hydroxyl groups, but causes gelling after exposure to air, or after the addition of water or alcohol. Grignard reagents do not gel "dry" sols containing zinc amyl, nor does zinc amyl peptize "dry" gels obtained with Grignard reagents. (7) A benzene gel of pure sol rubber incompletely vulcanized with sulfur (*i. e.*, with 0.24% combined sulfur) is peptized by the addition of phenylmagnesium bromide. Acetic acid de-peptizes it but an excess of acid does not revert the resulting gel to a sol.

Imperfect technique has prevented so far accurate quantitative data, but the following approximations have been noted. (1) The amount of C_6H_5MgBr required to complete the gel reaction (assumed to be the amount required to produce what appears to be the stiffest gel) varies from about one mole of C_6H_5MgBr per 500 isoprene units to one molecule per 6 isoprene units depending upon the degree of "break down" in the rubber, more being required for greater break down with a stiffer gel resulting. (2) Approximately an equal amount of C_6H_5MgBr is required to complete peptization as is required to produce maximum stiffness. (3) Approximately equal molecular amounts of acetic acid are required to reverse either the gelling or peptizing reactions as were originally used of the gelling or peptizing reagents.

Incomplete as the study now stands, it nevertheless justifies the following interpretations. (1) The introduction of the organo-metallic group does not produce polymerization, because carbon to carbon linkages would persist after the destruction of the organo-metallic complex and the polymerized product would differ markedly from the original material, which is not the case. (2) Since organo-metallic compounds, such as those used, do not form bridges between molecules, this new type of vulcanization results from the formation of one or several complex groups at one or more points of the rubber molecule. (3) Since the organo-metallic reagents show very slight or no action on oxygen-free rubber, it follows that the combined oxygen of the rubber molecule is the point of attack. Corollary: *combined* oxygen is present in "broken down" (degenerated) rubber. (4) Since the complex obtained with organo-metallic compounds is vulcanized rubber, since its destruction devulcanizes the rubber, and since this complex probably contains polar groups, the theory that the formation of polar groups on the rubber molecule is essential to produce vulcanization is given considerable support.

Summary

Rubber has been vulcanized with organo-metallic compounds; this vulcanization has been reversed, then repeated. An interpretation of the experiments is proposed and the bearing on sulfur vulcanization is pointed out.

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

Ring Opening of Galactose Acetates[1]

BY JACK COMPTON AND M. L. WOLFROM

For some time it has been postulated that the reactivity of the hexoses was greatly enhanced by an equilibrium that is believed to exist in solution between the normal or pyranose (1,5) oxidic linkage; the free aldehyde (open chain) form or its hydrate; and some other oxidic linkage, usually referred to as the gamma, (*h*) or furanose (1,4).[2] It is known that the methyl furanosides of the sugars form and hydrolyze with greater ease than the methyl pyranosides. Interesting quantitative data have been given by Levene, Raymond and Dillon[3] for these rates of formation and by Haworth[4] for the relative rates of hydrolysis. The sugar galactose presents an opportunity for comparing the reactivities of these three postulated equilibrium structures by the use of certain derivatives, namely, β-galactopyranose tetraacetate (I),[5] aldehydo-galactose pentaacetate, which in aqueous solution exists as the alde-

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[1] The part of this work dealing with the phenylhydrazine reactions was presented before the Division of Organic Chemistry at the 85th Meeting of the American Chemical Society, Washington, D. C., March 28, 1933.

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

[3] P. A. Levene, A. L. Raymond and R. T. Dillon, *J. Biol. Chem.*, **95**, 699 (1932).

[4] W. N. Haworth, *Ber.*, **65A**, 43 (1932).

[5] Unna, Inaugural Dissertation, Berlin, 1911.

hydrol (VI),[6] and β-galactofuranose tetraacetate (III).[7] Each of these derivatives possesses a free potential aldehyde group and differs primarily in that the first contains a (1,5) oxidic linkage, the second an open chain structure and the third, what is certainly another ring that is very probably (1,4).

