case positive,

TABLE I.

	<i>Tetramethyl γ-mannonolactone.</i>					<i>Tetramethyl γ-gluconolactone.</i>				
	H ₂ O.	EtOH.	CHCl ₃ .	Dioxan.	C ₆ H ₆ .	H ₂ O.	EtOH.	CHCl ₃ .	Dioxan.	C ₆ H ₆ .
$[\alpha]_D$...	+59·8°	-0·78°	-3·48°	-14·7°	-31·7°	+59·38°	+58·91°	+46·60°	+65·87°	+72·83°
λ_1^2	—	0·027	0·020	0·022	0·026	0·0267	0·029	0·035	0·034	0·035
λ_2^2	0·049	0·058	0·064	0·063	0·061	0·075	0·075	0·075	0·075	0·08
k_1	—	-12·25	-9·84	-13·15	-19·04	+22·09	+19·47	+16·53	+22·345	+23·78
k_2 ...	+17·8	+10·89	+6·52	+7·26	+7·85	-2·56	-0·59	-1·66	-1·35	-0·82

(The values of k_1 and k_2 refer to specific rotations. Full details of the observations summarised above will be found in Part IV and in the experimental section below.)

and the possibility arose that in the methylated γ -lactones a correlation (comparable with Hudson's rule for the unmethylated γ -lactones) might exist between the configuration of



the carbon atom involved in lactone formation and the sign of the induced dissymmetry. It is clear, however, that the second as well as the fourth carbon atom influences the induced effect, and it appeared probable that by comparing the rotatory dispersion constants of (I) and (II) information would be gained concerning the relative effects of these carbon atoms on the "induced" rotation term.

The experimental results now recorded reveal an unexpected contrast between the dispersions of the two epimerides. In all the solvents investigated (Table I) the rotatory dispersion of tetramethyl γ -gluconolactone departs comparatively slightly from simplicity and the rotation values are all strongly positive. The deviations from simplicity are sufficiently great to permit of the computation of two-term Drude equations which give satisfactory agreement between the observed and calculated values. Reference to the collected results (Table I) shows that the terms of the Drude equation are opposite in sign and that the positive term is much the greater numerically. This term in all cases has a value for λ_1^2 not far removed from 0·035, corresponding to an absorption band situated approximately at λ 1900. This wave-length is considerably higher than that of the Schumann band normally associated with C-C, C-H, and -C-O-R linkages which are the origin of the high-frequency term appearing in the rotatory dispersion of tetramethyl γ -mannonolactone. On the other hand, the wave-length is lower than that of the low-frequency term of the latter lactone (λ_2 ca. 2500). It is well known, however, that one of the absorption bands of the carboxyl group is situated in this neighbourhood (λ 1900), and it seems probable that the term having λ_1^2 ca. 0·035 in the equations for tetramethyl γ -gluconolactone is to be correlated with the induced dissymmetry of the lactonic carboxyl group. Should this be the case, it follows that in tetramethyl γ -gluconolactone the induced dissymmetry originating mainly from the fourth carbon atom controls the direction of rotation in all the solvents investigated. In this case, no term with λ^2 ca. 0·02 is evident, and it may be concluded that the high-frequency terms contributed by the centres of dissymmetry other than the induced centre almost or entirely cancel out. In contrast with this condition, the ordinary (non-induced) term is important in tetramethyl γ -mannonolactone, with the result that in the visual region the rotation is positive in some solvents and negative in others. For the latter substance, the value of the induced frequency constant calculated from the rotational data was λ^2 0·065, corresponding with absorption at λ 2500—2600. It would appear, therefore, that the effect of the *cis*-methoxy-groups in the methylated mannonolactone is seen in the displacement, relative to its position in the case of the *trans*-modification, of the absorption wave-length by approximately 600 Å. The movement brings the absorption band of tetramethyl γ -mannonolactone into a position much nearer the characteristic band of the carboxyl group (λ 2900 approx.). This difference in the position of the

absorption band may be correlated with another important difference manifested by substances having methoxy-groups respectively *cis* and *trans* to one another on carbon atoms 2 and 3. In comparison with their epimerides, all lactones which possess *cis*-2 : 3-methoxy- (or hydroxy-) groups are extraordinarily resistant to hydrolysis.

Two points in connexion with the present observations require further discussion. The calculations lead inevitably to the conclusion that a small negative term is present in which λ_2^2 has approximately the value 0.075. The origin of this term is obscure, and within the spectral region examined its influence on the total rotation is slight. We have considered its possible association with the carbonyl group of the lactone, but the evidence at present warrants no definite assignment to any particular group, more especially as an exactly similar term has been discovered in the rotatory dispersion of tetramethyl α -methylglucoside, a substance having no carboxyl group.

