

5. Toxicarol kills goldfish in a dilution of 1–20,000,000 at 27° in four and one-half hours. The $C_{23}H_{22}O_6$ compound at the same dilution and temperature is lethal in three hours.

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

THE FIFTH PENTA-ACETATE OF GALACTOSE, ITS ALCOHOLATE AND ALDEHYDROL

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In the work herein reported, the methods employed in the synthesis of the crystalline free aldehyde form of glucose¹ have been extended to galactose, and we have obtained this form of galactose penta-acetate and also its crystalline hydrate and ethyl alcoholate. This penta-acetate is of particular interest because it adds a fifth isomer to the series of four already known. Erwig and Koenigs² prepared the first form, m. p. 142°, of galactose penta-acetate. This beta ring form was isomerized to the alpha form of the same ring structure by Hudson and Parker³ on heating with acetic anhydride and zinc chloride. Hudson⁴ then reported a third form found in small yield in the acetylation mother liquors from the preparation of the first form. This was prepared in larger quantity by Hudson and Johnson⁵ and isomerized to the fourth form by the acetic anhydride and zinc chloride reaction. These four forms were found by Hudson to conform in rotation to two alpha and beta pairs of two different ring structures and constituted the first proof, based on the isolation of crystalline derivatives, that a sugar could exist in more than one lactal or ring structure. The third form of galactose penta-acetate has been prepared in higher yield by a method recently reported by Schlubach and Prochownick.⁶ The properties of the five forms of galactose penta-acetate are shown in Table I.

TABLE I
PROPERTIES OF THE FIVE PENTA-ACETATES OF GALACTOSE

Form	M. p., °C.	$[\alpha]_D$ CHCl ₃ , ^a U. S. P.
First galactose penta-acetate, β -form	142	+ 23.0
Second galactose penta-acetate, α -form	96	+107.0
Third galactose penta-acetate, β -form	98	- 42.0
Fourth galactose penta-acetate, α -form	87	+ 61.0
Fifth galactose penta-acetate, μ -form	121	- 25 (Initial)

^a The first four forms were measured at 20°, the fifth at 26°.

¹ M. L. Wolfrom, *THIS JOURNAL*, **51**, 2188 (1929).

² E. Erwig and W. Koenigs, *Ber.*, **22**, 2207 (1889).

³ C. S. Hudson and H. O. Parker, *THIS JOURNAL*, **37**, 1589 (1915).

⁴ C. S. Hudson, *ibid.*, **37**, 1591 (1915).

⁵ C. S. Hudson and J. M. Johnson, *ibid.*, **38**, 1223 (1916).

⁶ H. H. Schlubach and Vilma Prochownick, *Ber.*, **62**, 1502 (1929).

We have suggested¹ the name μ -glucose penta-acetate for the free aldehyde sugar acetates. This is convenient in briefly distinguishing from the α - and β -forms, as in Table I, but it has the disadvantage of not being a very rational prefix. We believe that the prefix aldehydo overcomes this difficulty and we will accordingly designate the fifth penta-acetate of galactose as aldehydo galactose penta-acetate.

Aldehydo galactose penta-acetate very readily combines with one molecule of ethyl alcohol and of water to form compounds that we do not believe are in the nature of ordinary addition compounds. Both compounds are stable to calcium chloride desiccation and it was found that the alcohol could not be removed from the alcoholate by heating at various temperatures under highly reduced pressure without decomposition of the acetate. As regards the hydrate, it need only be pointed out that the ordinary forms of sugar acetates show no tendency at all toward hydrate formation. We accordingly believe that these compounds are similar to the corresponding ones of chloral and it is interesting to note that their melting points fall in the same order, as is shown in Table II. It has been well established that these compounds of chloral are not ordinary addition compounds.