Buffered solutions of substituted hydrazines react with these three galactose tetraacetates to given open chain derivatives and the rates of these reactions furnish a direct comparison of the reactivity of the carbonyl groups in the different structures. The proof that only open chain hydrazones are obtained is furnished by the reactions outlined in Diagram 1. The reaction VI ⟶ V has been reported previously by Wolfrom and Christman.[8]

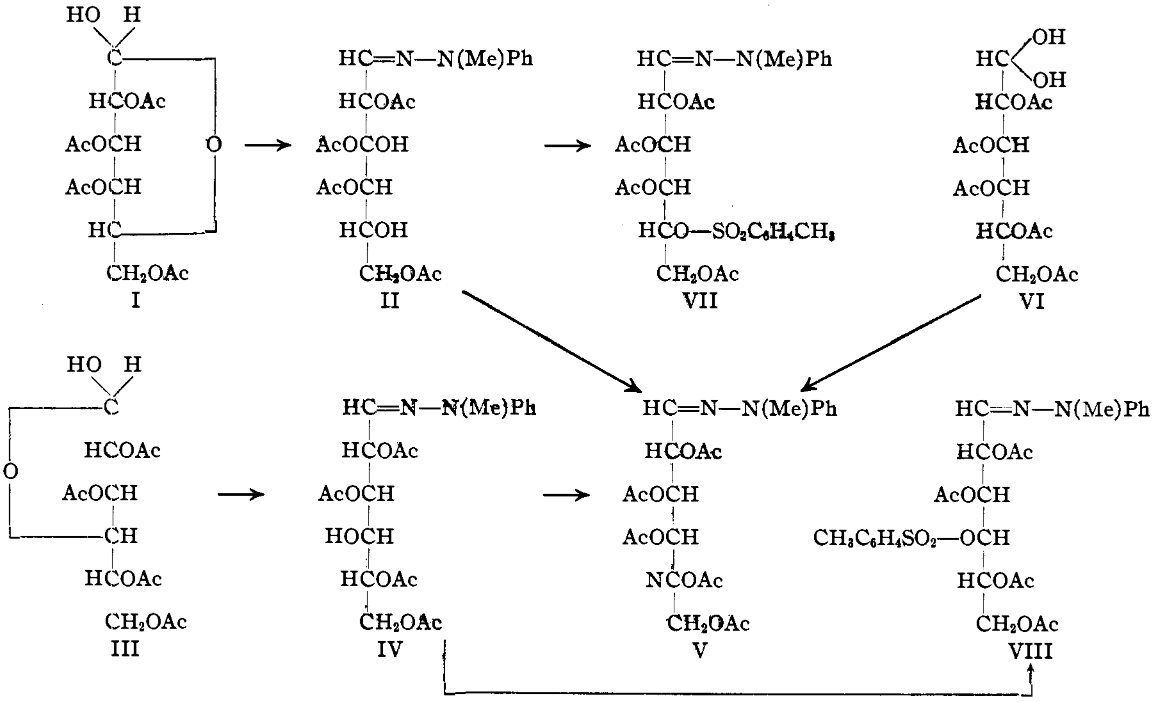
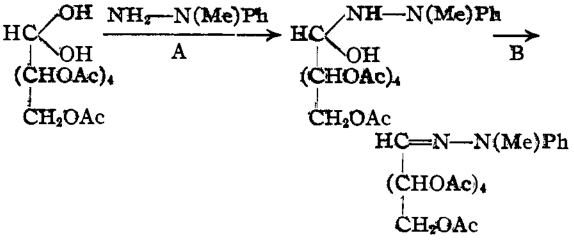


DIAGRAM 1

The rate of hydrazone formation for each of the three structures (I, III and VI) was determined under strictly comparable conditions and at a temperature of 0°. The method used was direct weighing of the hydrazone formed, this product being in each case extremely water-insoluble. The two tetraacetates exist in interconvertible α and β forms and show mutarotation. Under the experimental conditions used this equilibrium was probably attained immediately. At any rate, no difference was found between the data so obtained and those found by using aqueous solutions of the tetraacetates that had been given time to come to equilibrium. The results are tabulated in Table I and this table also includes data obtained with phenylhydrazine. With this reagent the open chain structure of the hydrazone tetraacetates was also proved by the fact that the hydrazone pentaacetate obtained by further mild acetylation was identical with that obtained directly from the aldehydo-galactose pentaacetate and phenylhydrazine. The phenylhydrazone of the galactopyranose tetraacetate unfortunately was an amorphous product.

