

174. Optical Rotatory Dispersion in the Carbohydrate Group. Part VIII.
Tetramethyl δ -Gluconolactone and Tetramethyl δ -Galactonolactone.

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IN Part IV (J., 1934, 1825) it was shown that the rotatory dispersion of tetramethyl γ -mannonolactone in various solvents could be expressed by a two-term Drude equation, the low-frequency term of which was attributed to induced dissymmetry at the lactonic carbonyl group. When the investigations were extended to the epimeric substance tetramethyl γ -gluconolactone (J., 1935, 295) the dispersion was found to be nearly simple in character, and when attempts were made to derive two-term equations it appeared that a positive term having λ_1^2 *ca.* 0.035 was predominant, and that the comparatively small negative term had λ_2^2 *ca.* 0.075. The former (positive) term corresponds to an active absorption band at λ 1900 A. and can be readily interpreted in terms of induced dissymmetry of the carbonyl group, but the physical meaning of the low-frequency term is still uncertain. We have, therefore, examined other members of the group of lactones which display dispersions not far removed from simplicity. Two such members, specially suitable for accurate measurements on account of high solubilities and rotatory powers, are tetramethyl δ -gluconolactone (I) and tetramethyl δ -galactonolactone (II). These substances possess six-membered ring systems, and we have been able, therefore, to compare the rotatory dispersions of typical δ -lactones with those of γ -lactones containing five-membered ring systems.



The results of the eight series of observations now published show that the rotatory dispersion of both lactones in all the solvents employed can be represented by single-term equations of the Drude-Natanson type :

$$\alpha_{\lambda} = \frac{k(\lambda^2 - \lambda_0^2)}{(\lambda^2 - \lambda_0^2)^2 + \lambda'^2 \lambda^2}$$

Reference to Table I reveals that the values of λ_0^2 are all close to 0.04, corresponding to an active absorption band in the neighbourhood of λ 2000. The carbonyl group of carboxylic acids and esters is known to exhibit absorption bands in this region. The band controlling the rotation of the lactones may, therefore, be ascribed to the lactonic carbonyl group. This implies that the whole of the observed rotation is due to induced dissymmetry and that the partial rotations due to the remaining centres of dissymmetry cancel out amongst themselves, leaving a negligible residual rotation. We have found by further calculations based on the data previously published (J., 1935, 295) that the dispersion of tetramethyl γ -gluconolactone can be expressed by similar single-term equations in which λ_0^2 is approximately 0.04 and λ'^2 *ca.* 0.008. The three lactones are exactly similar in behaviour, and in each case only the term due to induced dissymmetry is observed. These lactones follow the Hudson rotation rule in all solvents, and we have therefore another instance of the connection between rotation rules and induced dissymmetry (see J., 1934, 1826).

The absence of terms occasioned by absorption at shorter wave-lengths (*ca.* λ 1400) is surprising, although a similar case has been encountered amongst the aldehyde-sugars (Hudson, Wolfrom, and Lowry, J., 1933, 1179). On the other hand, in the rotatory dispersion of tetramethyl γ -mannonolactone, the high-frequency term due to the ordinary centres of dissymmetry is prominent, and even predominant under certain conditions. The only structural difference between corresponding mannose and glucose derivatives lies in the configuration of the groups attached to C_2 , and in view of the results now disclosed, we intend to examine other lactones in both the mannose and the glucose series in order to determine (*a*) the extent to which the induced dissymmetry is governed severally

by the dissymmetry of C_2 and by that at C_4 (in the γ -lactones : C_5 in the δ -lactones), and (b) the types of configuration which render the partial rotation due to induced dissymmetry preponderant in the total observed rotation.

