278. *The Rotatory Dispersion of Organic Compounds. Part XXIII. Rotatory Dispersion and Circular Dichroism of Aldehydic Sugars.*

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The aldehydic formula suggested by von Baeyer (*Ber.*, 1870, **3**, 67) and used by Emil Fischer in his classical researches on the stereoisomerism of the reducing sugars, has now been displaced almost universally by formulæ of the cyclic oxide type, first suggested in the same year by Colley (*Compt. rend.*, 1870, **70**, 403) and subsequently by Tollens (" Handbuch der Kohlenhydrate," 1883, p. 32). Thus, it has been clearly established that the

crystalline α- and β-sugars are of similar structure to the cyclic α- and β-glucosides and are therefore themselves cyclic (Simon, *Compt. rend.*, 1901, **132**, 487; E. F. Armstrong, J., 1903, **83**, 1305). The interconversion of these stereoisomeric sugars (which gives rise to mutarotation in aqueous solution) appears likely, however, to proceed by opening of the ring, with formation of an aldehyde or aldehydrol as an intermediate product (Lowry, J., 1903, **83**, 1314; 1904, **85**, 1565), just as the Lobry de Bruyn transformation (*Rec. trav. chim.*, 1895, **14**, 203) appears to proceed through the formation of a trace of an intermediate enol which is common to glucose, mannose, and fructose (Lowry, J., 1903, **83**, 1316); and on this basis, the velocity of isomeric change has been correlated with the extent to which the ring may be " hydrolysed " in aqueous alcohols of different concentrations (Lowry, *Z. physikal. Chem.*, Cohen Festband, 1927, 125). Exceptional interest therefore attaches to the genuine aldehydic or μ-sugars (Lowry, *Z. physikal. Chem.*, 1928, **130**, 125) prepared by Levene and Meyer (*J. Biol. Chem.*, 1926, **69**, 175; 1927, **74**, 695), by Wolfrom (*J. Amer. Chem. Soc.*, 1929, **51**, 2188, *et seq.*), and by Brigl and Mühlschlegel (*Ber.*, 1930, **63**, 1551), in which the formation of a ring is prevented by methylating, acetylating, or benzoylating the five hydroxyl radicals of von Baeyer's formula, the sugar being held meanwhile in an open-chain form by conversion into a thioacetal.

The present experiments were made in Cambridge with specimens of the crystalline acetates of the aldehydic forms of glucose, galactose, and arabinose, prepared in the laboratories of the Ohio State University. A specimen of the liquid pentamethyl derivative of aldehydo-glucose, supplied by Dr. Levene, developed a yellow tint which rendered it unsuitable for spectrophotometric work.

The primary result of our experiments has been to show that these sugars exhibit all the characteristic optical properties of the carbonyl group, so that the structure assigned to them by Wolfrom is fully confirmed in each case; but we have also been able to use them as test cases in regard to the real form of the curves of absorption, circular dichroism, and rotatory dispersion.

(a) *Absorption.*—It has been known for 20 years that the absorption bands of organic compounds cannot be represented by the formula which was developed by Ketteler and Helmholtz to represent the broadening of a spectral line resulting from " damped vibrations," and that an exponential formula, of the same general type as a probability curve, must be substituted for it (Bielecki and Henri, *Physikal. Z.*, 1913, **14**, 516). Three such equations have already been put forward, since Kuhn and Braun (*Z. physikal. Chem.*, 1930, *B*, **8**, 281) have postulated a probability distribution of frequencies, Lowry and Hudson (*Phil. Trans.*, 1933, *A*, **232**, 117) have postulated a probability distribution of wave-lengths, whilst the equation of Bielecki and Henri is of an intermediate type. It is unfortunately not possible to compare the relative merits of these different equations as applied to Kuhn and Braun's compounds, since no numerical data are given, and discrimination by graphical analysis is not practicable on account of the small scale on which their graphs are reproduced; but an investigation of the absorption bands of the xanthates (Lowry and Hudson, *loc. cit.*) has shown conclusively that these are definitely *symmetrical on a scale of wave-lengths*, in strict agreement with the formula of Lowry and Hudson. They cannot therefore be represented accurately by the formulæ of Bielecki and Henri or of Kuhn and Braun.

Our new absorption equation, however, can only be regarded as an ideal limiting case, since absorption curves which are steeper on the side of longer wave-lengths have long been familiar in nicotine, etc.; but a long personal experience has not yet produced any similar evidence of the existence in the absorption spectra of organic compounds of curves which are steeper on the side of shorter wave-lengths, as required by the other two equations. Molecular xenon, however, gives absorption curves of this type in the Schumann region (McLennan and Turnbull, *Proc. Roy. Soc.*, 1930, **129**, 266), as also do the diatomic molecules of potassium, zinc, cadmium, and mercury. This form of absorption curve appears, indeed, to be a peculiar attribute of molecules which are held together by very weak forces, possibly of the van der Waals type, but form more stable molecules when one of the component atoms has been activated. The conditions which prevail in the aldehydes and ketones are, however, directly opposite to these, and there are theoretical reasons for

thinking that the type of electronic transition which gives rise to the ultra-violet absorption bands of unsaturated organic compounds may produce bands which are extended in the direction of the Schumann region, but not bands which are extended towards the visible spectrum.

The work now described has confirmed us in the belief that the two earlier equations, which are referred to above, do not represent a normal type of absorption curve, and that dispersion curves based upon them are therefore not likely to provide the best interpretation of the optical properties of organic compounds. The aldehydic sugars, indeed, provide particularly favourable conditions for an investigation of this problem, since there is no overlapping of the absorption bands, such as was observed in the xanthates and in

FIG. 1.

Aldehydic d-glucose penta-acetate.
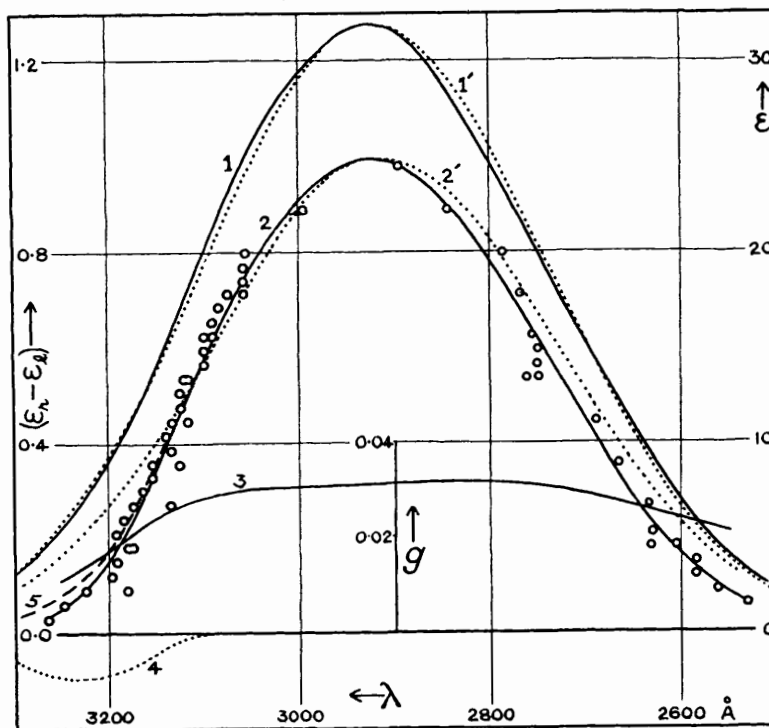
1, *Absorption (experimental)*; 1′, *absorption (theoretical), deduced from equation* (i); 2, *circular dichroism (experimental)*; 2′, *circular dichroism (theoretical), deduced from equation* (ii); 3, *dissymmetry factor*; 4, *subsidiary circular dichroism component (theoretical)*; 5, *algebraic sum of curves 2′ and 4.*