The reaction between the substituted hydrazines and each of the three acetates was monomolecular in every case. With aldehydo-galactose pentaacetate aldehydrol, the reaction very probably passes through the steps



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[6] M. L. Wolfrom, THIS JOURNAL, 52, 2464 (1930); *ibid.*, 53, 2275 (1931).

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

[8] M. L. Wolfrom and C. C. Christman, *ibid.*, 53, 3413 (1931).

TABLE I

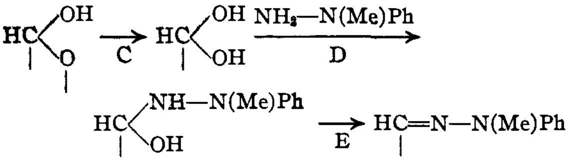
RATE OF HYDRAZONE FORMATION OF GALACTOSE ACETATES

Temp., 0°. a, 7.2×10^{-4} moles. 0.06 molar sugar acetate soln. Molar ratio of sugar acetate : substituted hydrazine hydrochloride : potassium acetate = 1 : 1.5 : 1.75. $k = 1/t\ (\text{min.}) \log_e a/(a - x)$

	Phenylhydrazone			Methylphenylhydrazone	
t, min.	Hydrazone, g.	*k*	*t*, min.	Hydrazone, g.	*k*
ALDEHYDO-GALACTOSE PENTAACETATE					
6	0.0966	0.055	6	0.0978	0.050
9	.1493	.060	12	.1769	.058
12	.1714	.057	18	.2264	.056
18	.2310	.061	24	.2523	.051
24	.2596	.058		Av.	.054
	Av.	.058			
GALACTOFURANOSE TETRAACETATE					
10	0.1181	0.047	12	0.0530	0.014
			12	.0506	.014
20	.1928	.047	24	.1258	.020
40	.2639	.047	36	.1584	.018
40	.2682	.047	48	.1798	.017
	Av.	.047	72	.2070	.015
				Av.	.016
GALACTOPYRANOSE TETRAACETATE					
180	0.0524	0.00101	180	0.0321	0.00057
180	.0511	.00099			
360	.0992	.00106	360	.0637	.00060
540	.1157	.00086	720	.1050	.00048
720	.1495	.00087	1080	.1354	.00050
1080	.1787	.00078	1440	.1530	.00044
	Av.	.00093		Av.	.00052

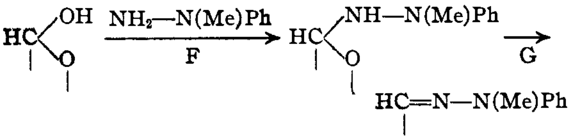
Now Bodforss,[9] following a suggestion made by Wieland[10] has shown that the reaction between aromatic aldehydes and an equivalent or deficient amount of phenylhydrazine as free base is monomolecular, being controlled by the slowest reaction (B, above). Our conditions were different from those of Bodforss in that the hydrazine hydrochloride and an excess of potassium acetate were used. This results in the formation of a solution of the phenylhydrazine acetate which is certainly very slightly dissociated into free phenylhydrazine. Since the amount of free phenylhydrazine remains minute and constant, the source of phenylhydrazine is acting here as a large reservoir and thus reaction A, and hence the complete reaction, would be apparently monomolecular.

The reaction between a substituted hydrazine and either of the ring tetraacetates may proceed as follows



It is axiomatic that the over-all speed of a series of consecutive reactions is controlled by the slowest. *A priori* we would not know which of the above three reactions is the slowest. But reactions D and E are the same as reactions A and B above. Now in all cases, the speed of reactions A and B between the substituted hydrazine and the aldehydo acetate exceeded the rates of the two ring tetraacetates. Accordingly the above series of reactions is governed by C or by the rate of lactal opening.

An alternative explanation leading to the same conclusion but which is more in accordance with the results of Isbell and Hudson[11] on the course of aldose oxidation, would be as follows



In the above case, the nature of reaction F would be sufficiently similar to the rapid reaction A to be ruled out as the controlling reaction. The over-all speed would be controlled by G or by the rate of lactal opening in the cyclic hydrazone structure. This would allow for slight differences in rates of reaction with the nature of the substituted hydrazine, as was found to be the case.