TABLE II

COMPARISON OF THE MELTING POINTS OF CHLORAL AND ITS HYDRATE AND ALCOHOLATE WITH THOSE OF ALDEHYDO GALACTOSE PENTA-ACETATE

	Chloral ^a	Aldehydo galactose penta-acetate
Ethyl alcoholate, m. p., °C.	55	133
Hydrate, m. p., °C.	47.4	125
Free form, m. p., °C.	-57.5	121

^a J. C. Olsen, "Chemical Annual," D. Van Nostrand, Co., Inc., New York, 1926, 6th ed.

If these two compounds of aldehydo galactose penta-acetate are not ordinary addition compounds, then they must be the aldehydrol and the ethyl-hemi-acetal. Galactose aldehydrol has been postulated by Lowry and Smith⁷ as an intermediate in mutarotation and an analysis of data has led these authors to conclude that this form exists at equilibrium to the extent of 12% of the sugar present. Levene and Meyer⁸ prepared the liquid aldehydo pentamethylgalactose, and by using methyl alcohol containing hydrogen chloride, were able to obtain the dimethyl acetal (b. p., 118–120°, 0.6 mm.).

The alcoholate and hydrate of aldehydo galactose penta-acetate show rotation changes in U. S. P. chloroform solution that are probably due to dissociation of the alcohol and water, respectively. These are plotted in Fig. 1 and Fig. 2 and both curves exhibit a distinct break in the early

⁷ T. M. Lowry and G. F. Smith, *J. Phys. Chem.*, **33**, 9 (1929).

⁸ P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **74**, 695 (1927).

course of the change. The free form shows a continuous change of rotation in chloroform. That this change is due to combination with the ethyl alcohol in the U. S. P. chloroform used is made probable by the fact that the rotation of this form was constant in pure acetylene tetrachloride solution. The final rotation of the free form in chloroform approached but did not equal that of the alcoholate in the same solvent. This may be due to a difference in the ethyl alcohol concentration present, although further work would be required to show this definitely. The properties of the three acetates are listed in Table III.

TABLE III

PROPERTIES OF THE FREE FORM, HYDRATE, AND ALCOHOLATE OF ALDEHYDO GALACTOSE PENTA-ACETATE

Form	M. p., °C.	$[\alpha]_D^{25}$, CHCl ₃ , U. S. P.
Aldehydo galactose penta-acetate	121	-25 (Initial)
Aldehydo galactose penta-acetate hydrate	125	+19.5 (Initial)
Aldehydo galactose penta-acetate ethyl alcoholate	133	- 0.5 (Initial)

Aldehydo galactose penta-acetate and its hydrate and alcoholate all readily reduce Fehling's solution on heating and their aqueous solutions give a strong Schiff test for the aldehydo group. Since the alcoholate reduces Fehling's solution, the ethyl alcohol cannot be present in any stable glycosidic linkage. The Schiff test given by the hydrate and alcoholate in aqueous solution denotes dissociation of the water and alcohol in combination. An aqueous solution of the alcoholate readily gave a crystalline semicarbazone, identical with that obtained in the same way from the free form. This semicarbazone showed a normal molecular weight by the Rast⁹ method.

In the experimental work recorded in this paper, it was found convenient to prepare the aldehydo-galactose penta-acetate through the alcoholate, although it should also be possible to prepare the free form directly.

Further work on the synthesis and reactivity of the free aldehyde forms of sugar acetates is in progress in this Laboratory.

Experimental

Preparation of Galactose-ethylmercaptal.—The procedure of E. Fischer¹⁰ always produced low yields when repeated in this Laboratory. The procedure to be described gave good results and is essentially that used by Levene and Meyer⁸ in the preparation of mannose-ethylmercaptal except that more acid is required to dissolve the galactose. Fifty grams of galactose was placed in a 500-cc. glass-stoppered wide-mouthed bottle and dissolved at room temperature in 75 cc. of concentrated hydrochloric acid (sp. gr. 1.19). Fifty cc. of technical ethyl mercaptan was then added and the mixture vigorously shaken, releasing the pressure occasionally. After three to five minutes a definite temperature increase was noted. A little ice and ice water was then added. The con-

⁹ K. Rast, *Ber.*, **55**, 1051 (1922).