Kuhn's α-azidopropionic esters, as well as in his α-chloro- and α-bromo-esters where only a " step-out " was observed. On the contrary, the characteristic absorption band of the aldehydic group is separated so widely from that of the acetate radicals that no " general absorption " could be detected within the range of our observations, chloroform being used as a solvent. The ultra-violet band, therefore, stood out as a detached peak, apparently unaffected by the presence of other absorbing centres. It was consequently possible to plot both sides of the band over a wide range of intensities, and to make a precise study of its symmetry by the method of rectilinear diameters. In this way it was established that the aldehydic penta-acetate of glucose gives a band which is definitely symmetrical on a scale of wave-lengths, whilst the aldehydic tetra-acetate of arabinose deviates from our ideal curve in the same direction as nicotine, but in the opposite direction from that required by the two alternative equations.

The experimental absorption data are shown graphically as curves 1 in Figs. 1, 2, and

3. Theoretical curves, 1′, are also shown, which are symmetrical on a scale of wave-lengths, as calculated from the equation

$$\varepsilon = \varepsilon_{max.} \, e^{-[(\lambda - \lambda_0)/\theta]^2} \qquad \qquad \text{(i)}$$

where ε and $\varepsilon_{max.}$ are the molecular extinction coefficients at λ and λ_0 respectively, λ_0 is the wave-length corresponding to the maximum absorption, and θ is a distribution parameter, related to the half-width λ' of the band by $\lambda' = 1.66510$. The values of λ_0, λ', and $\varepsilon_{max.}$ are summarised in Table I.

TABLE I.

Parameters of Aldehydic Absorption Band.

	Aldehydic *d*-glucose penta-acetate.	Aldehydic *d*-galactose penta-acetate.	Aldehydic *l*-arabinose tetra-acetate.
Head of band (λ_0), Å.U.	2920	2900	2900
Maximum intensity (log $\varepsilon_{max.}$)	1·505	1·460	1·580
Half-width (λ'), Å.U.	423	500	470

(b) *Circular Dichroism.*—Measurements of circular dichroism of camphor in hexane (Kuhn and Gore, *Z. physikal. Chem.*, 1931, *B*, **12**, 389) and of aqueous solutions of camphor-β-sulphonic acid (Lowry and French, J., 1932, 2654) have shown that the maximum of circular dichroism occurs at longer wave-lengths than the maximum of absorption of unpolarised light, and that the ketonic absorption band in these two compounds is therefore composite in character. On the other hand, the maximum of circular dichroism in the aldehydic acetates is not displaced by more than 10 Å.U. relatively to the maximum of ordinary absorption; but the ratio of circular dichroism to absorption, or the " dissymmetry factor " as we have proposed to call it (Lowry and Hudson, *Phil. Trans.*, 1933, *A*, **232**, 119, footnote), instead of being strictly proportional to the frequency, falls off substantially at either end, but especially on the side of shorter wave-lengths. This suggests that there is a tendency for the optical activity to be concentrated on the long wave-length side of the aldehydic band, but not nearly so markedly as in the ketonic band of camphor.

In Figs. 1, 2, and 3, the experimental values for the circular dichroism are represented graphically as curve 2. The corresponding dissymmetry factor, $(\varepsilon_r - \varepsilon_l)/\varepsilon$, is plotted as curve 3 in each figure. Theoretical values of the circular dichroism, deduced by means of the equation :

$$(\varepsilon_r - \varepsilon_l) = (\varepsilon_r - \varepsilon_l)_{max.} \, \lambda/\lambda_0 \, . \, e^{-[(\lambda - \lambda_0)/\theta]^2} \qquad \qquad \text{(ii)}$$

are represented in the same figures by curve 2′. In this expression $(\varepsilon_r - \varepsilon_l)$ and $(\varepsilon_r - \varepsilon_l)_{max.}$ are the circular dichroism at wave-lengths λ and λ_0 respectively, λ_0 and λ' have a corresponding significance to that in (i) and, as before, $\lambda' = 1.66510$.

The experimental and the theoretical curves 2 and 2′ are similar in form, though the agreement between them is not completely satisfactory. The most marked divergence occurs on the long wave-length side of the aldehydic band of μ-glucose penta-acetate. This divergence can be interpreted by assuming the existence of a weak band of circular dichroism of opposite sign, as represented by curve 4 in Fig. 1. Curve 5, which is the algebraic sum of curves 2′ and 4, then agrees closely with the experimental data ; and a still more remarkable agreement is found in the corresponding curves of rotatory dispersion in this region. This component of opposite sign may represent the optical activity of a weak subsidiary band, which has been observed at 3100—3300 Å.U. in solutions of acetaldehyde and propaldehyde in hexane by Schou (*Compt. rend.*, 1926, **182**, 965 ; *J. Chim. physique*, 1929, **26**, 60).

The parameters of the curves of circular dichroism are given in Table II.

TABLE II.

Parameters of Curves of Circular Dichroism.

	Aldehydic *d*-glucose penta-acetate.	Aldehydic *d*-galactose penta-acetate.	Aldehydic *l*-arabinose tetra-acetate.
Position of maximum (λ_0), Å.U. ...	2920	2910	2910
Maximum circular dichroism $[(\varepsilon_r - \varepsilon_l)_{max.}]$	1·00	2·25	1·80
Half-width (λ'), Å.U.	420	400	400