TABLE I.

$$\alpha_\lambda = k(\lambda^2 - \lambda_0^2)/[(\lambda^2 - \lambda_0^2)^2 + \lambda^2\lambda'^2]$$

Tetramethyl δ -gluconolactone.				Tetramethyl δ -galactonolactone.			
Solvent.	k ,*	λ_0^2 .	λ' , A.	Solvent.	k ,*	λ_0^2 .	λ' , A.
CHCl_3	34.0	0.0415	760	CHCl_3	32.3	0.0456	915
C_6H_6	33.9	0.0429	770	C_6H_6	39.9	0.046	885
Dioxan	35.7	0.0429	845	Dioxan	35.1	0.0415	865
Ether	37.3	0.0388	695	Ether	31.7	0.0412	895

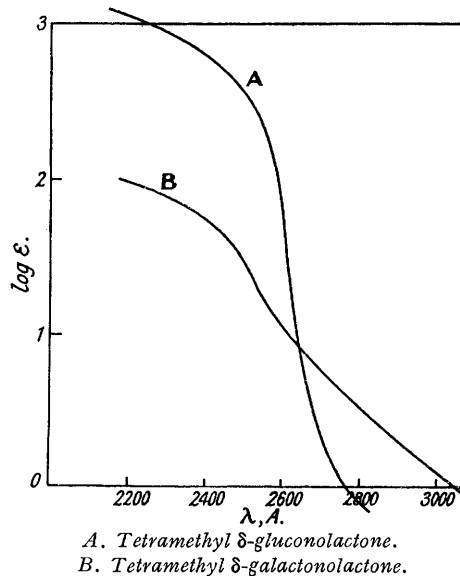
* Calculated for specific rotation values.

The constant λ' in the Drude-Natanson equation gives a measure of the half-width of the active absorption band, and it is apparent from Table I that the values of λ' are large, indicating broad absorption bands. For tetramethyl δ -galactonolactone, the calculated half-width is about 750 A., and for tetramethyl δ -galactonolactone, about 880 A. The corresponding value for tetramethyl γ -gluconolactone is about 900 A. These values are comparable with those (*ca.* 500 A.) measured directly by Hudson, Wolfrom, and Lowry (*loc. cit.*) for the absorption bands of aldehyde-sugar acetates. Moreover, the calculated values of λ' are compatible with the observed absorption spectra of the lactones which display strong general absorption at wave-lengths lower than about 2600 A., without evidence of discrete bands (see fig.).

It is recognised that the Drude-Natanson equation does not represent with complete accuracy the dispersion phenomena at wave-lengths near the head of the active absorption band (compare *idem, ibid.*), but in the present instances observations which would permit the use of more exact equations are unobtainable because the rotation values, although measurable for wave-lengths on the edge of the absorbing region, are not available for wave-lengths throughout the region of absorption.

In these circumstances, the Drude-Natanson equation gives a much closer approximation to the shape of the dispersion curve than does the ordinary Drude equation, which is valid only in regions of complete transparency. We have previously given examples of this (J., 1935, 1658; 1936, 1403) and it has been shown by Sørensen and Trumpy (*Z. physikal. Chem.*, 1935, B, 28, 135) that the dispersions of various sugar acetates, which possess a carbonyl group similar to that of the lactones now under investigation, may be expressed by single-term Drude-Natanson equations having λ_0^2 *ca.* 0.036 and λ' approximately 900 A.

Another feature of the present results requires comment. The induced dissymmetry in the examples now under discussion depends on absorption at λ 2000 approximately, whereas in the case of tetramethyl γ -mannonolactone (when the data were specially favourable for accurate analysis owing to the anomalous dispersion) the induced term depended upon absorption at λ 2500. An intermediate condition is shown by methyl dimethoxysuccinate (Harris, Hirst, and Wood, J., 1935, 1658), the corresponding wave-length being λ 2300. The reason for these divergences is not yet known. Reference to p. 850 shows that the rotations recorded there can be expressed also with considerable accuracy by two-term Drude equations, one term of which is obviously the same in origin as



A. Tetramethyl δ -gluconolactone.
B. Tetramethyl δ -galactonolactone.

TABLE II.

