304. *Optical Rotatory Dispersion in the Carbohydrate Group. Part VII. The Glucal Series.*

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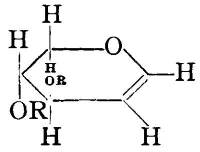
The rotatory powers of substances in the glucal series are of special interest because of the extraordinary contrast between the rotations of xylal and its derivatives and those of corresponding members in the glucal series. For example, xylal (I, R = H) has $[\alpha]_D$ $-$ 254° whereas the value for glucal (II, R = H) is $-$ 7°. This distinction is all the more remarkable since corresponding derivatives of xylose and glucose generally possess similar rotatory powers. Reference to the formulæ shows that in the pyranose series the only structural difference between the two series of substances lies in the substitution of one of the hydrogen atoms on C_5 of xylose by the group $-CH_2 \cdot OH$. This involves one additional centre of dissymmetry in the glucose molecule as compared with xylose, but the rotational effect of this centre appears to be small in derivatives of the reducing sugar, where C_1 exerts a preponderating influence.

On the other hand, in the glucal series both C_1 and C_2 have lost their ordinary dissymmetry, and the rotational effects depend on the centres at C_3, C_4, and C_5 in glucal and on those at C_3 and C_4 in xylal. The rotational difference between xylal and glucal might therefore depend solely on the altered conditions due to the presence of the extra dissymmetric centre in glucal, but in view of recent work on induced dissymmetry other possibilities arise also. Both xylal and glucal possess an unsaturated double bond situated in close proximity to a centre of dissymmetry. It was conceivable, therefore, that this double bond might acquire induced dissymmetry and so give rise to a partial rotation dependent on the absorption band of the unsaturated linkage. The head of this band being in the neighbourhood of 2000 A., the corresponding partial rotation in regions remote from the band would be of the form $k/(\lambda^2 - 0{\cdot}04)$. Furthermore, since the inductive effect is caused mainly by the nearest dissymmetric centre, it would be expected, in view of the stereochemical arrangements at C_3 and C_4 in glucal and in xylal, that the induced term would have the same sign for both substances. The remaining partial rotations due to the saturated centres could obviously differ in both sign and magnitude for reasons explained above.

(I.)



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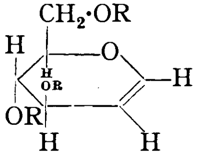

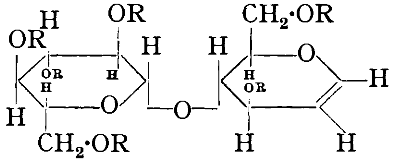

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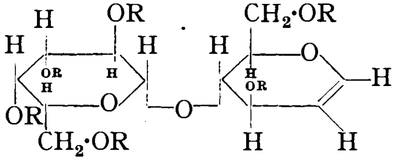


(IV.)

In order to gain definite information on these points, we decided to investigate the optical rotatory dispersion and absorption spectra of a selected group of substances in the glucal series. These included diacetyl xylal (I, R = Ac), triacetyl glucal (II, R = Ac), cellobial (III, R = H), hexa-acetyl cellobial (III, R = Ac), lactal (IV, R = H), and hexa-acetyl lactal (IV, R = Ac). The observations were made by methods described in earlier papers and the detailed figures are given in the experimental section. Analysis of the results revealed that the data for acetyl xylal could be expressed by a single-term equation of the Drude–Natanson type having $\lambda_0^2 = 0{\cdot}049$ approx. and k_0 negative in sign. The data for each of the other substances required for their quantitative expression a two-term Drude equation of the ordinary type, $\alpha_\lambda = k_1/(\lambda^2 - \lambda_1^2) - k_0/(\lambda^2 - \lambda_0^2)$, in which λ_0^2 was again *ca.* 0·045, and the low-frequency term was negative in sign. The value of λ_1^2 was approximately 0·025, and in view of results described in previous papers, this high-frequency term can be ascribed to absorption of light at the saturated linkages of the molecule.

Rotatory Dispersion Constants.