(c) *Rotatory Dispersion in the Region of Transparency.*—Wolfrom and Brode (*J. Amer. Chem. Soc.*, 1931, **53**, 2279) have investigated the rotatory dispersion in the visible spectrum of these three aldehydic sugars. After plotting the reciprocals of the molecular rotations against the squares of the wave-lengths, these authors concluded that the rotatory dis-
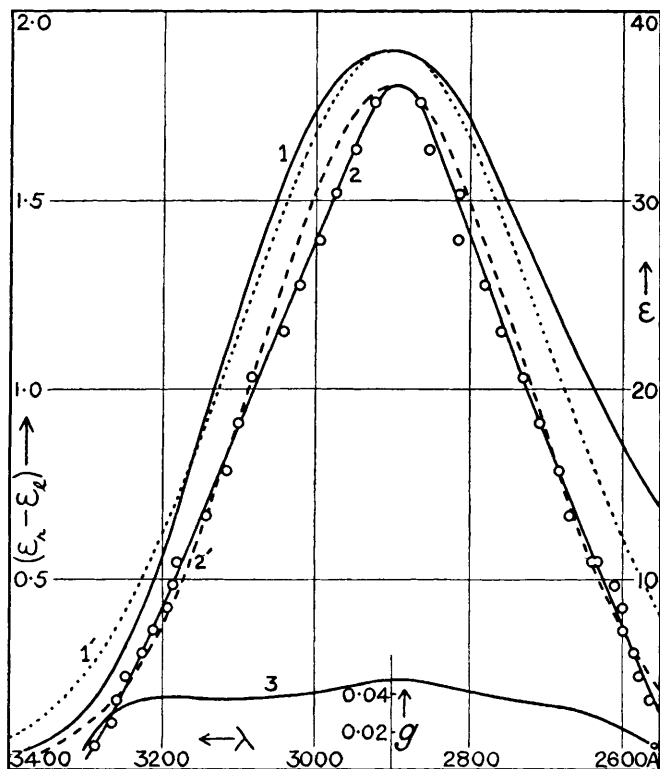
FIG. 2.

Aldehydic d-*galactose penta-acetate.*
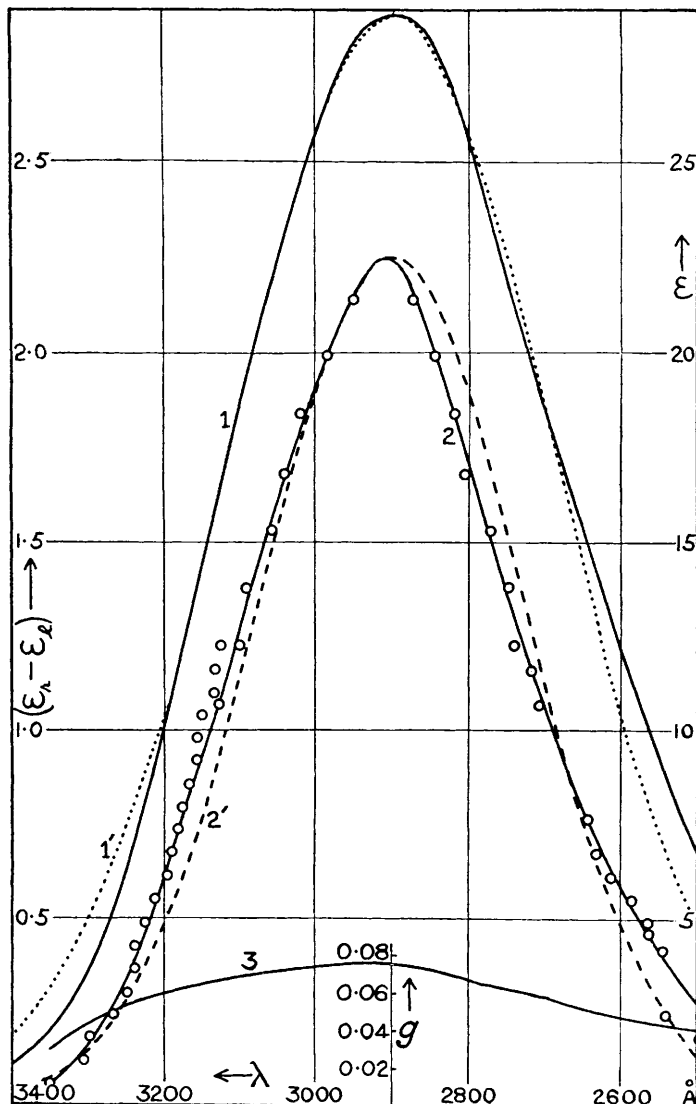
1, *Absorption* (*experimental*); 1', *absorption* (*theoretical*), *deduced from equation* (i); 2, *circular dichroism* (*experimental*); 2', *circular dichroism* (*theoretical*), *deduced from equation* (ii); 3, *dissymmetry factor.*

persion of the aldehydic acetates of galactose and arabinose was simple, whilst that of the aldehydic acetate of glucose was complex.

Our experiments confirm the earlier conclusion as regards the simple rotatory dispersion of the arabinose compound in the region of transparency, but they show that the rotatory dispersions of the glucose and galactose derivatives are complex, and can only be represented by two terms of opposite sign. The *negative partial rotation* in each equation is

obviously due to the " induced dissymmetry " (Lowry and Walker, *Nature*, 1924, **113**, 565; Lowry, *ibid.*, 1933, **131**, 566) of the aldehydic group, whilst the *positive partial rotation*, which has a characteristic frequency in the Schumann region, may be attributed to the fixed asymmetry of the $>CH \cdot O \cdot CO \cdot CH_3$ groups. This positive rotation is obviously composite in character, and must be regarded as the algebraic sum of a series of positive and negative terms with similar dispersion constants. The simple rotatory dispersion of the aldehydic acetate of arabinose is due to the fact that this algebraic sum is zero; but this internal compensation does not prevent the development of induced dissymmetry in the aldehydic group, since this phenomenon is determined mainly by the fixed asymmetry

FIG. 3.

Aldehydic l-*arabinose tetra-acetate.*

1, *Absorption* (*experimental*); 1′, *absorption* (*theoretical*), *deduced from equation* (i); 2, *circular dichroism* (*experimental*); 2′, *circular dichroism* (*theoretical*), *deduced from equation* (ii); 3, *dissymmetry factor.*

of the carbon atom to which the carbonyl group is directly attached. The Drude equations and the wave-lengths given by the dispersion constants, together with the positions of the maxima of circular dichroism for comparison, are given below :

(i) *Aldehydic* d-*glucose penta-acetate.*

$$[\alpha] = -\,3.7844/(\lambda^2 - 0.09126) + 3.3063/\lambda^2.$$

Wave-length given by dispersion constant = 3021 Å.U.
  ,,   of maximum circular dichroism = 2920 Å.U.

(ii) *Aldehydic* d-*galactose penta-acetate.*

$$[\alpha] = -\,12.3419/(\lambda^2 - 0.08946) + 8.4438/\lambda^2.$$

Wave-length given by dispersion constant = 2991 Å.U.
  ,,   of maximum circular dichroism = 2910 Å.U.

(iii) *Aldehydic* l-*arabinose tetra-acetate.*

$$[\alpha] = -\,16 \cdot 1571/(\lambda^2 - 0 \cdot 08575).$$

Wave-length given by dispersion constant = 2928 Å.U.

,, of maximum circular dichroism = 2910 Å.U.

As in many preceding cases (see first footnote, Lowry and Hudson, *loc. cit.*, p. 118), there is a marked divergence between the characteristic frequency deduced by extrapolation from the curves of rotatory dispersion and that deduced directly from measurements of absorption or circular dichroism, but this difference is relatively small in the case of the arabinose compound.

TABLE III.

Specific Rotations of Aldehydic d-*Glucose Penta-acetate in Chloroform Solution at* 20°.

Concentration (c, in g./100 c.c.) and length (l, in dcm.) of column of solution. : (a) c = 3·9848, l = 4; (b) c = 3·9848, l = 1; (c) c = 3·9848, l = 0·1; (d) c = 1·3283; l = 0·1; (e) c = 0·6641, l = 0·1.