According to the above explanations the velocity constants for the two tetraacetates as given in Table I are a fair measure of the rate of lactal opening in each. It is seen that the pyranose structure has by far the lowest reactivity and rate of opening, the time being a matter of hours as against minutes for the other ring structure. The ratio of speeds for the pyranose to the other is about one to forty-five, or the furanose lactal opens about forty-five times as rapidly as the pyranose, at the relatively low temperature of 0°. As the reaction is very sensitive to temperature, it is to be expected that this difference might widen appreciably with an increase in temperature.

A phenylhydrazone of galacto-furanose tetraacetate has been recorded previously by Hudson and Johnson.[7] The phenylhydrazone we obtained had a higher melting point (139–140°) and

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[9] S. Bodforss, *Z. physik. Chem.*, **109**, 223 (1924).

[10] H. Wieland, "Die Hydrazine," Stuttgart, 1913.

[11] H. S. Isbell and C. S. Hudson, *Bur. Standards J. Research*, **8**, 327 (1932); *cf.* H. S. Isbell, *ibid.*, **8**, 615 (1932).

a much different rotation ([α]$_D$ +80°, $CHCl_3$) than the compound (m. p. 95°; [α]$_D$ +15.5°, $CHCl_3$) described by these workers. As these differences are too great to be for the same substance, the most reasonable explanation is that Hudson and Johnson had isolated an unstable isomer, probably one of the *syn-anti* forms. A similar experience was reported by Wolfrom and Thompson[12] with aldehydo-glucose oxime hexaacetate which was first isolated as a low melting (m. p. 79°) substance. This later changed over into a higher melting (m. p. 119.5°) form and all experiments to produce the lower melting isomer thereafter failed.

Further work is in progress in this Laboratory on the extension of the synthetic reactions herein reported.

Experimental

Preparation of β-Galactopyranose Tetraacetate (I).—Unna, in an unpublished dissertation[5] first reported the preparation of this compound by a method similar to that given by Fischer and Hess[13] for β-glucose tetraacetate. In the present work β-galactopyranose tetraacetate has been prepared successfully according to this general procedure.

From 20 g. of acetobromogalactose (m. p. 83°), 16–17 g. of crude product was obtained. Recrystallization of this product from 8 cc. of ethyl malonate gave 7 g. of pure material (m. p. 112°).[14] Further purification from this solvent did not change the melting point or optical rotation [α]$^{20}_{D}$ +23.3° (*c*,[15] 5.0, $CHCl_3$), changing slowly in the dextro direction; [α]$^{24}_{D}$ +25° ⟶ +76° (H_2O).

Anal. Calcd. for $C_6H_8O_6(COCH_3)_4$: acetyl, 23.0 cc. of 0.1 *N* NaOH per 100 mg.; reducing sugar (Munson-Walker), 0.5172 g. galactose. Found: acetyl, 23.1 cc.; reducing sugar, 0.5177 g. (determined by comparison with pure galactose control).

Aldehydo-galactose Methylphenylhydrazone 2,3,4,6-Tetraacetate (II).—Two grams (1 mole) of β-galactopyranose tetraacetate (m. p. 112°) was dissolved in 100 cc. of hot water and cooled to 0°. Two grams (3 moles) of α-methyl-α-phenylhydrazine was dissolved in 40 cc. of water containing 8 cc. of glacial acetic acid and 1 g. (2 moles) of potassium acetate. This solution was added with stirring to the cold tetraacetate solution. After standing at room temperature for fifteen to twenty minutes the hydrazone began to separate in crystalline form and this crystallization was practically complete after about four hours; yield, 2.1 g.; m. p. 117–118°. After one recrystallization from 95% ethanol the substance melted at 122–123° and the melting point and rotation were unchanged after further recrystallization. The rotation of this compound showed a difference in sign in pyridine and chloroform solutions. A very slow mutarotation in the dextro direction was observed in both solvents, this being more rapid with pyridine. Although we believe that the crystalline form of this compound has an open chain structure, the fact that it has an unsubstituted hydroxyl on the carbon chain might lead to ring formation in solution. Mutarotation into *syn-anti* forms with differing rotation is also not excluded. [α]$^{20}_{D}$ −12.0° ⟶ +37.5° (72 hours; *c*, 2.0, pyridine). [α]$^{25}_{D}$ +56.5° (*c*, 4.0, $CHCl_3$, changing very slowly in the dextro direction.