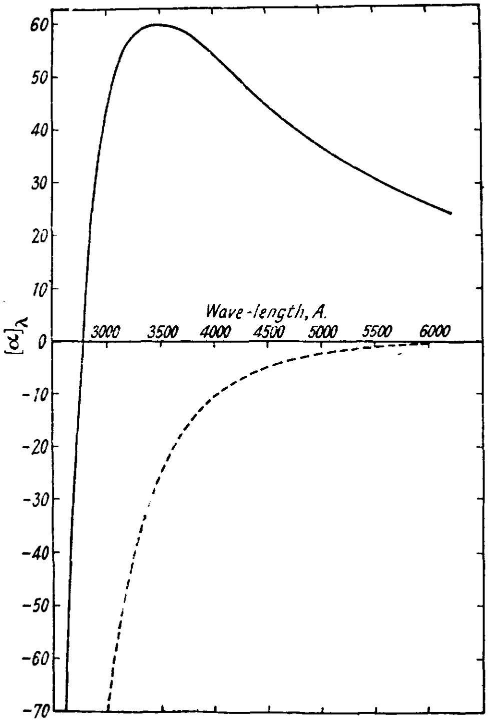
Substance.	Solvent.	*c*.	$[\alpha]_D$.	λ_0^2.	λ_1^2.	k_0/k_1.
Diacetyl xylal	$CHCl_3$	18·6	−315°	0·049	—	—
	EtOH	19·0	−299	0·049	—	—
Triacetyl glucal	$CHCl_3$	15·6	− 23	0·045	0·028	−1·189
	EtOH	6·1	− 14	0·047	0·021	−1·130
Hexa-acetyl lactal	$CHCl_3$	10·0	− 17	0·04	0·02	−1·249
Hexa-acetyl cellobial	$CHCl_3$	11·7	− 22	0·047	0·02	−1·615
Lactal	H_2O	10·4	+ 27·2	0·0405	0·026	−0·714
Cellobial	H_2O	7·6	− 0·3	0·045	0·02	−0·933

The low-frequency term with λ_0^2 *ca.* 0·045 corresponds to an absorption band in the region λ 2000—2200 A. It cannot therefore be associated with the saturated bonds, and since the same value of λ_0^2 appears in the equations for lactal, cellobial, and their hexa-acetyl derivatives, it cannot be ascribed to induced dissymmetry of the carbonyl group in the acetates. It must therefore be connected with the double bond, which is known to absorb strongly in the region of λ 2000, and the results now published provide clear evidence that in the glucal series the unsaturated linkage ·C:C· can become dissymmetric under the influence of adjoining centres of dissymmetry.

The observation that the sign of the induced term is the same in all the derivatives of glucal and xylal referred to in this paper is in accord with expectation (see above), and moreover, the absorption spectra of the various substances can be directly correlated with the character of the rotatory dispersion. It is apparent from Figs. 2 and 3 that solutions of lactal and cellobial are remarkably transparent for wave-lengths above λ 2300, below which the absorption curve rises with extreme steepness until at about λ 2050 (log ε, 3·6) there is change of direction suggesting a maximum. The acetylated derivatives display a similar behaviour, giving curves which commence to rise steeply at λ 2400.

Reference to the detailed results shows that the rotations of substituted glucals in the visual region vary markedly with the substituent, and lactal and cellobial provide a specially interesting contrast in this connection. In the visual region, the rotation of lactal is positive ($[\alpha]_D$ + 27°) and rises with diminishing wave-length to the maximum value, $[\alpha]_{3500}$ + 60°, after which it decreases, crosses the axis, and reaches — 168° at λ 2505 (Fig. 1). On the other hand, the rotation of cellobial is negative even in the visual region, and becomes increasingly negative as the wave-length decreases (Fig. 1). Now, cellobial differs structurally from lactal only in the disposition of the hydrogen and the hydroxyl group round C_4 of the second hexose residue. In the ordinary saturated derivatives of the sugars, this difference entails a smaller positive rotation for glucose derivatives as compared with the corresponding galactose derivatives, and in the present example it should operate therefore by diminishing the effect of the high-frequency term ($\lambda_1^2 = 0{\cdot}02$) relative to that of the induced low-frequency term ($\lambda_0^2 = 0{\cdot}04$). The equations show that this is actually what takes place, the ratio k_0/k_1 being 0·93 for cellobial and 0·71 for lactal.

FIG. 1.