¹⁰ E. Fischer, *ibid.*, **27**, 673 (1894).

tents of the bottle almost at once solidified to a mass of white crystals. More ice water was added and the mass filtered immediately, washing with a little ice water. The material was recrystallized from absolute alcohol and then from hot water; yield, 37 g.; m. p. 140–142°.

D-Galactose-ethylmercaptal Penta-acetate.—Fifty grams of galactose-ethylmercaptal was treated with 175 cc. of dry pyridine and cooled in ice. After nearly all of the mercaptal had dissolved, 250 cc. of acetic anhydride was gradually added. This addition caused the separation of a considerable quantity of solid. The mixture was allowed to stand in ice for about an hour and then kept at room temperature for eighteen hours. The undissolved material went into solution on occasional shaking. The solution was then poured into about 10 liters of ice water. The sirup thrown out readily crystallized; yield, 85 g., or 98%. Pure material was obtained by dissolving in methyl alcohol and adding water to opalescence, placing in the ice box, and from time to time adding more water until no further crystallization took place; yield, 81 g., m. p. 77–78°, $[\alpha]_D^{25} +9.8^\circ$ in chloroform (U. S. P.) solution. After two further recrystallizations the melting point was 77.5–78.5° and the specific rotation in chloroform (U. S. P.) solution was $+9.7^\circ$ at a temperature of 25°. The substance crystallizes in prismatic needles and is readily soluble in chloroform, ether, benzene, acetone and methyl alcohol; it is less soluble in ethyl alcohol and is practically insoluble in petroleum ether and water.

Anal. Subs., 0.2029: 20.4 cc. of 0.1 *N* KOH. Calcd. for $(C_2H_5S)_2C_6H_7O_5(CH_3CO)_5$: 20.4 cc. of 0.1 *N* KOH.

Aldehyde Galactose Penta-acetate Mono-ethyl Alcoholate.—The procedure followed in the preparation of aldehyde-glucose penta-acetate¹ was modified in order to obtain this compound. Twenty-five grams of galactose-ethylmercaptal penta-acetate (1 mol.) was dissolved in 90 cc. of acetone and 45 cc. of water added. The clear solution was held in a 3-necked round-bottomed flask provided with a good mechanical stirrer. An excess, 45–50 g., of washed and finely powdered cadmium carbonate was added and under rapid stirring a solution of 49 g. (3.6 mols) of mercuric chloride dissolved in 72 cc. of acetone was gradually added. Stirring was maintained at room temperature for twenty-four hours, with occasional additions of small amounts of finely powdered cadmium carbonate. This was then filtered, an excess of fresh cadmium carbonate being placed in the suction flask, and the precipitate washed with acetone. The filtrate was then concentrated to dryness at 35° under reduced pressure and in the presence of excess cadmium carbonate. The residue was dried by adding absolute ethyl alcohol and distilling under reduced pressure, this being repeated. The residue was extracted with warm chloroform, filtered, 50 cc. of absolute alcohol added to the filtrate and the resulting solution evaporated at room temperature in a vacuum desiccator. The product crystallized completely during the course of this evaporation. An amount of 20.4 g. was obtained. This was dissolved in about four parts of hot absolute ethyl alcohol, norite added and the solution filtered from a small amount of insoluble material. On cooling slowly to room temperature crystallization began and was allowed to continue for eighteen hours at room temperature. The crystals were removed by filtration and washed with cold absolute ethyl alcohol; yield, 11.5 g.; m. p. 132–133°. Further amounts of pure material were obtainable by repeated recrystallization from absolute ethyl alcohol of the material obtained by evaporating the mother liquor either to dryness or to low volume. From 72.9 g. of crude product, 56.2 g. of material melting at 132–133° was so obtained in six crops.

The substance crystallizes in diamond-shaped six-sided plates. It is soluble in warm water and in acetone, very soluble in chloroform, very slightly soluble in warm ether and practically insoluble in petroleum ether. The room temperature solubility in methyl alcohol is about 1.5 g. per 100 cc.; in ethyl alcohol, less than 1 g. per 100 cc.

