

Dehydrorotenol is reduced with catalytic hydrogen to a mixture of dehydrodihydrorotenol and dehydrodihydrorotenolic acid.

Dehydrodihydrorotenolic acid is not cleaved with alkaline hydrogen peroxide.

With zinc and alkali dehydrorotenol and dehydrodihydrorotenol are reduced quantitatively to rotenol and dihydrorotenol.

Isorotenol ($C_{23}H_{24}O_6$) on reduction with Clemmensen reagent (amalgamated zinc) yields a compound of formula $C_{23}H_{26}O_5$, indicating the reduction of a carbonyl group.

Dihydrorotenonic acid is reduced with zinc and alkali to dihydrorotenolic acid.

WASHINGTON, D. C.

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

THE MUTAROTATION OF THE ALCOHOLATE AND ALDEHYDROL OF ALDEHYDO-GALACTOSE PENTAACETATE

BY M. L. WOLFROM

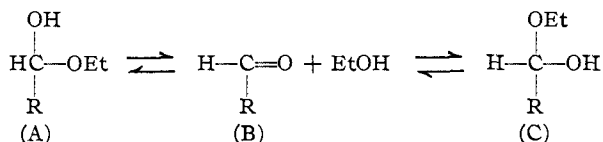
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The open chain or aldehyde sugar acetates synthesized in this Laboratory show mutarotation in alcohol but not in such non-hydroxylated solvents as acetylene tetrachloride. The mutarotation in alcohol is indicative of chemical combination of some kind between the solvent and the carbonyl group of the sugar acetate. In the case of galactose,¹ well-defined crystalline compounds with ethanol and water were isolated. At the time of the isolation of these two compounds, we were interested only in determining their initial rotation in chloroform and the U. S. P. grade of this solvent was used. The rotations were thus determined in chloroform containing an appreciable amount of ethanol. In both cases mutarotation curves which passed through a minimum were obtained. The unusual nature of these mutarotation curves has been pointed out to us by Professor T. M. Lowry and we have accordingly repeated the experiments using alcohol-free chloroform. In this solvent we find a minimum only in the curve for the ethanol compound (Fig. 1). Data for two experiments with the ethanol compound are given in Table I. The actual speeds for the two experiments are widely different but values identical within the limits of experimental error are obtained for the minimum and final rotations. This variation in speed is probably due to the catalytic effect of hydrogen chloride produced by the slight photochemical decomposition of the alcohol-free chloroform used, the amount of acidity present being apparently different in the two cases.

¹ M. L. Wolfrom, *THIS JOURNAL*, **52**, 2464 (1930).

The nature of the mutarotation curve for the ethanol compound indicates a rapid initial reaction followed by a slower one and is also indicative of the presence of three substances with differing rotations. This can be adequately explained on the basis of structural theory as follows



The fact that the free aldehyde form (B, $[\alpha]_D -25^\circ$) and the known ethanol compound (A, $[\alpha]_D +1.5^\circ$) have widely differing rotations in chloroform is proof that the ethanol is constitutionally combined and is not present as alcohol of crystallization. In the hemi-acetal structure (A)

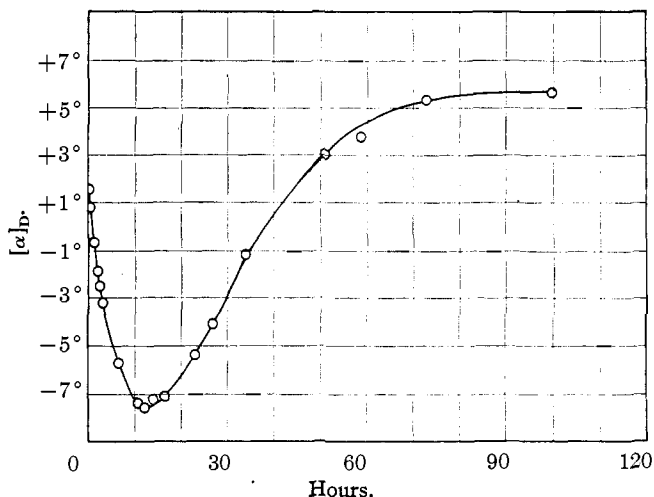
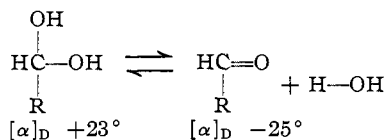


Fig. 1.—Mutarotation of the ethyl hemi-acetal of aldehydo-galactose pentaacetate in chloroform, Expt. 1.

the aldehydo carbon atom becomes asymmetric and can exist in two forms, (A) and (C). From the nature of the mutarotation curve the form (C) must be more dextro-rotatory than (A). Experiments to find conditions for the isolation of the second form (C) are now in progress in this Laboratory.

The mutarotation curve obtained for aldehydo-galactose pentaacetate aldehydol in ethanol-free chloroform is shown in Fig. 2. This is now a smooth exponential curve and differs widely in form from that obtained for the ethanol compound. In the case of the aldehydol, the aldehydo carbon atom is not asymmetric and only one form is possible. The nature of the mutarotation is indicated by the following simple reaction



As the rotations of both the forms indicated above are known, the data obtained may be analyzed mathematically. The data of Table II show that the reaction is a simple monomolecular decomposition, as would be predicted on the basis of an aldehydol structure for the hydrate. The value obtained for the final rotation indicates that the change to the free aldehyde form ($[\alpha]_D -25^\circ$) is nearly complete. When a 4% chloroform solution of the aldehydol was used the solution became turbid in about thirty minutes due to the separation of water.