Anal. Calcd. for $C_{13}H_{16}O_5N_2(COCH_3)_4$: N, 6.20; acetyl, 8.85 cc. 0.1 *N* NaOH per 100 mg. Found: N, 6.11; acetyl, 8.91 cc. (Freudenberg[16] method).

Preparation of Aldehydo-galactose Methylphenylhydrazone Pentaacetate (V) from its 2,3,4,6-Tetraacetate.—Aldehydo-galactose methyl phenylhydrazone 2,3,4,6-tetraacetate (0.72 g. of m. p. 122–123°) was dissolved in 36 cc. of pyridine, cooled to 0° and 5 cc. of acetic anhydride added. After standing for two hours at 0° the solution was poured into 200 cc. of ice water with vigorous stirring, whereupon it separated immediately in crystalline form; yield, 0.57 g.; m. p. 137–138°. After three recrystallizations from alcohol the melting point was 138–139° (unchanged on admixture with an authentic specimen of the same substance).[8] [α]$^{24}_{D}$ +25.2° (*c*, 2.0, pyridine), without mutarotation. Previously this compound has been reported[8] as having [α]$_D$ +27°. Comparison of materials prepared by the present and the earlier procedure left no doubt of their identity, the lower rotation value being the more nearly correct.

Aldehydo-galactose Methylphenylhydrazone 2,3,4,6-Tetraacetate 5-*p*-Toluene Sulfonate (VII).—One gram of aldehydo-galactose methyl phenylhydrazone 2,3,4,6-tetraacetate was dissolved in 3 cc. of dry pyridine and 1.0 g. of *p*-toluene sulfonyl chloride added with cooling and the mixture shaken for about five minutes to complete the solution of the chloride. The solution was then kept at ice-box temperature for fifteen hours, after which the dark mixture was poured into 100 cc. of ice water with vigorous stirring. The gummy mass first separating became solid after standing in an ice-bath for about two hours; yield, 1.1 g. This was obtained crystalline as fine needles from hot ethanol and was further purified by dissolving in pyridine and pouring into a large volume of water; m. p. 143–144°. The rotation and melting point were unchanged by further recrystallization from pyridine–water; [α]$^{27}_{D}$ +21.4° (*c*, 2.0, pyridine).

Anal. Calcd. for $C_{20}H_{22}O_7N_2S(COCH_3)_4$: S, 5.26; acetyl, 6.60 cc. of 0.1 *N* NaOH per 100 mg. Found: S, 5.07; acetyl, 6.58 (Freudenberg).

Aldehydo-galactose Phenylhydrazone 2,3,4,6-Tetraacetate.—Two grams (1 mole) of β-galactose tetraacetate (m. p. 112°) was dissolved in 30 cc. of hot water and cooled to 0°. One gram (2 moles) of potassium acetate and 1.2 g. (1.5 moles) of phenylhydrazine hydrochloride was dissolved in 10 cc. of hot water. This solution was cooled to room temperature and added with stirring to the ice-cold tetraacetate solution. After about ten minutes the solution became cloudy and the hydrazone slowly separated

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[12] M. L. Wolfrom and A. Thompson, THIS JOURNAL, **53**, 622 (1931).

[13] E. Fischer and K. Hess, *Ber.*, **45**, 912 (1912).

[14] In de-alkalinated glass, as per A. Georg, *Helv. Chim. Acta*, **15**, 924 (1932), the melting point was 127–128°.

[15] *c* = g. subs. per 100 cc. soln.

[16] K. Freudenberg and M. Harder, *Ann.*, **433**, 230 (1923).

as an amorphous solid. After about twelve hours at 0° the reaction was complete. The solid first separating became a gummy, amber-colored material at room temperature. The mother liquor was separated from the solid by decantation. After washing with water several times by decantation the product was dried in a vacuum desiccator, whereby it became solid; yield, 2.3 g.; 91.6%. Despite numerous attempts using various solvents this material could not be induced to crystallize; $[\alpha]^{23}_{D}$ +5.0° (*c*, 4.0, pyridine).