It is soluble in about seven parts of boiling absolute ethyl alcohol. As the melting points of this substance and of the others here reported, were all very sensitive to slight impurities, this constant was used throughout this work as a criterion of purity. The

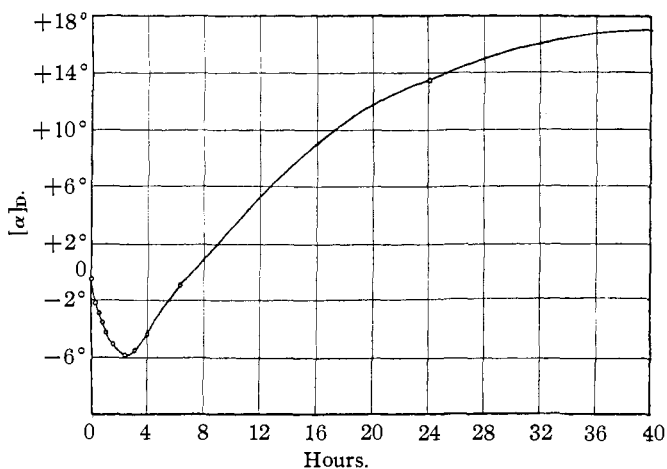


Fig. 1.—Rotation change of aldehyde galactose penta-acetate alcoholate in U. S. P. chloroform (Expt. 2).

melting point of the pure substance is 133–134° when it is very rapidly heated to near the melting point. This melting point was unchanged by further recrystallization.

TABLE IV
ROTATION CHANGES OF ALDEHYDO GALACTOSE PENTA-ACETATE ALCOHOLATE IN U. S. P.
CHLOROFORM SOLUTION
 l , 1.1 dm. λ , 5892 Å.

Time, min.	Experiment 1 t , 25° c , 5.021		Time, min.	Experiment 2 t , 21° c , 5.013	
	α , degrees	$[\alpha]_D$, degree		α , degrees	$[\alpha]_D$, degrees
0		-0.6 ^a	0		-0.5 ^a
1.5	-0.05	-0.9	2	-0.05	-0.9
5	- .10	-1.8	5	- .09	-1.6
10	- .11	-2.0	10	- .11	-2.0
15	- .14	-2.5	15	- .12	-2.2
30	- .27	-4.9	30	- .16	-2.9
45	- .36	-6.5	45	- .19	-3.5
Hours			Hours		
1	- .37	-6.7	1	- .23	-4.2
			1.5	- .28	-5.1
			2.3	- .32	-5.8
3	- .19	-3.4	3	- .30	-5.5
			4	- .24	-4.4
6	+ .28	+5.1	6.3	- .05	-0.9
30	1.03	18.7	24	+ .74	+13.4
50	1.04	18.8	48	.92	16.7
			98	1.05	19.0
			124	0.92	16.7

^a Interpolated.

The initial specific rotation of material of this purity in chloroform (U. S. P.) is -0.5° . This rotation changes in the levo direction and then reverses sign and becomes dextro, reaching equilibrium at a specific rotation of $+18^\circ$. This behavior is probably due to dissociation of the ethyl alcohol. The rotation change is plotted in Fig. 1 and the data are tabulated in Table IV. It was determined that this change was not mainly, at least, in the nature of a deep-seated isomerization involving an acetyl shift with the possible formation of a penta-acetate of lactal structure. The equilibrated chloroform solution was concentrated to dryness in a vacuum desiccator. The residue was but slightly changed in appearance from the original material, being slightly sticky, probably due to incomplete alcoholate formation. On one recrystallization from 95% ethyl alcohol, the original material was obtained in good yield. The melting point was $131-133^\circ$ and was not depressed on admixture with known material of this same purity.

In methyl alcohol at room temperature the pure substance has no detectable initial rotation. The specific rotation gradually increases, reaching the equilibrium value of $+14.5^\circ$. This rotation change is tabulated in Table V.