In chloroform: c , 14.455; l , 1 dm.; t , 20°; $[\alpha]_D^{20} + 109.3$; $[\alpha]_\lambda^{20} = 6.918\alpha_\lambda$.
$$(A) \alpha_\lambda = \frac{5.4756}{\lambda^2 - 0.037} - \frac{0.53}{\lambda^2 - 0.064}; (B) \alpha_\lambda = \frac{4.9345(\lambda^2 - 0.0415)}{(\lambda^2 - 0.0415)^2 + 0.00578\lambda^2}$$

λ	6708	6292	6104	5893	5805	5515	5225	4887	4548	4252
a	+11.95°	13.73°	14.65°	15.80°	16.33°	18.34°	20.71°	24.08°	28.45°	33.45°
Diff. (A) ...	+0.06	+0.07	+0.05	+0.02	+0.02	+0.05	+0.04	-0.02	-0.08	-0.09
Diff. (B) ...	+0.06	+0.06	+0.03	± 0	-0.01	-0.02	± 0	-0.07	-0.14	-0.16
λ	4021	3835	3676	3542	3423	3315	3226	3138	3065	
a	+38.45°	43.45°	48.45°	53.45°	58.45°	63.45°	68.45°	73.43°	78.42°	
Diff. (A) ...	-0.04	+0.08	+0.10	+0.17	+0.12	-0.12	+0.04	-0.27	-0.04	
Diff. (B) ...	-0.11	+0.02	+0.06	+0.16	+0.14	-0.07	+0.09	-0.26	-0.16	

In benzene: c , 16.89; l , 1 dm.; t , 20°; $[\alpha]_D^{20} + 108.9$; $[\alpha]_\lambda^{20} = 5.922\alpha_\lambda$.
$$(A) \alpha_\lambda = \frac{6.2838}{\lambda^2 - 0.0365} - \frac{0.5138}{\lambda^2 - 0.065}; (B) \alpha_\lambda = \frac{5.7245(\lambda^2 - 0.0429)}{(\lambda^2 - 0.0429)^2 + 0.0060\lambda^2}$$

λ	6708	6292	6104	5893	5805	5515	5225	4887	4548	4252
a	+13.89°	15.90°	17.04°	18.39°	18.99°	21.27°	24.08°	28.45°	33.45°	38.45°
Diff. (A)	+0.03	-0.03	+0.01	-0.01	-0.03	-0.06	-0.02	-0.02	-0.02	-0.02
Diff. (B)	+0.05	-0.01	+0.03	± 0	-0.03	-0.07	-0.05	-0.07	-0.05	-0.05
λ	4844	4830	4580	4365	4157	4002	3758	3542	3423	3315
a	+28.68°	28.95°	32.95°	36.95°	41.45°	45.45°	53.45°	58.45°	63.45°	68.45°
Diff. (A)	± 0	+0.07	+0.23	+0.25	+0.11	+0.03	+0.19	+0.19	+0.19	+0.19
Diff. (B)	-0.07	+0.01	+0.14	+0.12	-0.05	-0.17	-0.06	-0.06	-0.06	-0.06
λ	3649	3542	3433	3345	3265	3193	3108	3065	3065	3065
a	+57.45°	62.45°	67.45°	72.45°	77.45°	82.44°	88.43°	93.42°	98.41°	103.40°
Diff. (A)	-0.03	+0.31	-0.07	+0.06	+0.15	+0.34	+0.13	+0.13	+0.13	+0.13
Diff. (B)	-0.30	+0.03	-0.38	-0.24	-0.15	± 0	-0.30	-0.30	-0.30	-0.30