Soln.	λ	[α]	Soln.	λ	[α]	Soln.	λ	[α]	Soln.	λ	[α]
Visual readings.			*Photographic readings.**			(e)	3298	−230°	(d)	3000	−190°
(a)	Li 6708	− 3·20°	(a)	4301	− 22·40°	(c)	3298	−238	(e)	3000	−150
	Cd 6438	− 3·83		4202	− 25·54		3292	−264		2990	− 80
	Zn 6362	− 4·08		4132	− 28·67	(d)	3287	−260		2969	± 0
	Li 6104	− 4·58		4062	− 31·81	(c)	3274	−288	(d)	2969	−115
	Na 5893	− 5·02		4005	− 34·94		3271	−314	(e)	2957	+ 80
	Cu 5782	− 5·46		3966	− 38·08	(e)	3266	−300	(d)	2954	− 40
	Hg 5780	− 5·46		3917	− 41·22	(c)	3258	−338		2937	+ 40
	Cu 5700	− 6·15		3879	− 44·35		3257	−338	(e)	2929	+150
	Ag 5468	− 7·35		3840	− 47·49	(d)	3248	−330	(d)	2918	+115
	Hg 5461	− 7·35		3809	− 50·63	(c)	3248	−364		2912	+190
	Cu 5219	− 8·66		3776	− 53·76		3236	−388	(e)	2912	+230
	Ag 5209	− 8·91		3754	− 56·90	(e)	3229	−380	(d)	2874	+260
	Cu 5153	− 9·35		3728	− 60·03	(c)	3197	−414	(e)	2872	+380
	Cu 5106	− 9·85		3687	− 63·16	(d)	3180	−415		2864	+300
	Cd 5086	− 9·79	(b)	3648	− 71·6	(c)	3175	−440	(d)	2852	+330
	Zn 4811	−12·74		3640	− 71·6		3126	−464	(e)	2844	+450
	Cd 4800	−12·67		3570	− 84·0		3100	−464	(d)	2829	+415
	Zn 4722	−13·93	(c)	3530	− 88		3076	−440		2823	+490
	Zn 4680	−14·81	(b)	3514	− 96·6	(d)	3075	−415	(e)	2823	+530
	Cd 4678	−14·74		3466	−109·0	(c)	3059	−414		2804	+600
	Li 4602	−15·75	(c)	3445	−112		3059	−390	(d)	2797	+565
	Hg 4358	−20·95	(b)	3440	−121·8	(e)	3048	−380		2788	+640
			(d)	3440	−115	(d)	3048	−330	(e)	2772	+680
			(c)	3393	−138	(e)	3047	−300	(d)	2768	+715
				3367	−164	(c)	3042	−364	(c)	2600	+716
			(d)	3338	−190		3021	−338	(d)	2598	+755
			(c)	3329	−188	(e)	3021	−230	(c)	2588	+690
				3315	−214	(d)	3016	−260		2539	+665

(d) *Rotatory Dispersion in the Region of Absorption.*—The results of this preliminary analysis by means of Drude's equation have been confirmed by extending the observations right through the aldehydic absorption band, where the curves of total rotation assume the characteristic form first observed by Cotton in the coloured tartrates. Beyond a wave-length of 2500 Å.U., however, observations were rendered impossible by the general absorption of the solvent. The results are set out in Tables III, IV, and V, and are plotted as curve 1 in Figs. 4, 5, and 6.

The partial rotation due to the aldehydic band was deduced from its circular dichroism by means of the equation of Lowry and Hudson, as follows :

$$[\alpha] = \frac{[\phi]}{m}\frac{\lambda_\phi}{\lambda}\left[e^{-[(\lambda-\lambda_0)/\theta]^2} \int_0^{(\lambda-\lambda_0)/\theta} e^{x^2} \cdot dx + \frac{\theta}{2(\lambda+\lambda_0)} \right]. \qquad (iii)$$

where [α] = partial specific rotation at wave-length λ, m = maximum value of the terms inside the bracket, [φ] = maximum value of [α], which occurs at wave-length λ_φ, and is given by $[\phi] \simeq \dfrac{201400}{M}\dfrac{(\varepsilon_r - \varepsilon_l)_{max.}}{}$ (degrees), M being molecular weight. The other symbols have the same significance as in equation (ii). This partial rotation is represented

graphically as curve 2 in Figs. 4, 5, and 6, where the total specific rotation is plotted as curve 1.

TABLE IV.

Specific Rotations of Aldehydic d-*Galactose Penta-acetate in Chloroform Solution at 20°.*

(a) $c = 7\cdot8864$, $l = 2$; (b) $c = 7\cdot8864$, $l = 0\cdot1$; (c) $c = 1\cdot3144$, $l = 0\cdot1$.

Visual readings. (a)

Soln.	λ	[α]
Li	6708	−15·47°
Cd	6438	−17·56
Zn	6362	−18·51
Li	6104	−20·80
Na	5893	−23·84
Cu	5782	−25·17
Hg	5780	−25·49
Cu	5700	−26·37
Ag	5468	−30·75
Hg	5461	−30·81
Cu	5219	−36·33
Ag	5209	−36·33
Cu	5153	−37·91
Cu	5106	−39·75
Cd	5086	−40·32
Zn	4811	−49·96
Cd	4800	−50·40
Zn	4722	−54·27
Zn	4680	−56·68
Cd	4678	−56·55
Li	4602	−60·86
Hg	4358	−78·36

Photographic readings.*

Soln.	λ	[α]
(a)	4144	−100·30°
	4032	−116·15
	3942	−132·00
	3879	−147·85
	3816	−163·70
	3760	−179·55
	3716	−195·40
	3678	−211·25
	3640	−227·10
	3607	−242·95
	3582	−258·80
	3557	−274·65
	3535	−290·50
	3514	−306·35
(b)	3485	−321
	3450	−346
	3427	−371
	3407	−397
	3393	−422
	3379	−448
	3355	−473
	3348	−498
	3338	−524
	3329	−549
	3324	−574
	3317	−600

Soln.	λ	[α]
(b)	3315	− 625°
	3306	− 650
	3298	− 676
	3292	− 701
	3287	− 727
	3280	− 752
(c)	3280	− 785
(b)	3275	− 777
	3271	− 803
	3266	− 828
(c)	3254	− 860
	3222	− 935
	3180	−1010
	3175	−1010
	3151	−1090
	3076	−1090
	3067	−1010
(c)	3067	−1010
	3048	− 935
	3032	− 785
	3021	− 860
	3008	− 710
	3000	− 630
	2984	− 555
	2973	− 480
	2967	− 405

Soln.	λ	[α]
(c)	2960	− 325°
	2954	− 250
	2937	− 175
	2929	− 100
	2929	− 25
	2918	+ 60
	2912	+ 130
	2895	+ 205
	2895	+ 280
	2884	+ 360
	2874	+ 435
	2864	+ 510
	2851	+ 585
	2844	+ 660
	2838	+ 740
	2825	+ 815
	2813	+ 890
	2804	+ 965
	2788	+1040
	2778	+1120
	2772	+1195
	2762	+1270
	2667	+1420
	2631	+1420
	2563	+1270
	2524	+1195

* All the lines hereunder are those of Fe.