TABLE V
ROTATION CHANGES OF ALDEHYDO GALACTOSE PENTA-ACETATE ALCOHOLATE IN METHYL ALCOHOL

Experiment 1				Experiment 2	
Time, min.	$t, 25^\circ, c, 1.012$ α , degrees	$[\alpha]_D$, degrees	Time, min.	$t, 23^\circ, c, 1.015$ α , degrees	$[\alpha]_D$, degrees
5	0	0	10	0	0
15	0	0	20	0	0
30	0	0	30	0	0
Hours		Hours		Hours	
5.5	+0.11	+5.5	3	+0.04	+2
9	.15	7.5	6	.08	4
24	.22	11.0	24	.23	11.5
49	.24	12.0	48	.29	14.5
76	.28	14.0	98	.31	15.5
147	.28	14.0	123	.28	14.0

The presence of ethoxyl in this compound was qualitatively determined by the procedure of Willstätter and Utzinger.¹¹ This consists in treating the substance with hydriodic acid and passing the alkyl iodide evolved into undiluted dimethylaniline. The resulting crystals were filtered, washed with cold acetone and recrystallized once from hot acetone. The crystals are very deliquescent and must be dried in a desiccator over sulfuric acid. The melting point was 136° and showed no depression on being mixed with an authentic specimen of dimethylethylphenylammonium iodide. The melting point of trimethylphenylammonium iodide is 232° (corr.)¹²

The alcohol in this compound dissociates very readily in solution, as the substance reduces hot Fehling's solution and gives a very strong Schiff aldehyde test. These tests were obtained by using dilute aqueous solutions of the substance formed by dissolving it in warm water and cooling to room temperature. The Schiff reagent used was that recommended by Alyea and Bäckström.¹³ The substance also reacts instantaneously in aqueous solution with semicarbazide to form an insoluble semicarbazone.

¹¹ R. Willstätter and M. Utzinger, *Ann.*, **382**, 148 (1911).

¹² Max Phillips, *THIS JOURNAL*, **52**, 793 (1930).

¹³ H. N. Alyea and H. L. J. Bäckström, *ibid.*, **51**, 97 (1929).

The substance is stable in the air and in a calcium chloride desiccator. It was not found possible to remove the alcohol by heating at various temperatures and under highly reduced pressure without decomposition of the acetate.

Anal. Subs., 0.2201: CO_2 , 0.3970; H_2O , 0.1334. Subs., 0.3133: AgI , 0.1709. Subs., 0.1000: 11.41 cc. of 0.1 *N* KOH . Calcd. for $\text{C}_6\text{H}_7\text{O}_6(\text{CH}_3\text{CO})_5\text{C}_2\text{H}_5\text{OH}$: C, 49.52; H, 6.47; OC_2H_5 , 10.33; 11.46 cc. of 0.1 *N* KOH . Found: C, 49.19; H, 6.78; OC_2H_5 , 10.46; 11.41 cc. of 0.1 *N* KOH ; S, absent.

In the ethoxyl determination, a double Zeisel apparatus was used, the vapors from the first being passed through the second before being absorbed in the silver solution.

Aldehyde Galactose Semicarbazone Penta-acetate.—It was found possible to dissolve the alcoholate of aldehyde galactose penta-acetate in water and readily obtain the semicarbazone of this aldehyde from the solution. An amount of aldehyde galactose penta-acetate mono-ethyl alcoholate (m. p. 133–134°) equal to 0.56 g. (1 mol) was dissolved in 5 cc. of hot water and the solution cooled to room temperature. A mixture of 0.12 g. (0.9 mol) of semicarbazide hydrochloride and 0.20 g. (1.6 mols) of potassium acetate was added to the solution and the whole shaken vigorously. After a few minutes