——— *Rotatory dispersion of lactal in water.*
– – – – *Rotatory dispersion of cellobial.*

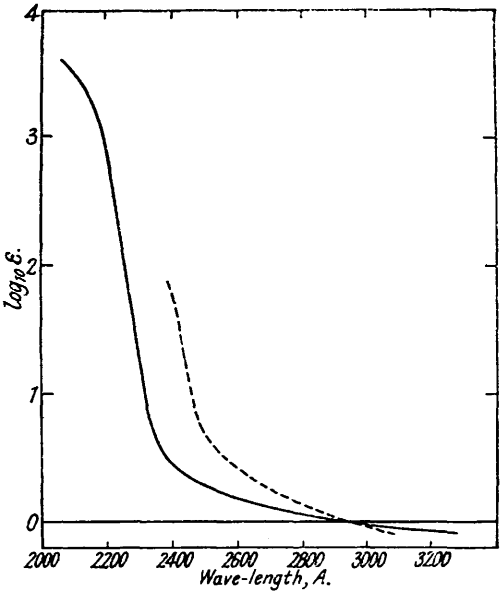
The results indicate also that the difference in rotatory power between diacetyl xylal and triacetyl glucal is complex in origin. In the former, the partial rotations due to the saturated centres cancel out, leaving only the induced term, which then displays its full value in the observed rotation; in the latter, which possesses an additional saturated centre, this compensation does not take place, with the result that the total rotation is made up of two terms of opposite sign, and the effect of the induced term is much less evident.

EXPERIMENTAL.

Diacetyl Xylal.—Diacetyl xylal was prepared from tetra-acetyl xylose by Levene and Mori's method (*J. Biol. Chem.*, 1929, **83**, 803). After purification by repeated distillation under diminished pressure (bath temp. 93—95°/0·1 mm.), it was a clear colourless syrup, $n_D^{15^\circ}$ 1·4670. Its absorption spectrum in alcohol is shown in Fig. 3.

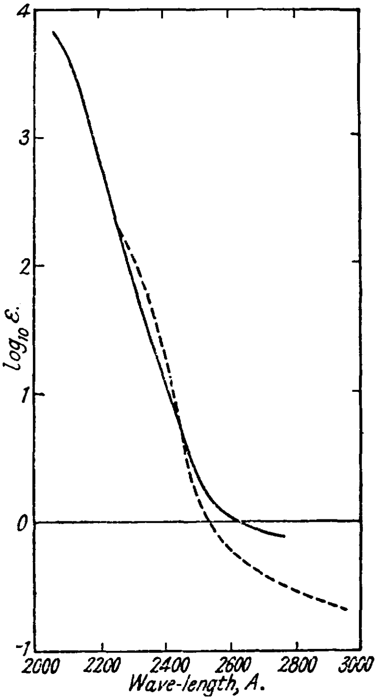
3 : 4 : 6-*Triacetyl Glucal.*—This was prepared by Fischer's method (*Ber.*, 1914, **47**, 1, 199), and recrystallised from absolute alcohol–light petroleum; m. p. 54—55°. Its absorption spectrum in alcohol is shown in Fig. 3.

FIG. 2.



——— *Lactal in water and cellobial in water.*
– – – – *Hexa-acetyl lactal in chloroform and hexa-acetyl cellobial in chloroform.*

FIG. 3.



——— *Triacetyl glucal in alcohol.*
– – – – *Diacetyl xylal in alcohol.*

Data for diacetyl xylal.

(*a*) In chloroform : *c*, 18·639; *l*, 1 dm.; *t*, 20°; $[a]_D^{20°} = -315·4°$;

$$a_\lambda^{20°} = -\frac{17·673(\lambda^2 - 0·0485)}{(\lambda^2 - 0·0485)^2 + 0·00107\lambda^2};\ [a]_\lambda^{20°} = 5·365a_\lambda.$$

λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.	λ.	$a_{obs.}$.	$a_{calc.}$.	Diff.
6708	−43·70°	−43·89°	+0·19°	3904	−167·55°	−167·65°	+0·10°
6292	50·67	50·69	+0·02	3691	197·55	197·69	+0·14
6104	54·18	54·32	+0·14	3578	217·55	217·53	−0·02
5893	58·79	58·91	+0·12	3436	247·55	247·60	+0·05
5805	60·96	61·00	+0·04	3349	269·55	269·64	+0·09
5515	68·79	68·79	±0	3256	297·55	297·09	−0·46
5225	78·33	78·27	−0·06	3169	327·55	327·31	−0·24
4887	92·41	92·21	−0·20	3119	347·55	347·11	−0·44
4595	107·55	107·74	+0·19	3051	377·55	377·47	−0·08
4311	127·55	127·33	−0·22	3012	397·55	396·97	−0·58
4085	147·55	147·42	−0·13	2974	417·55	417·60	+0·05