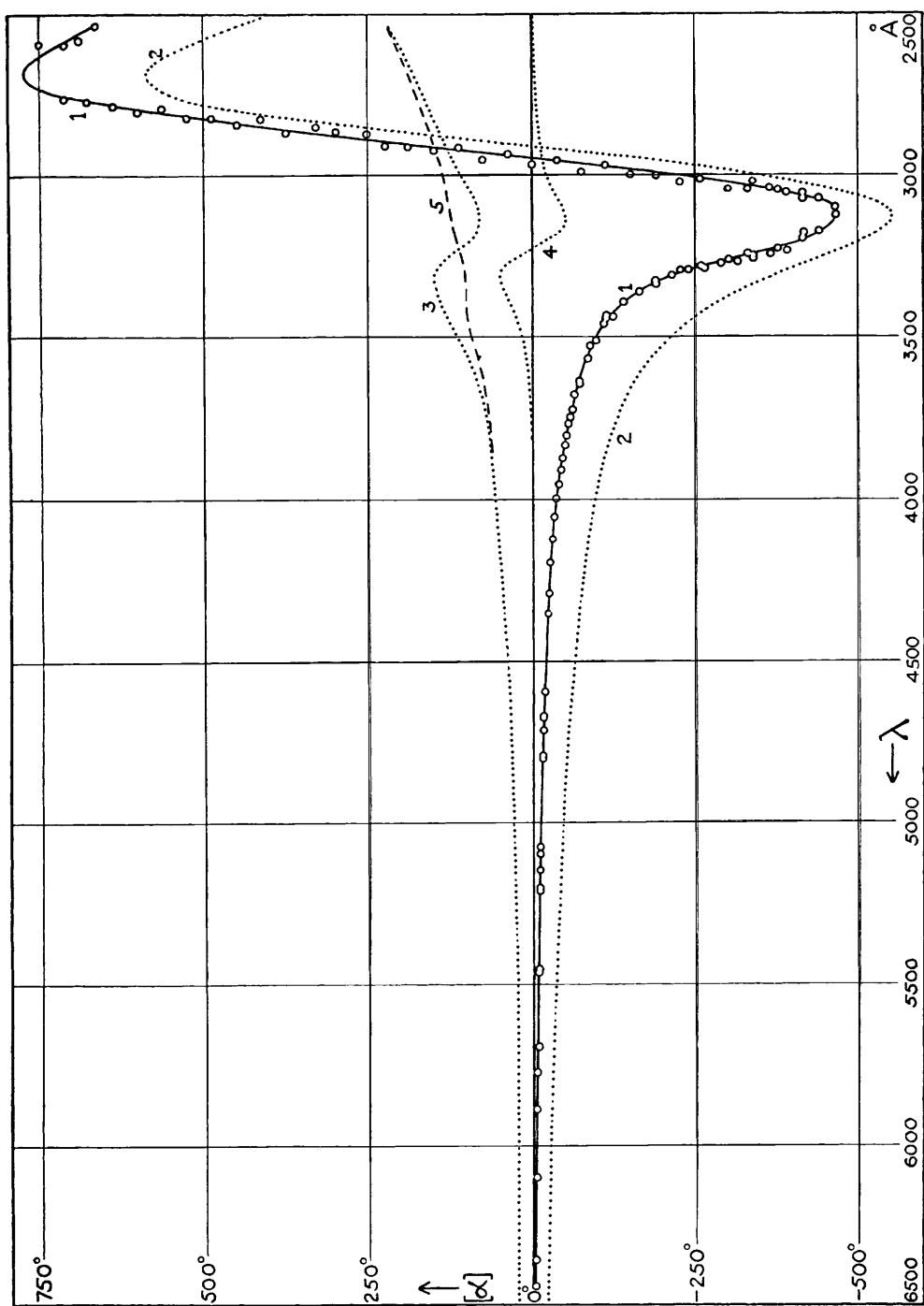## TABLE V.

Specific Rotations of Aldehydic l-*Arabinose Tetra-acetate in Chloroform Solution at 20°.*

(a) $c = 8\cdot3748$, $l = 2$; (b) $c = 8\cdot3748$, $l = 0\cdot1$; (c) $c = 1\cdot3958$, $l = 0\cdot1$.

Visual readings. (a)

Soln.	λ	[α]
Li	6708	− 44·36°
Cd	6438	− 49·25
Zn	6362	− 50·87
Li	6104	− 56·30
Na	5893	− 61·79
Cu	5782	− 65·14
Hg	5780	− 65·31
Cu	5700	− 67·52
Ag	5468	− 76·48
Hg	5461	− 76·48
Cu	5219	− 86·57
Ag	5209	− 87·05
Cu	5153	− 90·09
Cu	5106	− 92·54
Cd	5086	− 93·26
Zn	4811	−110·81
Cd	4800	−111·82
Zn	4722	−117·61
Zn	4680	−121·08
Cd	4678	−121·44
Li	4602	−127·70
Hg	4358	−155·05

Photographic readings.*

Soln.	λ	[α]
(a)	4204	−176·96°
	4119	−191·89
	4046	−206·81
	3986	−221·74
	3928	−236·66
	3872	−251·59
	3826	−266·51
	3781	−281·44
	3746	−296·37
	3707	−311·29
	3676	−326·22
	3646	−341·14
	3621	−356·07
	3595	−370·99
	3572	−385·92
	3552	−400·84
(b)	3541	−394
(a)	3525	−415·77
	3507	−429·86
(b)	3498	−418
(a)	3485	−444·79
(b)	3477	−442
(a)	3466	−459·71
(b)	3450	−466
(a)	3450	−474·64
	3440	−489·56

Soln.	λ	[α]
(b)	3427	− 490°
	3413	− 513
	3384	− 537
	3371	− 561
	3355	− 585
	3348	− 609
	3342	− 633
	3338	− 657
	3329	− 681
	3324	− 705
	3315	− 728
	3306	− 752
	3298	− 776
(c)	3292	− 790
(b)	3292	− 800
	3286	− 824
	3280	− 848
(c)	3271	− 860
	3254	− 930
	3248	−1005
	3193	−1075
	3161	−1145
	3084	−1145
	3067	−1075
	3026	−1005

| Soln.	λ	[α]
(c)	3026	− 930°
	3010	− 860
	2987	− 790
	2973	− 715
	2965	− 645
	2960	− 575
	2954	− 500
	2948	− 430
	2937	− 360
	2937	− 285
	2929	− 215
	2918	− 145
	2912	− 70
	2895	+ 285
	2844	+ 575
	2826	+ 860
	2805	+ 930
	2788	+1005
	2721	+1075
	2689	+1145
	2667	+1145
	2636	+1075
	2592	+1005
	2543	+ 930
	2512	+ 860

FIG. 4.

Aldehydic d-glucose penta-acetate.