Anal. Calcd. for $C_{12}H_{14}O_5N_2(COCH_3)_4$: acetyl, 36.40 cc. of 0.1 *N* NaOH. Found: acetyl, 36.52 cc. (by distillation at constant volume with 15% phosphoric acid).

Preparation of Aldehydo-galactose Phenylhydrazone Pentaacetate from the Phenylhydrazone of Galactopyranose Tetraacetate.—Galactose phenylhydrazone 2,3,4,6-tetraacetate (2.2 g.) was dissolved in 10 cc. of pyridine at 0°, and 8 cc. of acetic anhydride added. After two hours of standing at room temperature the solution was poured into 100 cc. of ice water with vigorous stirring and the mixture kept for one hour at 0°. The gummy mass that separated was washed several times with water by decantation and crystallized by the addition of a small amount of ethanol: yield 0.73 g., m. p. 133°. On one recrystallization from ethanol the melting point was 135–136° and the rotation was $[\alpha]^{26}_{D}$ +41.9° (*c*, 4.0, pyridine). Aldehydogalactose phenylhydrazone pentaacetate was first prepared by Hofmann[17] and its open chain structure determined by Wolfrom and Christman.[8]

Comparison of the above product with material prepared according to the previous methods left no doubt of their identity. The pyridine addition compound was prepared; m. p. 108–110°. A chloroform solution of the substance decomposed rapidly in the characteristic manner noted by Wolfrom and Christman.

Preparation of β-Galactose-*h*-Tetraacetate (III) from β-Galactose-*h*-pentaacetate.—With slight modifications, β-galactose-*h*-tetraacetate was prepared according to the procedure of Hudson and Johnson,[7] with much improved yields. Six grams of β-galactose-*h*-pentaacetate (m. p. 98°; $[\alpha]_{D}$ −42.2°, $CHCl_3$), prepared according to the procedure of Schlubach and Prochownick,[18] was transformed into the sirupy acetobromo compound and this changed to the tetraacetate according to the procedure of Fischer and Hess.[13] The thick sirup obtained after removal of the acetone crystallized on nucleation; yield, 3.0 g.; m. p. 72–74° (74–76° in dealkalinated glass); $[\alpha]^{27}_{D}$ −19.3° (*c*, 4.9, alcohol-free $CHCl_3$); $[\alpha]^{28}_{D}$ −17.0° (U. S. P. $CHCl_3$), both values changing slowly in the dextro direction. Hudson and Johnson recorded the melting point of 73° and $[\alpha]^{20}_{D}$ −17.8° (U. S. P. $CHCl_3$).

A rigorous proof of the ring structure of this tetraacetate has not as yet been made. The pyranose structure of the first tetraacetate may be considered as established because of its relation to β-methyl galactopyranoside through the acetobromo compound. As it is held generally at present that only the furanose and pyranose ring structures are readily formed, we will consider that the tetraacetate of the second ring form of galactose has the former ring structure (furanose).

Aldehydo-galactose Methylphenylhydrazone 2,3,5,6-Tetraacetate (IV).—β-Galactofuranose tetraacetate (0.5 g. or 1 mole) was dissolved in 15 cc. of warm water and the solution cooled to 0°. To this was added an ice-cold solution of 0.5 g. (3 moles) of α-methyl-α-phenylhydrazine in 10 cc. of water containing 2 cc. of glacial acetic acid and 0.5 g. (4 moles) of potassium acetate. In less than five minutes the solution became cloudy and the crystalline hydrazone began to separate. The reaction progressed much more rapidly than in the case of the pyranose tetraacetate, being practically complete in about forty-five minutes; yield 0.53 g., m. p. 102–103°. After two recrystallizations from ethyl acetate by the addition of petroleum ether this substance gave a melting point of 126°, unchanged after a third recrystallization; $[\alpha]^{23}_{D}$ +59.1° (*c*, 2.0, pyridine); $[\alpha]^{23}_{D}$ +59.5° (*c*, 2.0, $CHCl_3$), both values remaining constant.