(*b*) In alcohol : *c*, 19·037; *l*, 1 dm.; *t*, 20°; $[a]_D^{20°}$ −298·6°; $[a]_\lambda^{20°} = 5·253a_\lambda$;

$$a_\lambda = -\frac{17·04(\lambda^2 - 0·049274)}{(\lambda^2 - 0·049274)^2 + 0·001544\lambda^2}.$$

6708	−42·26	−43·34	+0·08	3940	−157·56	−157·47	−0·09
6292	48·87	48·91	+0·04	3778	177·56	177·84	+0·28
6104	52·34	52·42	+0·08	3590	207·56	207·54	−0·02
5893	56·85	56·84	−0·01	3441	237·56	237·41	−0·15
5805	58·87	58·86	−0·01	3314	269·06	268·97	−0·09
5515	66·38	66·37	−0·01	3246	289·06	288·85	−0·21
5225	75·55	75·53	−0·02	3204	302·06	302·38	+0·32
4887	89·05	88·98	−0·07	3148	322·56	322·14	−0·42
4885	89·06	89·07	+0·01	3061	357·56	357·38	−0·18
4533	107·56	107·69	+0·13	2941	417·56	417·55	−0·01
4322	122·06	122·05	−0·01	2833	487·56	487·07	+0·49
4081	142·56	142·64	+0·08	2768	537·56	538·03	−0·47

Data for 3 : 4 : 6-*triacetyl glucal.*

(*a*) In chloroform : *c*, 15·579; *t*, 20°; *l*, 1 dm.; $[\alpha]_D^{20°} = -23·4°$; $[\alpha]_\lambda^{20°} = 6·419\alpha_\lambda$;
$\alpha_\lambda = 4·568/(\lambda^2 - 0·0281) - 5·431/(\lambda^2 - 0·04475)$.

λ.	$\alpha_{obs.}$	$\alpha_{calc.}$	Diff.	λ.	$\alpha_{obs.}$	$\alpha_{calc.}$	Diff.	λ.	$\alpha_{obs.}$	$\alpha_{calc.}$	Diff.
6708	−2·61°	−2·58°	−0·03°	4921	−6·15°	−6·17°	+0·02°	3267	−29·56°	−29·54°	−0·02°
6495	2·88	2·80	−0·08	4707	7·05	7·11	+0·06	3166	34·57	34·57	±0
6137	3·20	3·26	+0·06	4294	9·55	9·67	+0·12	3085	39·58	39·52	−0·06
6104	3·29	3·31	+0·02	4085	11·55	11·56	+0·01	3003	46·09	45·97	−0·12
5893	3·65	3·64	−0·01	3916	13·55	13·54	−0·01	2925	53·61	53·60	−0·01
5805	3·77	3·79	+0·02	3788	15·55	15·42	−0·13	2847	63·62	63·35	−0·27
5616	4·15	4·17	+0·02	3625	18·55	18·46	−0·09	2783	73·63	73·54	−0·09
5515	4·35	4·39	+0·04	3499	21·55	21·50	−0·05	2732	83·64	83·57	−0·07
5225	5·07	5·14	+0·07	3371	25·55	25·44	−0·11				

(*b*) In alcohol; *c*, 6·097; *t*, 20°; *l*, 1 dm.; $[\alpha]_D^{20°} = -13·8°$; $[\alpha]_\lambda^{20°} = 16·40\alpha_\lambda$;
$\alpha_\lambda = 1·1902/(\lambda^2 - 0·02082) - 1·3447/(\lambda^2 - 0·04658)$.

6708	−0·64	−0·56	−0·08	4580	−1·95	−1·94	−0·01	3261	−8·56	−8·58	+0·02
6495	0·73	0·62	−0·11	4405	2·25	2·25	±0	3162	10·07	10·15	+0·08
6137	0·75	0·73	−0·02	4262	2·55	2·56	+0·01	3067	12·07	12·07	±0
6104	0·76	0·74	−0·02	4107	2·95	2·96	+0·01	2987	14·09	14·14	+0·05
5893	0·84	0·83	−0·01	3998	3·35	3·31	−0·04	2912	16·60	16·58	−0·02
5805	0·87	0·87	±0	3864	3·85	3·83	−0·02	2840	19·61	19·57	−0·04
5616	0·98	0·96	−0·02	3747	4·35	4·38	+0·03	2763	23·63	23·75	+0·12
5515	1·02	1·02	±0	3647	4·95	4·95	±0	2706	27·63	27·76	+0·13
5225	1·22	1·22	±0	3508	5·95	5·94	−0·01	2652	32·64	32·58	−0·06
4887	1·54	1·54	±0	3384	7·05	7·09	+0·04	2609	37·65	37·39	−0·26
4785	1·65	1·66	+0·01								