The interpretation suggested above implies that the value of λ given by $\lambda_1^2 = 0.035$ has a definite physical meaning. This would not be the case if the term were fictitiously simple and in reality represented the sum of two or more terms having different values of λ . In view of the considerable spectral range covered by several of the sets of observations and the large numerical values of the observed rotations, it seems unlikely that any equation of three or more terms could be found in which λ^2 in the principal term differed appreciably from the value 0.035. It will be seen from the experimental results that in certain solvents the differences between the observed and calculated values are, although small, greater than the experimental error. It is probable, therefore, that this lactone requires at least a three-term equation to express fully its rotation, but we have been unable to devise any equation in which λ_1^2 differs seriously from the value 0.035.

2 : 3 : 5 : 6-Tetramethyl gluconic acid in water, like the corresponding mannonic acid, shows marked general absorption in the near ultra-violet. Within the spectral range available, its rotatory power can be represented by a one-term equation ($\lambda_0^2 = 0.027$). The results are recorded in the experimental section, but in view of the small numerical values of α_λ and the limited spectral range, we reserve for future discussion the interpretation of the values of λ_0^2 .

EXPERIMENTAL.

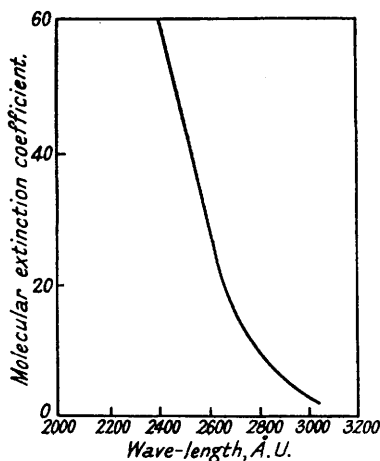
Calculation of the Constants of the Drude Equation.—The following tables show that the deviation from simplicity of the rotatory dispersion of this lactone is slight, amounting to some 12% of the value of α_λ at approximately λ 3100 (see, e.g., data for solutions in dioxan and chloroform). The possible experimental error, although small, is nevertheless an appreciable proportion of this divergence and renders almost impossible the direct calculation of the constants of a two-term Drude equation. Direct calculations (Lowry and Glyn Owen, *Trans. Faraday Soc.*, 1930, 26, 371) made with 4 points, distributed throughout the spectral range investigated, resulted generally in equations the solutions of which involved imaginary quantities.

The method of calculation adopted was to obtain the constant, λ_1 , of an approximate one-term equation by careful extrapolation of the graph of $1/\alpha$ against λ^2 . A value for λ_2 was then assumed, and four experimental points, A, B, C and D, were chosen, distributed as evenly as possible throughout the spectral range examined, measurements having been taken to the limits of transparency in a 2-dm. tube. By using these values of λ_1 and λ_2 , values of k_1 and k_2 were computed from the experimental points A and C, and a second pair, k_1' and k_2' , from the points B and D. If λ_1 and λ_2 had been correctly chosen, it would be found that $k_1 = k_1'$ and $k_2 = k_2'$ within the experimental error, but in general this would not be the case, so λ_1 was then varied by trial and error until the differences $k_1 - k_1'$ and $k_2 - k_2'$ were as small as possible; then λ_2 was varied with the same object, and finally, by repeating the whole process of successive approximation as often as necessary, the variation of k_1 and k_2 over the whole dispersion curve was reduced to less than the experimental error or to a minimum.

This method of obtaining a two-term (4 constant) Drude equation seems to be the only one available where variations from simplicity are small. The signs of k_1 and k_2 are readily ascertainable in the preliminary stage of the calculation, but the ultimate exact evaluation of λ_1 and λ_2 and consequent values of k_1 and k_2 is a very long process.

It will be noted that the frequency constants (λ_1) of the most satisfactory simple equations which are given for comparison) are less than the corresponding constants (λ_1) of the high-frequency term in the complex equations, and that the deviation from simplicity (α , obs.— α ,

calc.) is negative. It was found possible to derive more than one equation which gave reasonably close agreement between observed and calculated values. The possible variations in λ_1^2 and λ_2^2 are, however, inconsiderable, and there is no escape from the introduction of terms containing respectively a value of λ_2^2 not far removed from 0.07 and of λ_1^2 close to 0.035. This applies even for those alternative equations (the best of several calculated) given for the dioxan and benzene solutions of the lactone, none of which is within our recognised limits of experimental error. It is highly probable, however, that the rotation of this lactone requires a more complicated function for its exact representation. Attempts were made to follow the dispersion curves into the region of absorption, but even with 2-cm. columns of solution the absorption was too great to permit accurate observations. Photometric measurements on solutions of the lactone in water, alcohol, and dioxan showed slight absorption between λ 7000 and λ 3000. Beyond λ 3000, general absorption set in, rising steeply at about λ 2700. There was no indication of selective absorption (see fig.).



