TABLE II (*Concluded*)

t, min.	α, degrees	$[\alpha]_D$, degrees	x (Free form)	$a - x$ (Aldehydrol)	k[b]
35	−1.36	−17.0	0.869	0.131	0.058
40	−1.45	−18.1	.894	.106	.056
50	−1.56	−19.5	.924	.076	Av., 0.057 ±0.003
60	−1.62	−20.2	.939	.061	
90	−1.69	−21.1	.958	.042	
120	−1.68	−21.0	.956	.044	
240	−1.69	−21.1	.958	.042	

[a] Interpolated. [b] $k = (1/t) \log_e a/(a - x)$.

The author wishes to acknowledge his indebtedness to Professor Edward Mack, Jr., for counsel in analyzing the data presented in this communication.

Summary

1. The rotation changes of the aldehydrol and ethyl hemiacetal of aldehydo-*d*-galactose pentaacetate have been determined in alcohol-free chloroform solution.

2. The nature of the rotation changes observed is presented as evidence for the constitutional nature of these compounds.

3. New values for the rotations of these substances in chloroform have been determined.

4. Polarimetric evidence is given for the existence of two isomeric forms of aldehydo-galactose pentaacetate ethyl hemi-acetal.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE ROTATORY DISPERSION OF SEVERAL ALDEHYDO SUGAR ACETATES

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Rotatory dispersion work in the sugar series has not been carried on to any great extent. Lowry and Richards[1] have made a very accurate study of the dispersion of sucrose in water solution and have found it to be normal and simple. In the sugar acetate series, very complete data have been obtained by Levene and Bencowitz[2] for the ring pentaacetates of α- and β-mannose and of α- and β-glucose in a number of solvents, including chloroform. In all these cases they have found the dispersion in the visible region of the spectrum to be normal and simple. Wagner-Jauregg[3] has reported

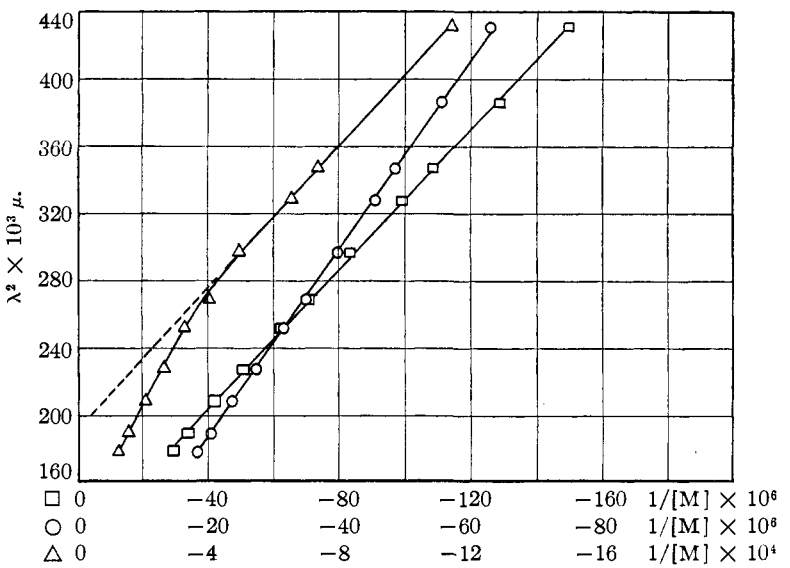
[1] T. M. Lowry and E. M. Richards, *J. Chem. Soc.*, **125**, 2511 (1924).

[2] P. A. Levene and I. Bencowitz, *J. Biol. Chem.*, **72**, 627 (1927); **73**, 679 (1927); **74**, 153 (1927).

[3] T. Wagner-Jauregg, *Helv. Chim. Acta*, **11**, 786 (1928).

the dispersions of a number of sugars in water solution and of some methylated sugars in chloroform. He has found them to be simple in every case except that of β-pentamethylglucose in chloroform, which was stated to be complex.

Optical rotations at 5892 Å. have been previously recorded for the open chain or aldehydo acetates of *d*-glucose,[4] *d*-galactose[5] and *l*-arabinose[6] in chloroform solution. We have now measured the complete optical dispersion of these substances in the visible region. This was done with the object of determining whether these compounds which are known to



⊡, Aldehydo-*d*-galactose pentaacetate; ○, aldehydo-*l*-arabinose tetraacetate; △, aldehydo-*d*-glucose pentaacetate.