Hexa-acetyl Lactal.—This was prepared from hepta-acetyl lactosidyl bromide by Bergmann's method (*Annalen*, **1923**, **434**, 86) as modified by Haworth, Hirst, Plant, and Reynolds (J., **1930**, 2647). After recrystallisation from chloroform–light petroleum, it had m. p. 114°, $[\alpha]_D^{20°}$ − 17·2° in chloroform (*c*, 10·0). Its absorption spectrum in chloroform is shown in Fig. 2.

Data for hexa-acetyl lactal.

In chloroform : *c*, 10·0; *l*, 1 dm.; *t*, 20°; $[\alpha]_\lambda^{20°} = 10·0\alpha_\lambda$;
$\alpha_\lambda = 1·702/(\lambda^2 - 0·02) - 2·126/(\lambda^2 - 0·04)$.

6292	−1·52	−1·45	−0·07	4887	−2·97	−2·91	−0·06	3330	−11·54	−11·27	−0·27
5893	1·72	1·72	±0	4512	3·53	3·72	+0·19	3175	13·95	13·92	−0·03
5805	1·83	1·80	−0·03	4000	5·53	5·56	+0·03	3138	14·55	14·69	+0·14
5515	2·00	2·06	+0·06	3680	7·54	7·54	±0	3100	15·55	15·53	−0·02
5225	2·40	2·40	±0	3475	9·54	9·39	−0·15				

Lactal.—Hexa-acetyl lactal (above) was de-acetylated by methyl-alcoholic ammonia. The crystalline product, m. p. 191°, $[\alpha]_D$ + 27·5° in water (*c*, 1·6), was the anhydrous form. It was analytically pure, but contained a trace of impurity which strongly absorbed ultra-violet light. The lactal was dissolved in water, the solution boiled with charcoal, and evaporated under diminished pressure, giving a crystalline mass. The pure monohydrate of lactal was then obtained by crystallisation from aqueous alcohol (cf. Fischer and Curme, *Ber.*, **1914**, **47**, 2047). The anhydrous form has m. p. 191°, but it is difficult to assign a definite m. p. to the hydrated form, which loses water when heated and melts between 160° and 190° according to conditions of heating. In making up the solutions for polarimetric work the hydrate was used, but for convenience, the concentrations quoted below are given in terms of anhydrous material. The maximum occurs at λ 3500 (obs. and calc.), the value of α_λ being 6·25° (calc., 6·14°). The absorption spectrum of lactal is shown in Fig. 2.

Data for lactal.

In water : *c*, 10·407; *l*, 1 dm.; *t*, 20°; $[\alpha]_D^{20°}$ +27·2°; $[\alpha]_\lambda^{20°} = 9·609\alpha_\lambda$;
$\alpha_\lambda = 3·68/(\lambda^2 - 0·026) - 2·627/(\lambda^2 - 0·0405)$.

6292	+2·49	+2·56	−0·07	4120	+5·45	+5·28	+0·17	3047	+ 4·93	+ 4·87	+0·06
5893	2·83	2·89	−0·06	3845	5·94	5·73	+0·21	2877	+ 2·41	+ 2·68	−0·27
5805	2·94	2·97	−0·03	3755	6·09	5·86	+0·23	2772	+ 0·0	+ 0·10	−0·10
5515	3·22	3·27	−0·05	3475	6·24	6·11	+0·13	2703	− 2·52	− 2·48	−0·04
5225	3·57	3·60	−0·03	3258	6·08	5·90	+0·18	2611	− 7·49	− 7·68	+0·19
4887	4·04	4·04	±0	3208	5·93	5·76	+0·17	2505	−17·46	−17·93	+0·47
4375	4·94	4·84	+0·10	3110	5·43	5·31	+0·12				

Cellobial.—Cellobiose octa-acetate was transformed into hexa-acetyl cellobial as described by Haworth, Hirst, Streight, Thomas, and Webb (J., 1930, 2638). The hexa-acetate was de-acetylated by methyl-alcoholic ammonia, and the cellobial so obtained was crystallised from methyl alcohol. This material, m. p. 177°, was colourless and analytically pure, but was contaminated like lactal. Further purification was effected by treatment with charcoal in aqueous solution, followed by crystallisation of the cellobial from methyl alcohol containing a little light petroleum. The substance then had m. p. 177°, $[\alpha]_{\mathrm{D}}^{20^\circ} - 0{\cdot}3^\circ$ in water (*c*, 7·57), and its aqueous solution was sufficiently transparent to permit measurement of the rotatory dispersion in the ultra-violet as far as 2978 A. Its absorption spectrum is given in Fig. 2.