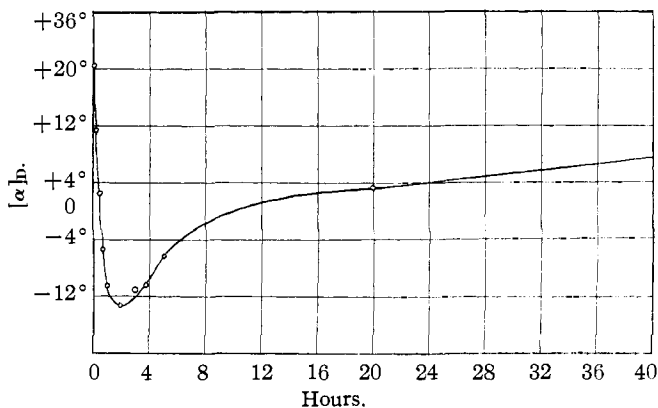


Fig. 2.—Rotation change of aldehyde galactose penta-acetate hydrate in U. S. P. chloroform (Expt. 2),

a heavy crystallization took place. The mixture was allowed to stand overnight and then filtered and washed with cold water; yield, 0.43 g. (75%); m. p. 200–201° (corr.) with decomposition. On recrystallization from boiling water the substance crystallized in glittering, prismatic needles which in some cases were over one centimeter in length. The melting point was unchanged on one recrystallization and also on three recrystallizations. This melting point is identical with that of *d*-galactose semicarbazone,¹⁴ but as both these values are more in the nature of decomposition points than true melting points, this fact need not be surprising. The substance is soluble in about 55 parts of boiling water, soluble in hot ethyl and methyl alcohol, and is very slightly soluble in chloroform, ether and acetone.

Anal. Subs., 0.2011: N_2 , 16.97 cc. (752 mm., 25°). Subs., 0.1147: 13.0 cc. 0.1 *N* KOH . Calcd. for $\text{C}_7\text{H}_{10}\text{O}_6\text{N}_3(\text{CH}_3\text{CO})_5$: N, 9.40; 12.8 cc. 0.1 *N* KOH . Found: N, 9.23; 13.0 cc. 0.1 *N* KOH .

The acetyl determination was performed by dissolving the weighed sample (0.1 g.) in 20 cc. of boiling water, cooling rapidly to room temperature, and adding an equal

¹⁴ Maquenne and Goodwin, *Bull. soc. chim.*, [3] 31, 1075 (1904).

volume of 0.2 *N* potassium hydroxide before crystallization was initiated. The alkaline solution was then allowed to stand for one hour at room temperature and the excess alkali determined by titration with 0.1 *N* hydrochloric acid, using phenolphthalein indicator.

Molecular weight:¹⁵ (Rast) 0.0102 g. of subs. in 0.1019 g. of camphor depressed the m. p. 9°. Mol. wt. calcd. for C₁₇H₂₅O₁₁N₃: 447. Found: 445.

Aldehyde Galactose Penta-acetate Monohydrate.—On several recrystallizations of the aldehyde galactose penta-acetate monoethyl alcoholate from boiling water the pure monohydrate was obtained. This substance crystallizes readily from water as prismatic

TABLE VI
ROTATION CHANGES OF ALDEHYDO GALACTOSE PENTA-ACETATE HYDRATE IN U. S. P.
CHLOROFORM SOLUTION
t, 27°. λ , 5892 Å.