1, Total specific rotation (experimental); 2, partial rotation associated with aldehydic absorption band (theoretical), deduced from equation (iii); 3, curve 1 minus curve 2; 4, partial rotation associated with subsidiary circular dichroism component (curve 4 of Fig. 1) (theoretical); 5, residual rotation associated with absorption bands in further ultra-violet and Schumann region (curve 3 minus curve 4).

(i) *Glucose and galactose.* The aldehydic radical in the penta-acetates of these two sugars gives rise to partial rotations (curve 2) which differ widely from the observed total rotations (curve 1). The differences, which are plotted as curve 3, represent the residual rotations due to the remainder of the molecule. These difference curves should
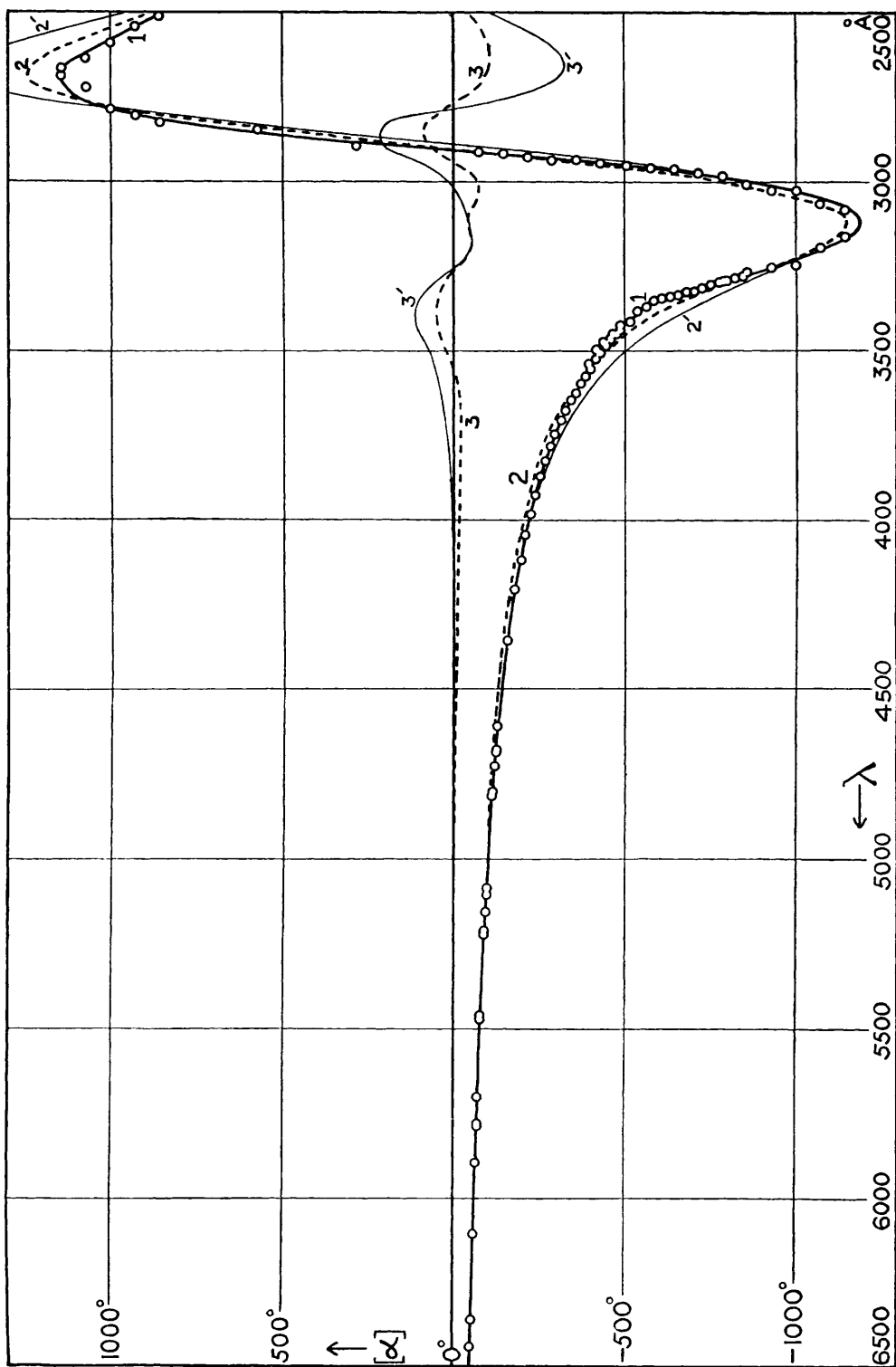
Fɪɢ. 5.

Aldehydic d-galactose penta-acetate.
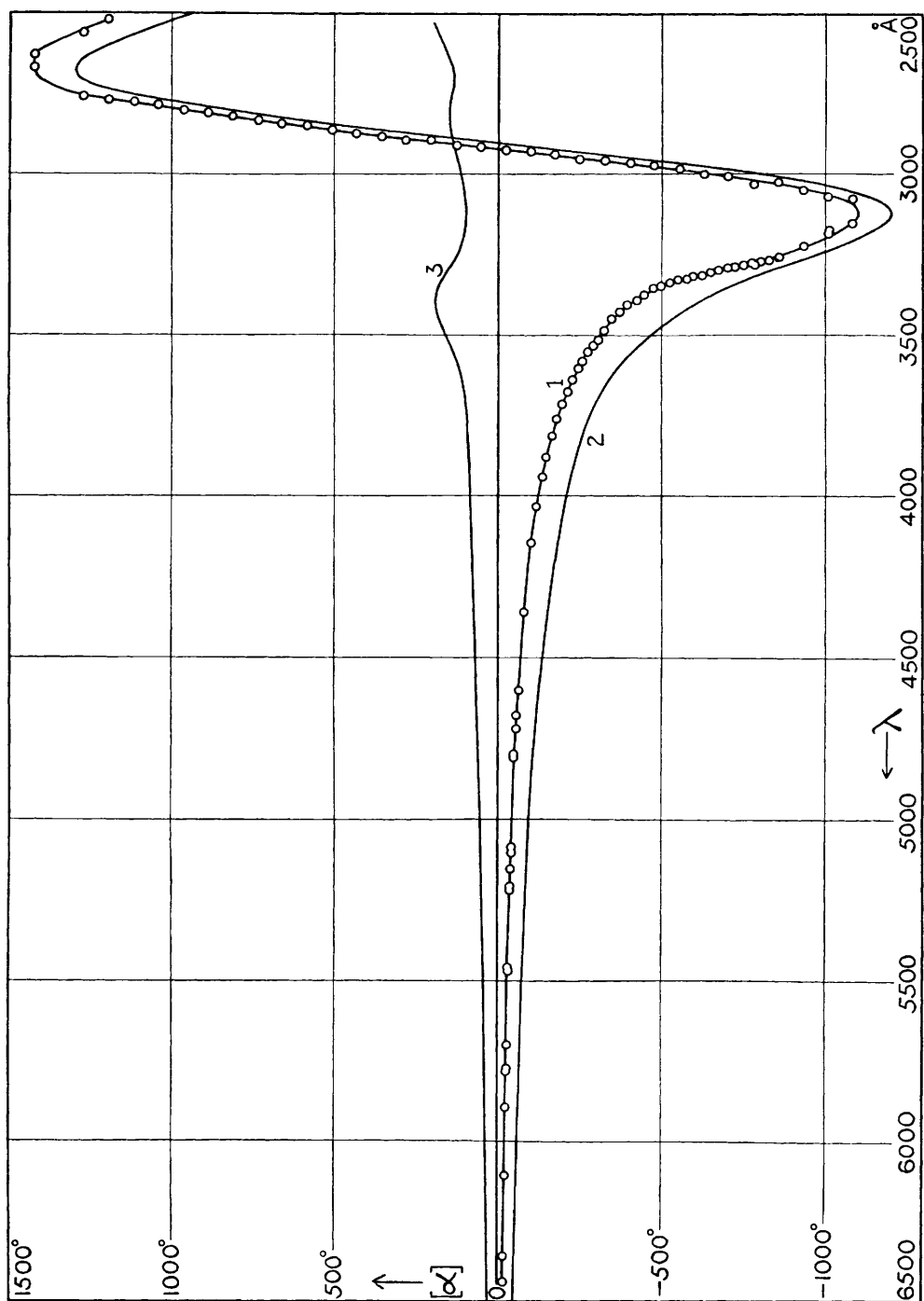
1, *Total specific rotation (experimental)*; 2, *partial rotation associated with aldehydic absorption band (theoretical), deduced from equation (iii)*; 3, *residual rotation associated with absorption bands in further ultra-violet and Schumann region (curve 1 minus curve 2)*.