Data for cellobial.

In water : *c*, 7·568; *l*, 2 dm.; *t*, 20°; $[\alpha]_{\lambda}^{20^\circ} = 6{\cdot}60\alpha_{\lambda}$;
$\alpha_{\lambda} = 1{\cdot}633/(\lambda^2 - 0{\cdot}02) - 1{\cdot}524/(\lambda^2 - 0{\cdot}045)$.

5893	−0·04	−0·05	+0·01	4294	−0·99	−1·00	+0·01	3246	−6·14	−6·12	−0·02
5515	0·13	0·13	±0	4009	1·55	1·56	+0·01	3172	7·14	7·14	±0
5225	0·23	0·23	±0	3711	2·56	2·57	+0·01	3105	8·14	8·27	+0·13
4887	0·39	0·40	+0·01	3530	3·56	3·53	−0·03	3014	10·16	10·20	+0·04
4680	0·55	0·55	±0	3392	4·56	4·57	+0·01	2978	11·17	11·11	−0·06
4490	0·75	0·74	−0·01	3292	5·57	5·57	±0				

Hexa-acetyl Cellobial.—Obtained by the method referred to above, this was prepared for spectro-polarimetric work by several crystallisations from alcohol; m. p. 135°. Its absorption spectrum is shown in Fig. 2.

Data for hexa-acetyl cellobial.

In chloroform : *c*, 11·67; *l*, 1 dm.; *t*, 20°; $[\alpha]_{\mathrm{D}}^{20^\circ} -21{\cdot}7^\circ$; $[\alpha]_{\lambda}^{20^\circ} = 8{\cdot}57\alpha_{\lambda}$;
$\alpha_{\lambda} = 1{\cdot}098/(\lambda^2 - 0{\cdot}02) - 1{\cdot}773/(\lambda^2 - 0{\cdot}047)$.

6292	−2·22	−2·16	−0·06	4054	−7·52	−7·50	−0·02	3106	−21·54	−21·48	−0·06
5893	2·53	2·55	+0·02	3902	8·52	8·54	+0·02	3048	23·55	23·56	+0·01
5805	2·65	2·65	±0	3776	9·52	9·59	+0·07	3000	25·55	25·54	−0·01
5515	3·04	3·03	−0·01	3595	11·53	11·49	−0·04	2957	27·55	27·56	+0·01
5225	3·52	3·51	−0·01	3449	13·53	13·56	+0·03	2921	29·56	29·46	−0·10
4887	4·22	4·23	+0·01	3338	15·53	15·52	−0·01	2852	33·57	33·74	+0·14
4774	4·52	4·52	±0	3247	17·53	17·47	−0·06	2802	37·58	37·51	−0·07
4467	5·52	5·51	−0·01	3166	19·54	19·62	+0·08	2744	42·58	42·79	−0·21
4219	6·52	6·58	+0·06								

Throughout the calculations, special attention was given to the possibility that equations having constants other than those given above might fit the data equally well. The observed rotations for diacetyl xylal reached the very high value of — 537° and it was soon obvious that no equation having λ_0^2 appreciably different from 0·049 could be considered. The data conform closely to the requirements of a single-term Drude equation and, as shown, can be accommodated precisely by a Natanson equation in which the value of the "damping factor" (0·001) corresponds approximately with an absorption band of half-width 300 A. This value is very reasonable, but it is of course possible that the deviations from the simple equation in regions remote from the band may be ascribed in part to small partial rotations due to other active bands. The total correction is, however, so small that such terms cannot be separated out, and it is clear that for this substance the character of the rotatory dispersion is accurately defined by the equation given. Each of the other substances investigated gave results which required for their expression two-term Drude equations, and, as explained in our previous papers, some variation in the calculated dispersion constants is then possible, especially when the observed rotations are small. Nevertheless, we have satisfied ourselves by numerous calculations that, in each equation given in the text, the constants recorded reveal correctly the general character of the dispersion, and that no serious variation in the values of the constants can be made without the introduction of discrepancies between observed and calculated rotation values, much beyond the range of possible experimental error.

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