Experiment 1 <i>l</i> , 2 dm. <i>c</i> , 2.011			Experiment 2 <i>l</i> , 1.1 dm. <i>c</i> , 4.003			Experiment 3 <i>l</i> , 1 dm. <i>c</i> , 2.011		
Time, min.	α , degrees	$[\alpha]_D$, degrees	Time, min.	α , degrees	$[\alpha]_D$, degrees	Time, min.	α , degrees	$[\alpha]_D$, degrees
0		+19.2 ^a	0		+20.2 ^a	5	+0.31	+15.4
2	+0.73	18.2	5	+0.76	17.3	10	.29	14.4
4	.71	17.7	7	.71	16.1	15	.22	10.9
6	.66	16.4	10	.63	14.3	20	.14	7.0
8	.62	15.4	13	.55	12.5	25	.11	5.5
10	.59	14.7	15	.52	11.8	30	.08	4.0
12	.55	13.7	17.5	.48	10.9	40	.02	1.0
14	.51	12.7	20	.44	10.0	55	-.08	-4.0
						Hours		
16	.48	11.9	25	.32	7.3	1	-.14	-7.0
20	.46	11.4	30	.10	2.3	1.2	-.16	-8.0
25	.38	9.5	35	.01	0.2	3	-.21	-10.4
30	.30	7.5	41	-.16	-3.6	5	-.28	-13.9
40	.17	4.2	45	-.25	-5.7	18	0	0
			Hours					
50	.06	1.5	1	-.46	-10.5	23	+.02	+1.0
Hours								
1	-.10	-2.5	2	-.59	-13.4	30	.08	4.0
1.3	-.15	-3.7	3	-.49	-11.1	45	.15	7.5
1.8	-.34	-8.5	3.8	-.47	-10.7	54	.18	9.0
3	-.51	-12.7	5	-.28	-6.4	71	.17	8.5
5	-.55	-13.7	20	+.14	+3.2			
8	-.57	-14.2	46	.39	8.9			
12	-.29	-7.2	56	.36	8.2			
27	+.05	+1.2	73	.38	8.6			
47	.35	8.7						

^a Interpolated.

NOTE.—The last values are somewhat uncertain due to evaporation of the chloroform on long standing and to an apparent decomposition that sometimes takes place after a period in this solvent.

¹⁵ We are indebted to Mr. Leonard Wise of this Laboratory for the determination of this molecular weight.

needles. The crystals are moderately soluble in chloroform, very slightly soluble in water at room temperature, but are soluble in hot water, very soluble in acetone and are practically insoluble in ether and petroleum ether. An aqueous solution of the substance readily reduced hot Fehling's solution and gave a strong Schiff test. The melting point was found to be 124–126°, on rapid heating to near the melting point, and this was unchanged by further recrystallization. Material of this purity showed an initial rotation in U. S. P. chloroform of +19.5°. This value changed to levo and then became dextro, becoming constant at +9°. These polarimetric data are plotted in Fig. 2 and are tabulated in Table VI.

Anal. Subs., 0.2110: CO₂, 0.3662; H₂O, 0.1174. Subs., 0.1000: 12.38 cc. of 0.1 *N* NaOH. Calcd. for C₆H₇O₆(CH₃CO)₅·H₂O: C, 47.04; H, 5.93; 12.25 cc. of 0.1 *N* NaOH. Found: C, 47.32; H, 6.23.

Aldehydo Galactose Penta-acetate.—On several recrystallizations of the aldehydo galactose penta-acetate mono-ethyl alcoholate from hot toluene, the pure free aldehyde form of the penta-acetate was obtained. This substance readily crystallizes from toluene

TABLE VII
ROTATION OF ALDEHYDO GALACTOSE PENTA-ACETATE

Expt. 1, U. S. P. CHCl ₃ <i>l</i> , 1.1 dm. <i>c</i> , 4.001			Expt. 2, U. S. P. CHCl ₃ <i>l</i> , 1.1 dm. <i>c</i> , 4.005			Expt. 3, CHCl ₂ —CHCl ₂ <i>l</i> , 1 dm. <i>c</i> , 3.990		
Time, min.	α , degrees	$[\alpha]_D$, degrees	Time, min.	α , degrees	$[\alpha]_D$, degrees	Time, min.	α , degrees	$[\alpha]_D$, degrees
0		-25 ^a	0		-25.5 ^a	3	-0.65	-16.3
3	-0.97	-22.0	2	-1.08	-24.5	5	-.65	-16.3
4	-.93	-21.1	3	-1.00	-22.7	10	-.63	-15.8
6	-.92	-20.9	4	-1.01	-23.0	15	-.64	-16.0
10	-.77	-17.5	6	-0.93	-21.1	30	-.62	-15.5
16	-.68	-15.5	8	-.87	-19.8	Hours		
20	-.66	-15.0	10	-.87	-19.8	1	-.64	-16.0
27	-.57	-13.0	15	-.81	-18.4	2	-.65	-16.3
35	-.43	-9.8	20	-.72	-16.4	6.5	-.65	-16.3
45	-.35	-8.0	30	-.61	-13.9	21.5	-.66	-16.5
Hours			45	-.35	-8.0	65.5	-.65	-16.3
1	-.28	-6.4	Hours					Av. -16.1
1.25	-.18	-4.1	1	-.19	-4.3			
1.5	-.08	-1.8	1.5	-.10	-2.3			
1.75	-.04	-0.9	2	-.01	-0.2			
2	+.04	+0.9	2.5	+.10	+2.3			
2.5	.08	1.8	3	+.23	+5.2			
3	.15	3.4	8	+.35	+8.0			
4.3	.29	6.6						
6	.36	8.2						
7	.38	8.6						
22	.46	10.5						
41	.43	9.8						