Rotatory Dispersion.—Tetramethyl γ -gluconolactone was prepared by the oxidation of tetramethyl glucofuranose (see Drew, Goodyear, and Haworth, J., 1927, 1237). It was purified for the present work by several successive distillations in a vacuum; b. p. $97^\circ/0.05$ mm., m. p. 27° . The rotational measurements were made by the methods given in Part I (J., 1930, 2108).

D = Algebraical difference between observed and calculated values.

2 : 3 : 5 : 6-Tetramethyl gluconic acid in water : $c = 7.228$; $t = 20^\circ$; $l = 2$ dm.; $[\alpha]_\lambda^{20^\circ} = 6.917\alpha_\lambda$; $[\alpha]_D^{20^\circ} = 22.90^\circ$; $\alpha_\lambda = 1.06/(\lambda^2 - 0.027)$.

λ .	α , obs.	D .	λ .	α , obs.	D .	λ .	α , obs.	D .	λ .	α , obs.	D .
6708	$+2.57^\circ$	$+0.06$	5515	$+3.82^\circ$	± 0	4538	$+5.91^\circ$	-0.01	4010	$+7.91^\circ$	-0.01
6292	2.87	± 0	5225	4.31	± 0	4376	6.41	-0.03	3920	8.41	$+0.04$
5893	3.31	± 0	4887	4.98	-0.02	4258	6.91	$+0.04$	3749	9.41	$+0.05$
5805	3.39	-0.03	4736	5.41	$+0.04$	4130	7.41	$+0.03$	3582	10.41	-0.05

2 : 3 : 5 : 6-Tetramethylgluconolactone.—In water : $c = 8.016$; $t = 20^\circ$; $l = 2$ dm.; $[\alpha]_\lambda^{20^\circ} = 6.238\alpha_\lambda$; $[\alpha]_D^{20^\circ} = 59.38^\circ$; $\alpha_\lambda = 3.54097/(\lambda^2 - 0.0267) - 0.410224/(\lambda^2 - 0.075)$.

6708	$+7.24^\circ$	-0.03	5225	$+12.24^\circ$	-0.07	4376	$+17.91^\circ$	-0.06	3720	$+25.41^\circ$	$+0.17$
6292	8.30	-0.01	4887	14.10	-0.09	4216	19.41	-0.04	3601	26.91	$+0.02$
6104	8.86	± 0	4844	14.41	-0.05	4072	20.91	-0.03	3498	28.41	$+0.05$
5893	9.52	-0.02	4694	15.41	-0.06	3952	22.41	$+0.11$	3352	30.41	$+0.05$
5805	9.81	-0.03	4568	16.41	$+0.02$	3822	23.91	$+0.02$	3200	32.41	$+0.60$
5515	10.96	-0.01									

In alcohol : $c = 11.2112$; $t = 25^\circ$; $l = 2$ dm.; $[\alpha]_\lambda^{25^\circ} = 4.46\alpha_\lambda$; $[\alpha]_D^{25^\circ} = 58.91^\circ$; $\alpha_\lambda = 4.365853/(\lambda^2 - 0.02895) - 0.131958/(\lambda^2 - 0.075)$.

6708	$+10.01^\circ$	-0.01	5515	$+15.29^\circ$	$+0.01$	4354	$+26.04^\circ$	± 0	3581	$+41.64^\circ$	$+0.15$
6292	11.45	-0.04	5225	17.22	± 0	4099	30.04	$+0.07$	3453	45.44	$+0.06$
6104	12.23	-0.03	4886	20.04	$+0.04$	3898	33.84	$+0.05$	3318	50.04	-0.01
5805	13.62	-0.05	4682	22.04	$+0.01$	3786	36.24	± 0	3235	52.44	-0.22

In chloroform : $c = 7.586$; $t = 25^\circ$; $l = 2$ dm.; $[\alpha]_\lambda^{25^\circ} = 6.591\alpha_\lambda$; $[\alpha]_D^{25^\circ} = 46.60$; $\alpha_\lambda = 2.5082/(\lambda^2 - 0.0346) - 0.251375/(\lambda^2 - 0.075)$ (Equation A); $\alpha_\lambda = 2.262/(\lambda^2 - 0.028)$ (Equation B).