In dioxan: c , 16.44; l , 1 dm.; t , 20°; $[\alpha]_D^{20} + 114.2$; $[\alpha]_\lambda^{20} = 6.083\alpha_\lambda$.
$$(A) \alpha_\lambda = \frac{6.646}{\lambda^2 - 0.0378} - \frac{0.756}{\lambda^2 - 0.067}; (B) \alpha_\lambda = \frac{5.8698(\lambda^2 - 0.0429)}{(\lambda^2 - 0.0429)^2 + 0.00718\lambda^2}$$

λ	6708	6292	6104	5893	5805	5515	5225	4887	4548	4252
a	+14.18°	16.29°	17.42°	18.78°	19.36°	21.77°	24.49°	28.45°	33.45°	38.45°
Diff. (A)	+0.03	+0.03	+0.08	± 0	-0.05	+0.01	-0.09	-0.09	-0.09	-0.09
Diff. (B)	+0.04	+0.03	+0.08	± 0	-0.06	± 0	-0.11	-0.11	-0.11	-0.11
λ	4887	4681	4545	4376	4179	4028	3896	3775	3670	3556
a	+28.52°	31.55°	33.95°	37.05°	41.45°	45.45°	49.45°	53.45°	57.45°	62.45°
Diff. (A)	-0.14	-0.13	-0.02	-0.12	-0.10	-0.01	+0.06	+0.06	+0.06	+0.06
Diff. (B)	-0.16	-0.15	-0.03	-0.14	-0.10	-0.03	+0.08	+0.08	+0.08	+0.08
λ	3775	3670	3556	3442	3355	3268	3186	3108	3065	3065
a	+53.45°	57.45°	62.45°	67.45°	72.45°	77.45°	82.44°	88.43°	93.42°	98.41°
Diff. (A)	-0.01	+0.03	+0.20	-0.24	+0.14	+0.12	-0.01	-0.01	-0.01	-0.01
Diff. (B)	+0.03	+0.09	+0.28	-0.15	+0.22	+0.11	-0.18	-0.18	-0.18	-0.18

In ether: c , 16.83; l , 1 dm.; t , 20°; $[\alpha]_D^{20} + 118.9$; $[\alpha]_\lambda^{20} = 5.925\alpha_\lambda$.
$$(A) \alpha_\lambda = \frac{6.7214}{\lambda^2 - 0.035} - \frac{0.4178}{\lambda^2 - 0.065}; (B) \alpha_\lambda = \frac{6.2956(\lambda^2 - 0.0388)}{(\lambda^2 - 0.0388)^2 + 0.00479\lambda^2}$$

λ	6708	6292	6104	5893	5805	5515	5225	4887	4548	4252
a	+15.12°	17.35°	18.54°	20.06°	20.68°	23.23°	26.22°	30.61°	35.45°	40.45°
Diff. (A)	+0.01	-0.01	-0.01	+0.02	-0.04	± 0	-0.01	+0.04	+0.04	+0.04
Diff. (B)	± 0	-0.02	-0.02	± 0	-0.06	-0.01	-0.03	+0.01	+0.01	+0.01
λ	4652	4427	4251	4098	3966	3844	3740	3645	3645	3645
a	+34.45°	38.45°	42.45°	46.45°	50.45°	54.45°	58.45°	62.45°	66.45°	70.45°
Diff. (A)	+0.16	-0.11	-0.07	-0.05	+0.02	-0.11	-0.06	-0.08	-0.08	-0.08
Diff. (B)	+0.13	-0.13	-0.08	-0.06	+0.02	-0.07	± 0	+0.01	+0.01	+0.01
λ	3559	3482	3413	3346	3267	3214	3186	3108	3065	3065
a	+66.45°	70.45°	74.45°	78.45°	83.45°	87.45°	91.45°	95.45°	99.45°	103.45°
Diff. (A)	-0.10	-0.06	+0.08	+0.01	-0.24	-0.05	-0.05	-0.05	-0.05	-0.05
Diff. (B)	+0.02	+0.10	+0.27	+0.24	+0.02	+0.23	+0.23	+0.23	+0.23	+0.23

TABLE III.