be free from anomalies and quasi-hyperbolic in form; but this ideal was not realised completely, since both curves show ripples in the region of the aldehydic band. The curve for the aldehydic acetate of glucose (which shows the most marked deviations from the ideal) can, however, be corrected by allowing for the influence of the small band of weak

FIG. 6.

Aldehydic l-arabinose tetra-acetate.

1, *Total specific rotation (experimental)*; 2, *partial rotation associated with aldehydic absorption band (theoretical), deduced from equation* (iii); 2', *partial rotation associated with aldehydic absorption band (theoretical), deduced from equation of Kuhn and Braun*; 3, *error curve (curve 1 minus curve 2), based on equation* (iii); 3', *error curve (curve 1 minus curve 2'), based on equation of Kuhn and Braun.*

circular dichroism of opposite sign (curve 4) in Fig. 1, the existence of which has already been postulated in order to account for the form of the curve of circular dichroism. The partial rotation of this weak component is shown as curve 4 in Fig. 4, and the difference curve 5, obtained by subtracting curve 4 from curve 3, is now almost completely smooth.

(ii) *Arabinose.* The theoretical and the experimental curves 1 and 2 for the aldehydic acetate of arabinose, unlike those of glucose and galactose, agree closely over the entire range of wave-lengths, thus confirming our conclusion that the whole of the observed rotatory power is due to the induced dissymmetry of the aldehydic group. This sugar is the first example that we have found of a compound in which the rotatory power can be attributed exclusively to a single accessible absorption band. It therefore provides ideal material for determining the precise character of the partial rotatory dispersion produced by an isolated band. For this purpose we have calculated a series of partial rotations from the equation of Kuhn and Braun; these are plotted as curve 2' in Fig. 6, and lead to the difference curve 3'. This curve contains three substantial loops, and shows a maximum difference of 300° near the positive maximum; but the differences are equally distributed on either side of the axis of zero rotation, so that it is impossible to say whether the residual rotation due to the $>CH\cdot O\cdot CO\cdot CH_3$ groups is positive or negative. The rotations calculated from our own equation are plotted as curve 2 in Fig. 6, and lead to the difference-curve 3. The maximum difference is now reduced to 90°, and the loops are therefore much smaller; but the difference-curve crosses the axis of zero-rotation at four (or five) points, and it is again impossible to say with certainty whether the residual rotation is positive or negative.

On the assumption that the residual rotation associated with the more distant absorption bands is so small as to be negligible, the experimental data plotted as curve 1 in Fig. 6 show that *the maximum positive and negative partial rotations associated with the aldehydic band are approximately equal in magnitude.* The experimental error in this region is, however, too great to make it possible to decide whether this equality is accidental or is a characteristic feature of an ideal curve of rotatory dispersion. This question could be answered most effectively by studying other compounds in which the whole of the observed rotatory power is associated with a single accessible absorption band. Unfortunately, no other case of this kind is at present known. It may be pointed out, however, that if the two theoretical curves 2 and 4 of Fig. 4 are added together, the partial rotation due to the two components of the aldehydic band can be expressed by a curve which has positive and negative maxima of equal magnitude. Moreover, the analysis of the rotatory power of this compound is exceptionally satisfactory, since the final difference curve 5 is entirely free from any gross anomaly.

Our theoretical equation makes the positive maximum rather greater than the negative, and this contrast is greatly exaggerated in the theoretical curve derived from the equation of Kuhn and Braun. An equation which gives rise to equal maxima can readily be derived by omitting the factor λ_φ/λ and the term $\theta/2(\lambda + \lambda_0)$ in equation (iii), but this no longer reduces to Drude's equation in the region of transparency on either side of the band. Although, therefore, it is possible that the data of Fig. 6 may have disclosed an essential feature of the ideal curve of rotatory dispersion, yet we have not been able to derive an equation which satisfies the experimental requirements both in the region of transparency and in that of absorption.

Optical Superposition and C. S. Hudson's Isorotation Rules.—The data now recorded are of unique value as a test of van 't Hoff's theory of optical superposition and of C. S. Hudson's isorotation rules, since in no previous case has it been possible to isolate, by physical instead of algebraic methods, any of the partial rotations which make up the total rotations of a series of sugars. The cyclic sugars, which provided the data on which C. S. Hudson's isorotation rules were originally based, contain no radical which is more unsaturated than the secondary alcohols, the rotatory dispersion of which is dominated by a characteristic frequency at about 1540 Å.U. (Lowry and Dickson, J., 1913, **103**, 1067), unless the $-C-O-C-$ group which closes the ring is more easily activated than the $>CH(OH)$ groups. In these cyclic sugars therefore the conditions are exceptionally

favourable for verifying van 't Hoff's principle of optical superposition, since the dispersion constants of the partial rotations are all approximately equal.

The isorotation rules appear to hold good when derivatives of glucose and galactose are compared, but not when comparing similar derivatives of glucose and mannose. It therefore appears that the terminal asymmetric atom, *e.g.*, the $>CH(OMe)$ group of the glycosides, by which the sign and magnitude of the rotation are mainly determined, is influenced not only by the contiguous $>CH(OH)$ group, but also by the next asymmetric atom, so that its partial rotation will only remain constant when the *two* adjacent asymmetric atoms are of constant sign (compare Freudenberg, *J. Soc. Chem. Ind.*, 1931, **50**, 287).