Anal. Calcd. for $C_{13}H_{16}O_5N_2(COCH_3)_4$: N, 6.20; acetyl, 8.9 cc. of 0.1 *N* NaOH per 100 mg. Found: N, 6.37; acetyl, 9.1 cc. (Freudenberg).

Preparation of Aldehydo-galactose Methylphenylhydrazone Pentaacetate (V) from its 2,3,5,6-Tetraacetate.—This substance was further acetylated as described under the preparation of aldehydogalactose methylphenylhydrazone pentaacetate from its 2,3,4,6-tetraacetate. An amount of 0.52 g. of starting material yielded 0.46 g. of crude substance of m. p. 136–137°. After one recrystallization from ethanol a melting point of 138–139° was obtained, unchanged after a second recrystallization; $[\alpha]^{23}_{D}$ +25.1° (*c*, 3.7, pyridine). A mixture of this material with an authentic specimen of aldehydogalactose methylphenylhydrazone pentaacetate[8] melted at 138–139°.

Aldehydo-galactose Methylphenylhydrazone 2,3,5,6-Tetraacetate 4-*p*-Toluenesulfonate (VIII).—Aldehydo-galactose methylphenylhydrazone 2,3,5,6-tetraacetate (1.6 g.) was dissolved in 5 cc. of dry pyridine and 1.6 g. of *p*-toluenesulfonyl chloride added. After thorough mixing and cooling during the preliminary heat of solution of the *p*-toluenesulfonyl chloride, the solution was kept at a temperature of 40° for forty-eight hours. The solution was then cooled to room temperature, 3 cc. of water added with thorough shaking and the mixture then allowed to stand for thirty minutes. A large volume of carbon tetrachloride was added and this washed thrice with a 5% sulfuric acid solution, twice with 0.1 *N* sodium hydroxide solution and finally twice with water, all solutions being kept at 0°. The resulting carbon tetrachloride solution was dried over calcium chloride, treated with Norite and filtered. The solvent was then removed under a bell jar with a stream of dry air and the resulting sirup crystallized by the addition of a small amount of ethanol; yield 0.82 g., m. p. 102–103°. Further recrystallizations from ethanol did not alter the melting point or rotation; $[\alpha]^{30}_{D}$ +60.7° (*c*, 2.0, pyridine). The constants of this substance were thus quite different from those (m. p. 143–144°, $[\alpha]_{D}$ +21.5°, pyridine) of the corresponding derivative obtained from the galactopyranose tetraacetate. The *p*-toluenesulfonate group entered the fourth position with some difficulty, a 40° temperature being required. This is in accordance with the experience of Levene and Raymond[19]

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[17] A. Hofmann, *Ann.*, **366**, 277 (1909).

[18] H. H. Schlubach and Vilma Prochownick, *Ber.*, **63**, 2298 (1930).

[19] P. A. Levene and A. L. Raymond, *J. Biol. Chem.*, **97**, 763 (1932).

in reaction of the same reagent on a partially acylated methyl glucoside with the fourth position open.

Anal. Calcd. for $C_{20}H_{22}O_7N_2S(COCH_3)_4$: S, 5.26; acetyl, 6.60 cc. 0.1 *N* NaOH per 100 mg. Found: S, 5.14; acetyl, 6.73 cc. (Freudenberg).

Aldehydo-galactose Phenylhydrazone 2,3,5,6-Tetraacetate.—One gram (1 mole) of β-galactofuranose tetraacetate was treated with phenylhydrazine, etc., as described under the preparation of the phenylhydrazone of the β-galactopyranose tetraacetate. After about two minutes a precipitate began to separate, gummy at first but later crystallizing to a white solid. After standing for one hour the reaction was complete; yield, 1.2 g.; m. p. 128–129°. This product, upon recrystallizing twice from ether–petroleum ether, was obtained as a snow white, fluffy material; m. p. 139–140°. The melting point and rotation were unchanged on further recrystallization; $[\alpha]^{24}_{D}$ +80.1° (*c*, 4.0, pyridine); $[\alpha]^{26}_{D}$ +45.5° (*c*, 2.0, $CHCl_3$).