In chloroform : c , 15.50; l , 1 dm.; t , 20°; $[\alpha]_D^{20} + 104.4^\circ$; $[\alpha]_\lambda^{20} = 6.454\alpha_\lambda$.

$$(A) \alpha_\lambda = \frac{7.279}{\lambda^2 - 0.043} - \frac{2.225}{\lambda^2 - 0.06}; \quad (B) \alpha_\lambda = \frac{5.0385(\lambda^2 - 0.0456)}{(\lambda^2 - 0.04556)^2 + 0.0084\lambda^2}$$

λ	6708	6292	5893	5805	5515	5225	4887	4415	4257	4062
α	+12.18°	14.01°	16.17°	16.74°	18.77°	21.19°	24.75°	31.45°	34.45°	38.45°
Diff. (A) ...	±0	+0.01	-0.01	+0.01	+0.01	+0.02	+0.02	+0.03	+0.16	-0.02
Diff. (B) ...	±0	+0.01	-0.01	+0.01	±0	-0.02	±0	+0.02	+0.14	-0.01
λ	3900	3735	3590	3460	3352	3290	3232	3130	3050	
α	+42.45°	47.45°	52.45°	57.45°	62.45°	65.45°	68.45°	73.45°	78.45°	
Diff. (A) ...	-0.11	+0.01	-0.02	-0.17	±0	±0	+0.06	-0.37	+0.32	
Diff. (B) ...	-0.06	+0.09	+0.11	-0.03	+0.18	+0.16	+0.14	-0.55	-0.39	

In benzene : c , 16.68; l , 1 dm.; t , 20°; $[\alpha]_D^{20} + 129.1^\circ$; $[\alpha]_\lambda^{20} = 5.994\alpha_\lambda$.

$$(A) \alpha_\lambda = \frac{8.7704}{\lambda^2 - 0.041} - \frac{2.0413}{\lambda^2 - 0.06}; \quad (B) \alpha_\lambda = \frac{6.669(\lambda^2 - 0.046)}{(\lambda^2 - 0.046)^2 + 0.00783\lambda^2}$$

λ	6708	6292	5893	5805	5515	5225	4887	4630	4390	4108
α	+16.16°	18.60°	21.53°	22.23°	24.95°	28.24°	32.87°	37.45°	42.45°	49.95°
Diff. (A) ...	-0.05	-0.04	±0	-0.03	-0.02	+0.02	-0.05	+0.08	+0.03	+0.07
Diff. (B) ...	±0	+0.01	+0.04	±0	+0.01	+0.04	-0.06	+0.06	-0.02	+0.02
λ	4024	3951	3878	3754	3645	3546	3456	3389	3326	
α	+52.45°	54.95°	57.45°	62.45°	67.45°	72.45°	77.45°	81.45°	85.45°	
Diff. (A) ...	-0.04	-0.01	-0.14	-0.10	±0	+0.01	-0.10	-0.09	-0.20	
Diff. (B) ...	-0.12	-0.11	-0.19	-0.15	-0.04	+0.05	+0.05	+0.02	-0.03	

In dioxan : c , 15.31; l , 1 dm.; t , 20°; $[\alpha]_D^{20} + 111.5^\circ$; $[\alpha]_\lambda^{20} = 6.533\alpha_\lambda$.

$$(A) \alpha_\lambda = \frac{7.126}{\lambda^2 - 0.04} - \frac{1.749}{\lambda^2 - 0.06}; \quad (B) \alpha_\lambda = \frac{5.3764(\lambda^2 - 0.0415)}{(\lambda^2 - 0.0415)^2 + 0.0075\lambda^2}$$