In addition to his isorotation rules for the sugars and their simplest derivatives, C. S. Hudson has put forward additional rules to correlate the configuration and rotatory power of the *lactones* (*J. Amer. Chem. Soc.*, 1910, **32**, 338) and *amides* (*ibid.*, 1918, **40**, 813; Hudson and Komatsu, *ibid.*, 1919, **41**, 1141) of the sugar acids. The rotatory power of these compounds is due only in part to the fixed centres of asymmetry, since the induced dissymmetry of the unsaturated radicals $-CO \cdot O-$ and $-CO \cdot NH_2$ may be expected to contribute a partial rotation of lower frequency, associated with absorption bands on the threshold of the Schumann region. Similar conditions prevail in the case of the acetates of the aldehydic sugars, data for which are given in the present paper, since their rotatory power is due mainly (and in one case almost exclusively) to the induced dissymmetry of the unsaturated aldehydic group. This group, however, has an absorption band in the middle ultra-violet, which makes it possible to investigate its partial rotation by direct measurements of rotatory power in the region of absorption, whereas in all the other cases cited above the partial rotations are associated with absorption bands in the far ultra-violet or in the inaccessible Schumann region, where measurements of optical rotatory power are no longer possible. Even under these conditions, however, it might be expected (i) that, in agreement with Hudson's amide rule for the $-CO \cdot NH_2$ group, the *sign* of this induced dissymmetry would be determined by that of the terminal asymmetric carbon atom, and (ii) that, when the *two* terminal asymmetric atoms were of fixed sign, the *magnitude* of the partial rotation might be independent of the configuration of the more distant atoms.

These conditions actually prevail in the three sugars now under consideration, of which the configurations and optical rotations are set out in Table VI, since the *two* terminal asymmetric atoms are of similar configuration in *d*-glucose, *d*-galactose, *l*-arabinose, and *d*-xylose.*

TABLE VI.

Partial Molecular Rotations of Aldehydic Sugar Acetates.

[For the sodium D line ($\lambda = 5893$ Å.U.).]

	d-Glucose. CHO	*d*-Galactose. CHO	*l*-Arabinose. CHO	*d*-Xylose. CHO
	+	+	+	+
	−	−	−	−
	+	−	−	+
	+	+		
Partial rotation of CHO group	−109°	−238°	−188°	
„ „ other groups	+ 89°	+145°	− 9° *	
Total molecular rotation	− 20°	− 93°	−197°	− 51° †

* This small negative rotation is within the limits of the discrepancy between the observed and calculated rotations and its real existence is doubtful.

† Wolfrom, Newlin, and Stahly, *J. Amer. Chem. Soc.*, 1931, **53**, 4379.

It will be seen that the induced dissymmetry of the aldehydic group gives rise to a partial rotation which is constant in sign, since in each case it is negative in the visible spectrum. The magnitude of this partial rotation, however, is more than doubled as a result of a reversal of sign in the *third* asymmetric carbon atom on passing from the glucose sugar to the galactose sugar. Moreover, the elimination of the *fourth* asymmetric carbon atom on passing from *d*-galactose to *l*-arabinose is accompanied by a decrease of about one-quarter in the partial rotation of the aldehydic group.

* The xylose compound was too unstable to be included in this series of measurements.

These results differ profoundly from those recorded in the cyclic sugars. They may, perhaps, indicate that the terminal aldehydic group is not separated so widely from the third and fourth asymmetric centres as would appear from the straight-chain formula. If this explanation is correct, the dissymmetric field of the asymmetric carbon atoms must act directly across the intervening space, instead of being transmitted only through the intermediate chain of atoms.

EXPERIMENTAL.

Specimens of the aldehydic sugar acetates, sent by post from Columbus, Ohio, were kept in desiccators in the dark. They are only slightly soluble in water, ethyl alcohol, light petroleum, benzene, and *cyclo*hexane, but readily soluble in acetone, chloroform, and acetylene tetrachloride. The last was tried as a solvent (cf. Wolfrom, *J. Amer. Chem. Soc.*, 1929, **51**, 2188), but was found not to be sufficiently transparent, since an intense general absorption began just beyond 2625 Å.U. Measurements were therefore made in alcohol-free chloroform; the first sample was purified through the salicylide compound (Anschütz, *Annalen*, 1893, **273**, 73), but later samples were purified sufficiently from alcohol, hydrogen chloride, carbonyl chloride, etc., by shaking them repeatedly with water, drying for some days over freshly-heated anhydrous potassium carbonate, and distilling them twice from an all-glass apparatus. The chloroform was purified in small portions as required, and distilled immediately before use. A fresh solution of the aldehydic sugar was prepared for each series of measurements, so that no observation was made with a specimen which had been in contact with the solvent longer than 10—12 hours.

The absorption spectra were measured by means of a polarisation photometer, an iron arc being used as a source of light.

The circular dichroism was measured by the method of Kuhn and Braun (*Z. physikal Chem.*, 1930. 8 *B*. 445), but using, in place of a water rhomb a rhomb of fused silica, cut by Messrs. Adam Hilger, Limited, from a block which we had tested and found to be free from double refraction.

The rotatory dispersion in the visible and the ultra-violet region was measured by methods which have already been described. All observations, except the visual measurements for u-glucose penta-acetate, were made with the help of quartz tubes, in order to prevent possible decomposition by alkali. As the absorption band was penetrated, the length of the column and the concentration of the solution were progressively diminished. At intervals, the rotatory power of solutions which had been used for ultra-violet work was checked by repeated reading in the visible spectrum.

SUMMARY.

(*a*) Measurements have been made of the absorption spectrum, circular dichroism, and rotatory dispersion of the acetates of the open-chain aldehydic μ-forms of glucose, galactose, and arabinose.

(*b*) These aldehydic sugars have a characteristic " carbonyl " absorption band at 2900 Å.U., which is optically active and gives rise to a lævorotation in the visible spectrum. This band is either symmetrical on a scale of wave-lengths or slightly steeper towards the visible spectrum.

(*c*) The " dissymmetry factor " $(\varepsilon_r \sim \varepsilon_l)/\varepsilon$, which measures the ratio of the circular dichroism to the absorption of unpolarised light, is approximately proportional to the frequency, but falls off slightly on the side of shorter wave-lengths, although this anomaly is much less marked than in the cases of camphor and of camphor-β-sulphonic acid.

(*d*) The rotatory dispersion of these μ-sugars includes (i) a lævorotation, due to the induced dissymmetry of the aldehydic group, (ii) a dextrorotation, with a characteristic frequency in the Schumann region, which is attributed to the fixed asymmetry of the $>CH \cdot O \cdot CO \cdot CH_3$ groups. In the case of tetra-acetyl μ-arabinose, however, the Schumann terms cancel out, and the whole of the observed rotation is due to the aldehydic group.

(*e*) The partial rotation of the aldehydic group can be represented by the equation of Lowry and Hudson, which agrees with the experimental data more closely than do the equations of Natanson and of Kuhn and Braun.

(*f*) The principle of optical superposition and the validity of Hudson's rules of isorotation are discussed in the light of the results obtained with the aldehydic sugars.