Anal. Calcd. for $C_{12}H_{14}O_5N_2(COCH_3)_4$: N, 6.39; acetyl, 9.1 cc. of 0.1 *N* NaOH per 100 mg. Found: N, 6.39; acetyl, 9.2 cc. (H_3PO_4 method).

Employment of the same conditions used by Hudson and Johnson[7] for preparing a hydrazone (m. p. 95°; $[\alpha]_D$ +15.5°, U. S. P. $CHCl_3$) of the same acetate from ethereal solution yielded the above compound possessing a higher rotation and melting point than the substance described by these workers.

Preparation of Aldehydo-galactose Phenylhydrazone Pentaacetate from the Phenylhydrazone of Galactofuranose Tetraacetate.—Galactose phenylhydrazone 2,3,5,6-tetraacetate (1.5 g. of m. p. 139–140°) was further acetylated as described under the corresponding pyranose compound, except that the acetylation mixture was allowed to stand for twenty hours at room temperature. The gum that first separated crystallized on standing at 0° for two hours; yield, 1.4 g.; m. p. 120°. After one recrystallization from ether by the addition of petroleum ether the melting point was 135–136° (mixed m. p. unchanged), $[\alpha]^{32}_{D}$ +41.8° (*c*, 4.0, pyridine). The substance was thus identified as aldehydo-galactose phenylhydrazone pentaacetate.

Determination of the Rate of Hydrazone Formation.—The following general procedure was rigorously observed in determining the rate of hydrazone formation for each of the three galactose acetates with both phenylhydrazine and α-methyl-α-phenylhydrazine. The acetates used were carefully purified. The galactose tetraacetate (0.2500 g.) was dissolved in 8 cc. of warm distilled water and cooled to 0° in an ice-bath. With the aldehydo-galactose pentaacetate aldehydrol an equivalent amount (0.2931 g.) was used. With constant stirring, 1 cc. of an ice-cold 1.274 molar potassium acetate aqueous solution was added from a pipet, followed by 3 cc. of an ice-cold 0.36 molar (Ph- or (Me)Ph-) hydrazine hydrochloride aqueous solution. This resulted in a 0.06 molar solution of the acetate containing 1.5 moles of (Ph- or (Me)Ph-) hydrazine hydrochloride and 1.75 moles of potassium acetate to each mole of the sugar acetate. The reaction was allowed to proceed for a given time, with stirring and maintenance of the ice-bath. At the end of the stated time, the precipitated hydrazone was immediately transferred quantitatively to a Gooch crucible of known weight. After washing with ice water several times the precipitate was dried to constant weight in a desiccator over calcium chloride. The weight of the hydrazone formed in a given time was thus directly ascertained. This procedure was repeated for each point determined.

The very pure phenylhydrazine hydrochloride used was prepared according to the directions of Ardagh, *et al.*[20] The α-methyl α-phenylhydrazine hydrochloride was prepared by passing dry hydrogen chloride into an ice-cold chloroform solution of the purified α-methyl α-phenylhydrazine until a heavy crystallization was obtained. The white crystals were filtered and washed with cold chloroform. The aqueous solutions of the hydrazines used were always freshly prepared. The data obtained are tabulated in Table I.

Summary

1. Further mild acetylation of the phenylhydrazones of the two different ring tetraacetates of galactose produces the same phenylhydrazone pentaacetate as is obtained directly from the open chain galactose pentaacetate and phenylhydrazine. The same has been shown for the methylphenylhydrazones.

2. The *p*-toluenesulfonates of the methylphenylhydrazones of the two ring tetraacetates of galactose were found to be different.

3. From 1 and 2 above it follows that the two ring tetraacetates of galactose react with these substituted hydrazines to form open chain hydrazones.

4. The reaction of buffered solutions of phenylhydrazine with the two different ring structures of galactose tetraacetate and with the open chain pentaacetate of galactose is in each case a reaction of the first order. The same is true with methylphenylhydrazine.

5. It is shown that the furanose ring structure of galactose opens at 0° approximately forty-five times more rapidly than the pyranose ring.

6. A number of new acetylated galactose hydrazone derivatives have been synthesized in pure crystalline form.

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[20] E. G. Ardagh, R. Kellam, F. C. Rutherford and H. T. Walstaff, THIS JOURNAL, 54, 721 (1932).