λ	6708	6292	5893	5805	5515	5225	4887	4640	4450
α	+12.95°	14.81°	17.07°	17.68°	19.81°	22.39°	26.05°	29.45°	32.45°
Diff. (A) ...	+0.05	±0	-0.03	±0	-0.01	+0.02	-0.01	+0.06	+0.03
Diff. (B) ...	+0.05	+0.01	-0.04	±0	-0.01	+0.02	±0	+0.09	+0.06
λ	4285	4102	3939	3799	3680	3568	3452	3337	3244
α	+35.45°	39.45°	43.45°	47.45°	51.45°	55.45°	60.45°	65.45°	70.45°
Diff. (A) ...	+0.01	+0.05	-0.05	-0.12	-0.04	-0.19	±0	-0.37	-0.12
Diff. (B) ...	+0.03	+0.12	+0.06	+0.21	+0.12	-0.01	+0.15	-0.27	-0.19

In ether : c , 14.61; l , 1 dm.; t , 20°; $[\alpha]_D^{20} + 100.4^\circ$; $[\alpha]_\lambda^{20} = 6.847\alpha_\lambda$.

$$(A) \alpha_\lambda = \frac{6.217}{\lambda^2 - 0.04} - \frac{1.60}{\lambda^2 - 0.06}; \quad (B) \alpha_\lambda = \frac{4.636(\lambda^2 - 0.0412)}{(\lambda^2 - 0.0412)^2 + 0.0080\lambda^2}$$

λ	6708	6104	5893	5805	5515	5225	4880	4620	4217
α	+11.06°	13.58°	14.67°	15.12°	16.97°	19.18°	22.43°	25.45°	31.45°
Diff. (A) ...	±0	±0	±0	-0.04	-0.01	+0.01	+0.03	+0.03	-0.10
Diff. (B) ...	-0.04	-0.04	-0.04	-0.08	-0.05	-0.03	±0	±0	-0.07
λ	4062	3929	3767	3632	3507	3399	3300	3211	3109
α	+34.45°	37.45°	41.45°	45.45°	49.45°	53.45°	57.45°	61.45°	66.45°
Diff. (A) ...	-0.04	+0.04	-0.03	+0.06	-0.06	-0.05	-0.10	±0	+0.37
Diff. (B) ...	-0.02	+0.08	+0.06	+0.17	+0.05	+0.03	-0.07	-0.15	-0.31

that occurring in the single-term Drude-Natanson equations, but the second has $\lambda_2^2 ca. 0.065$ and corresponds to absorption at $\lambda 2500$. We have previously commented upon the possibility and relative merits of these two methods of representing dispersions which are nearly "simple" (J., 1935, 1659), and we are of the opinion that this second term has no physical significance, and, in particular, is not to be identified with the induced term in the dispersion of tetramethyl γ -mannonolactone. It is probably no more than a numerical correction factor which, over the range of wave-lengths examined, varies fortuitously in the same way as a term of the Drude equation. But with the evidence at present available it is not possible to reject categorically the alternative view, which is nevertheless to be regarded as improbable, that in these lactones the carbonyl group may display two modes of absorption both of which may be capable of giving rise to induced dissymmetry. Further investigations directed towards the elucidation of this point are now being undertaken.

EXPERIMENTAL.

Tetramethyl δ-Gluconolactone.—Tetramethyl glucopyranose was oxidised in the usual way by bromine-water. The product was distilled, and then treated in aqueous solution with a small quantity of potassium permanganate to remove traces of reducing material. The lactone was extracted from the aqueous solution by chloroform, and was finally purified by seven distillations under diminished pressure; $n_D^{15^\circ}$ 1.4561; $[\alpha]_D^{20^\circ} + 99^\circ$ in water (c , 0.8). The rotation data are in Table II.

Tetramethyl δ-Galactonolactone.—Specially purified 2 : 3 : 4 : 6-tetramethylgalactose (obtained by hydrolysis of the crystalline anilide) was oxidised by bromine-water (compare Haworth, Ruell, and Westgarth, J., 1924, 125, 2473). The lactone was then purified and distilled exactly as in the preceding case; $n_D^{15^\circ}$ 1.4602. The relevant data are in Table III.

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