λ .	α , obs.	Diff. (A).	Diff. (B).	λ .	α , obs.	Diff. (A).	Diff. (B).	λ .	α , obs.	Diff. (A).	Diff. (B).
6708	$+5.40^\circ$	$+0.03^\circ$	$+0.04^\circ$	5225	$+9.23^\circ$	-0.02°	$\pm 0^\circ$	3821	$+19.01^\circ$	$+0.03^\circ$	-0.16
6292	6.15	-0.01	± 0	4887	10.73	-0.02	± 0	3660	21.01	$+0.03$	-0.34
6104	6.54	-0.04	$+0.03$	4589	12.41	$+0.01$	$+0.01$	3514	23.01	-0.03	-0.68
5893	7.07	$+0.03$	-0.01	4360	13.91	-0.04	-0.04	3322	26.01	$+0.01$	-1.46
5805	7.32	-0.01	± 0	4179	15.41	$+0.02$	-0.02	3188	28.01	$+0.03$	-2.71
5515	8.20	-0.01	$+0.01$	4000	17.01	-0.03	-0.13	3107	29.21	$+0.38$	-3.80

In dioxan: $c = 11.416$; $t = 25^\circ$; $l = 2$ dm.; $[\alpha]_{\lambda}^{25^\circ} = 4.38\alpha_{\lambda}$; $[\alpha]_{D}^{25^\circ} = 65.87^\circ$; $\alpha_{\lambda} = 5.10172/(\lambda^2 - 0.03415) - 0.337626/(\lambda^2 - 0.075)$ (Equation A); $\alpha_{\lambda} = 5.04994/(\lambda^2 - 0.0333) - 0.282324/(\lambda^2 - 0.075)$ (Equation B); $\alpha_{\lambda} = 4.73/(\lambda^2 - 0.032)$ (Equation C).

λ	α , obs.	Diff. (A).	Diff. (B).	Diff. (C).	λ	α , obs.	Diff. (A).	Diff. (B).	Diff. (C).
6708	+11.35°	-0.02°	-0.02°	+0.03°	4101	+34.43°	-0.01°	+0.02°	-0.30°
6292	13.03	-0.02	-0.02	+0.03	3983	37.08	+0.11	+0.17	-0.27
6104	13.91	-0.02	-0.02	+0.02	3850	40.06	±0	-0.02	-0.64
5893	15.04	-0.01	±0	+0.04	3720	43.46	-0.15	-0.14	-1.00
5805	15.52	-0.04	-0.03	+0.01	3588	47.64	-0.02	-0.02	-1.26
5515	17.42	-0.01	+0.01	+0.04	3520	50.04	+0.10	+0.07	-1.43
5225	19.60	-0.05	-0.04	-0.03	3444	52.64	+0.02	-0.08	-1.97
4887	22.84	-0.03	-0.01	-0.03	3364	55.64	-0.08	-0.19	-2.64
4681	25.27	+0.03	+0.05	-0.01	3285	58.84	-0.06	-0.26	-3.47
4564	26.84	+0.08	+0.10	+0.01	3200	62.44	+0.01	-0.34	-4.75
4445	28.44	-0.03	±0	-0.13	3144	64.84	+0.15	-0.36	-5.92
4259	31.44	-0.04	-0.01	-0.22	3097	67.24	+0.78	+0.09	-6.77
4216	32.28	+0.04	+0.07	-0.17	3020	69.64	+1.05	-0.15	-10.25

In benzene: $c = 10.662$; $t = 25^\circ$; $l = 2$ dm.; $[\alpha]_{\lambda}^{25^\circ} = 4.6896\alpha_{\lambda}$; $[\alpha]_{D}^{25^\circ} = 72.83^\circ$; $\alpha_{\lambda} = 5.354337/(\lambda^2 - 0.0398) - 0.511828/(\lambda^2 - 0.075)$ (Equation A); $\alpha_{\lambda} = 5.07/(\lambda^2 - 0.035) - 0.175/(\lambda^2 - 0.08)$ (Equation B).

λ	α , obs.	Diff. (A).	Diff. (B).	λ	α , obs.	Diff. (A).	Diff. (B).	λ	α , obs.	Diff. (A).	Diff. (B).
6708	+11.76°	+0.07°	+0.01°	4755	+25.41°	+0.06°	+0.08°	3694	+46.91°	-0.15°	+0.04°
6270	13.52	-0.02	-0.08	4603	27.41	+0.03	+0.08	3622	49.41	-0.07	+0.13
6104	14.35	-0.02	-0.07	4472	29.41	+0.07	+0.14	3551	51.91	-0.12	+0.05
5880	15.63	+0.02	-0.03	4293	32.41	+0.04	+0.13	3488	54.41	-0.03	+0.11
5805	16.08	-0.01	-0.03	4090	36.41	-0.04	+0.09	3415	57.41	+0.01	+0.07
5515	18.00	-0.02	-0.05	3957	39.41	-0.17	±0.00	3345	60.41	+0.01	-0.04
5225	20.35	-0.03	-0.04	3774	44.41	-0.17	+0.12	3259	64.41	+0.19	-0.11
4887	23.75	-0.03	-0.02	3709	46.41	-0.18	+0.03	3190	67.41	+0.13	-0.49

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