^a Interpolated.

NOTE.—(a) The last values in Expts. 1 and 2 are somewhat uncertain due to evaporation of the chloroform on long standing and to an apparent decomposition that sometimes takes place after a period in this solvent. (b) A second set of readings in acetylene tetrachloride solutions gave the average value of -16.3° for the specific rotation in this solvent.

as very characteristic clusters of elongated prisms. The crystals are very soluble in chloroform, soluble in acetone and hot water, slightly soluble in alcohol and benzene at room temperature, but more soluble in the warm, very slightly soluble in ether and practically insoluble in petroleum ether. An aqueous solution of the substance readily reduced Fehling's solution when heated and gave a strong Schiff test. The melting point was found to be 120–121°, unchanged by further recrystallization. Material of this purity showed an initial rotation in U. S. P. chloroform of -25° , changing to $+10^\circ$. That this change was very probably due to combination with the ethyl alcohol in the U. S. P. chloroform was shown by the fact that the rotation was constant in pure acetylene tetrachloride solution, $[\alpha]_D^{27}$, -16° (Table VII). Before use the acetylene tetrachloride was washed with sodium bicarbonate solution to remove the acidity present in this solvent on standing, then with water, and the liquid then dried and distilled. The polarimetric data obtained with this compound are tabulated in Table VII.

A mixed melting point of the compound, m. p. 120–121°, with the first form of galactose penta-acetate, m. p. 142°, gave the value 107–111°. The other three forms of galactose pentaacetate melt below 100°.¹⁶ The semicarbazone was prepared from this substance in accordance with the previously recorded procedure, and was found to have the same melting point as the semicarbazone prepared from the alcoholate and showed no melting-point depression on being mixed with material from this source.

That the penta-acetate was a derivative of galactose was determined by identification of the mucic acid formed from it by oxidation. An amount of 0.5 g. of the penta-acetate, m. p. 120–121°, was oxidized with nitric acid according to the Kent-Tollens¹⁷ procedure. After two recrystallizations performed by dissolving the substance in 10% sodium hydroxide and adding 50% hydrochloric acid in slight excess, the crystals of mucic acid melted at 213–214° (corr.) with decomposition and slight preliminary darkening.

Anal. Subs., 0.2429: CO₂, 0.4374; H₂O, 0.1291. Subs., 0.1000: 12.80 cc. of 0.1 N NaOH. Calcd. for C₆H₇O₈(CH₃CO)₅: C, 49.21; H, 5.68; 12.81 cc. of 0.1 N NaOH. Found: C, 49.11; H, 5.95.

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Summary

1. A fifth form of *d*-galactose penta-acetate has been prepared in pure condition.
2. Evidence is given that this compound possesses the open-chain, free aldehyde structure and the name aldehydo galactose penta-acetate is suggested for this substance.
3. The hydrate and ethyl alcoholate of this compound have been prepared in pure form and evidence is given that they represent the aldehydol and ethyl-hemi-acetal structures, respectively.
4. The crystalline semicarbazone of aldehydo galactose penta-acetate has been prepared in pure form.

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¹⁶ Cf. Table I.

¹⁷ A. W. van der Haar, "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydsäuren," 1920, p. 103.