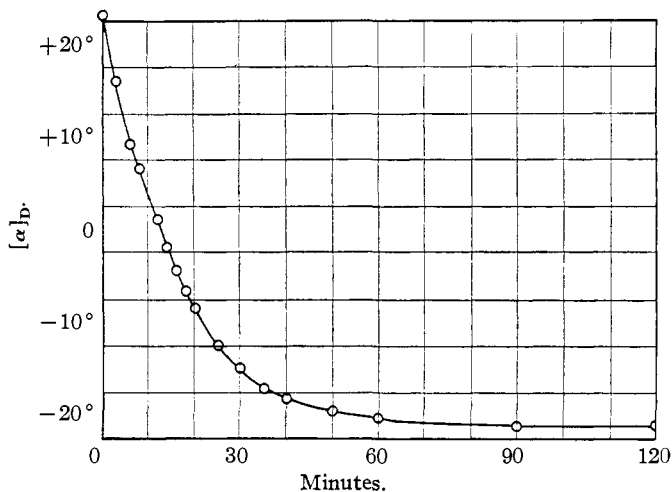


Fig. 2.—Mutarotation of the aldehydol of aldehydo-galactose pentaacetate in chloroform.

It may be stated that the material from the equilibrated chloroform solutions of both the aldehydol and ethyl hemiacetal can be recovered unchanged in good yield by recrystallization from the appropriate solvents. The rotation of the free form of aldehydo-galactose pentaacetate is stable in pure chloroform solution. This is also true of the aldehydo-acetates of *d*-glucose² and of *l*-arabinose³ recently isolated in this Laboratory. These facts show that the chloroform mutarotation of the aldehydol and ethyl hemiacetal of aldehydo-galactose pentaacetate is not in the nature of a profound structural change involving an acetyl shift to a ring form. It is believed that the pure chloroform mutarotation of these compounds offers good evidence of their constitutional structure.

² M. L. Wolfrom, *THIS JOURNAL*, **51**, 2188 (1929).

³ M. L. Wolfrom and Mildred R. Newlin, *ibid.*, **52**, 3619 (1930).

On the basis of the more accurate initial rotation data now reported, the specific rotation in chloroform solution of aldehydo-*d*-galactose pentaacetate aldehydrol is $+23^\circ$ and that for the ethyl hemiacetal is $+1.5^\circ$. The values previously obtained were $+19.5$ and -0.5° , respectively.

TABLE I

MUTAROTATION OF THE ETHYL HEMI-ACETAL OF ALDEHYDO-GALACTOSE PENTAACETATE IN PURE CHLOROFORM (*l*, 4 DM.; λ , 5892 Å.; *t*, 22°)

Experiment 1; <i>c</i> , 5.019			Experiment 2; <i>c</i> , 5.035		
Time, min.	α , degrees	$[\alpha]_D$, degrees	Time, min.	α , degrees	$[\alpha]_D$, degrees
4	+0.31	+1.6	3	-0.25	-1.2
10	.28	1.4	6	-.48	-2.4
14	.26	1.3	10	-.95	-4.7
30	.16	0.8	15	-1.24	-6.2
Hours			Hours		
1	-.04	-0.2	20	-1.35	-6.7
2	-.38	-1.9	27	-1.48	-7.4
4	-.80	-4.0	35.5	-1.56	-7.7
6.5	-1.13	-5.7	40	-1.59	-7.9
8	-1.32	-6.6	45	-1.45	-7.2
10.5	-1.47	-7.4	50	-1.40	-7.0
			Hours		
12	-1.53	-7.6	1	-1.09	-5.4
			(1, 2-dm.)		
14	-0.72	-7.2	1.25	-0.70	-3.5
17	-.71	-7.1	1.5	-.38	-1.9
23	-.54	-5.4	2	+.11	+0.6
34	-.12	-1.2	3	.70	3.5
59	+.37	+3.7	6.5	1.18	5.9
73	+.53	+5.3	9	1.18	5.9
100	+.56	+5.6			

TABLE II

MUTAROTATION OF THE ALDEHYDROL OF ALDEHYDO-GALACTOSE PENTAACETATE IN PURE CHLOROFORM (*l*, 4 DM.; λ , 5892 Å.; *t*, 23°; *c*, 2.006)

<i>t</i> , min.	α , degrees	$[\alpha]_D$, degrees	α (Free form)	$\alpha - \alpha$ (Aldehydrol)	k^b
0	$+23^a$	0	1.000	
3	+1.28	16.0	0.152	0.848	0.055
4	1.14	14.2	.191	.809	.054
6	0.74	9.2	.300	.700	.060
8	.52	6.5	.359	.641	.056
10	.28	3.5	.424	.576	.056
12	.08	1.0	.478	.522	.054
14	-.16	-2.0	.544	.456	.056
16	-.35	-4.4	.596	.404	.057
18	-.53	-6.6	.643	.357	.057
20	-.67	-8.4	.682	.318	.057
25	-.99	-12.4	.769	.231	.059
30	-1.19	-14.8	.822	.178	.058

TABLE II (Concluded)

<i>t</i> , 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 hemiacetal.

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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 Richards¹ 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 Bencowitz² 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-Jauregg³ 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).