Fig. 1.—Rotatory dispersion of several aldehydo sugar acetates.

possess a free aldehyde group would show any unusual optical rotatory properties. The data obtained are given in Table I and an analysis of the figures obtained has been made by the graphic method. When the reciprocals of the molecular rotations are plotted against the square of the wave lengths a straight line is obtained in the case of the aldehydo-acetates of galactose and arabinose (Fig. 1). On this basis, these dispersions are then normal and simple. In the case of aldehydo-*d*-glucose pentaacetate, a smooth curve without a maximum or minimum is obtained when the rotations are plotted against the wave length. When the reciprocal of the molecular rotation is plotted against the square of the wave

[4] M. L. Wolfrom, THIS JOURNAL, **51**, 2188 (1929).

[5] M. L. Wolfrom, *ibid.*, **52**, 2464 (1930).

[6] M. L. Wolfrom and Mildred R. Newlin, *ibid.*, **52**, 3619 (1930).

length (Fig. 1) a deviation from a straight line appears in the violet region. The dispersion is then apparently normal and complex. The rotations for the glucose acetate are low and consequently we do not wish to place much emphasis upon this deviation, as it may represent experimental error. However, since these substances possess a carbonyl group, they would be expected to show absorption in the ultraviolet with a consequent possible effect upon the rotatory dispersion in this region of the spectrum.

In the data herein reported, a Schmidt and Haensch polarimeter with spectrometer attachment was used. The spectrometer was calibrated by a method similar to that of Bencowitz.[7] A calibration was first made against the mercury arc. This was then verified by readings on a quartz plate calibrated by the National Bureau of Standards for two lines, using the data of Lowry and Coode-Adams[8] for the dispersion of quartz. The solvent used in determining the dispersion data was alcohol-free chloroform, in which the rotations of these acetates are stable. After dispersion readings were completed, the first reading taken was always checked.

TABLE I

ROTATORY DISPERSION IN CHLOROFORM SOLUTION OF THE ALDEHYDO-ACETATES OF *d*-GLUCOSE, *d*-GALACTOSE AND *l*-ARABINOSE (*l*, 4-DM.)

	Aldehydo-*d*-glucose pentaacetate		Aldehydo-*d*-galactose pentaacetate		Aldehydo-*l*-arabinose tetraacetate	
	c, 4.008	*t*, 27°	*c*, 4.000	*t*, 23°	*c*, 4.001	*t*, 23°
λ, mμ	α	[α]	α	[α]	α	[α]
656.3	−0.36	− 2.25	−2.73	−17.1	− 7.96	− 49.7
621			−3.17	−19.8	− 9.03	− 56.4
589.2	− .56	− 3.50	−3.77	−23.6	−10.29	− 64.3
573	− .63	− 3.94	−4.14	−25.9	−11.04	− 69.0
545	− .83	− 5.16	−4.93	−30.8	−12.64	− 79.0
519	−1.01	− 6.31	−5.77	−36.1	−14.27	− 89.2
502	−1.26	− 7.87	−6.70	−41.9	−15.94	− 99.6
477	−1.57	− 9.81	−8.15	−50.9	−18.30	−114.5
457	−1.99	−12.44	−9.91	−61.9	−21.13	−132.1
436	−2.71	−16.95	−12.24	−76.5	−24.7	−154
423	−3.24	−20.25	−14.1	−88.2	−27.4	−171

Summary

1. The rotatory dispersion in the visible region has been determined for the aldehydo acetates of *d*-glucose, *d*-galactose and *l*-arabinose in chloroform solution.

2. All these substances show normal dispersion. A graphic analysis of the data shows that the dispersion of aldehydo-glucose pentaacetate is apparently complex and that the others are apparently simple.

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[7] I. Bencowitz, *J. Phys. Chem.*, **32**, 1163 (1928).

[8] T. M. Lowry, *Phil. Trans.*, **212A**, 261 (1912); Lowry and Coode-Adams, *ibid.*, **226A**, 391 (1927).