

The mutarotations in pyridine and pyridine-alcohol mixture described above and shown graphically in Figs. 1 and 2 indicate that at least two changes take place under the conditions of the experiments. These reactions are obviously more complicated than that of rhamnose phenylhydrazone in water since in this case a constant minimum rotation was reached. Whether the results obtained in pyridine and pyridine-alcohol mixture are due to rearrangements involving structures I, II and III shown above or similar ones, to shifts in the ring structure of the compounds, or to reactions of the hydrazones with the solvent cannot be stated at present. A curve similar in shape to those given here was obtained by Wolfrom³ in the work on the alcoholate of aldehydo-galactose pentaacetate.

Summary

A polarimetric study of rhamnose and mannose phenylhydrazones was made. These substances, previously reported to have constant rotations, were found to mutarotate in an unusual manner.

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[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

THE OPTICAL ROTATION OF THE ISOMERIC NITROPHENYLHYDRAZONES OF RHAMNOSE AND MANNOSE

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Since the structure of the sugars and of most sugar derivatives is so complex, a strictly regular variation in the values for the optical rotation of isomeric sugar hydrazones might not be expected. The older data on the nitrophenylhydrazones, obtained by Van Ekenstein and Blanksma,¹ do in fact show peculiar variations. However, the published values for these compounds and for the unsubstituted derivatives vary so markedly in their relationship to each other, with the relationship found among other types of optically active position isomers, that further investigation of the subject appeared to be worth while.

Frankland,² after examination of the results of many investigations on the effect of position isomerism on rotation, deduced a rule which may be stated as follows. When the rotations of a monosubstituted benzene derivative and the three disubstitution products are compared, the para derivative has the highest rotation, the order of magnitude of the other three being meta, monosubstituted derivative, ortho. It was also pointed out by Cohen³ that the change in rotation due to substitution in the ortho

¹ Van Ekenstein and Blanksma, *Rec. trav. chim.*, **22**, 434 (1903); **24**, 33 (1905).

² Frankland, *J. Chem. Soc.*, **101**, 666 (1912).

³ Cohen, *ibid.*, **97**, 1737 (1910); **99**, 1060 (1911).

position is greater than the change caused by substitution in either the meta or para position. A summary of work done in this field and references to the literature may be found in standard texts on stereochemistry.⁴

The aim of the present work was to study the rotations of some isomeric sugar nitrophenylhydrazones so as to see to what extent the results varied with the rules stated above, and to find out whether peculiarities in the optical rotations, such as were noted in the preceding paper, exist in the nitrophenylhydrazone group. The rhamnose series was chosen for this study because the rotations found in the literature¹ of the meta and para nitrophenylhydrazones bear the relation to each other of optical antipodes, the value for the meta compound being -21.4° and for the para isomer $+21.4^\circ$. The mannose compounds were chosen because of the similarity of mannose to rhamnose in stereochemical structure. The old values are shown in Table I. The solvent was alcohol-pyridine mixture except as noted. No account was taken of the possibility of mutarotation in the older work. This is of importance in considering the feasibility of applying rules such as those stated above to these isomers.

TABLE I
DATA ON PHENYLHYDRAZONES

Hydrazone	Melting point, °C.	$[\alpha]_D$
Rhamnose phenyl ^a	160	$+54^\circ$ (in water) ^b
Rhamnose <i>o</i> -nitrophenyl	162	-59°
Rhamnose <i>m</i> -nitrophenyl	156	-21.4°
Rhamnose <i>p</i> -nitrophenyl	186	$+21.4^\circ$ (Ref. 1)
Mannose phenyl	199-201	$+26.6^\circ$ (in pyridine) ^c
Mannose <i>o</i> -nitrophenyl	171	$+16^\circ$
Mannose <i>m</i> -nitrophenyl	162	$+10.7^\circ$
Mannose <i>p</i> -nitrophenyl	190	... (Ref. 1)

^a Tanret, *Bull. soc. chim.*, 27, 392 (1902); ^b Jacobi, *Ann.*, 272, 170 (1893); ^c Hofmann, *Ann.*, 366, 277 (1909).

The Preparation of the Ortho, Meta and Para Nitrophenylhydrazones of Rhamnose and Mannose.—Two grams of sugar and 2 g. of the hydrazine were dissolved in 30 cc. of 95% alcohol and warmed for one-half hour on a water-bath under a reflux condenser. In most of the experiments the hydrazone separated out of the hot solution during the heating period. The reaction flask was then placed in the refrigerator until crystallization appeared to be complete.

The *o*- and *m*-nitrophenylhydrazones of rhamnose and the meta isomer of mannose did not crystallize until the reaction liquor was concentrated to about 15 cc. The hydrazones were then filtered and recrystallized to

⁴ Stewart, "Stereochemistry," Longmans, Green and Co., New York, 1919, p. 78; Cohen, "Organic Chemistry," Part II, Longmans, Green and Co., New York, 1928, p. 248; Wittig, "Stereochemie," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1930, p. 112.

constant melting points. The yields and melting points of the pure hydrazones are shown in Table II.

TABLE II
YIELDS AND MELTING POINTS

Hydrazone	Yield, g.	Melting point, °C.
Rhamnose <i>o</i> -nitrophenyl	2.8	152-153
Rhamnose <i>m</i> -nitrophenyl	3.0	158-159
Rhamnose <i>p</i> -nitrophenyl	2.5	191-192
Mannose <i>o</i> -nitrophenyl	3.5	172-173
Mannose <i>m</i> -nitrophenyl	1.8	162-163
Mannose <i>p</i> -nitrophenyl	3.5	202-203

The optical behavior of the nitrophenylhydrazones was found to be quite different from that of the simple phenylhydrazones. As shown in Table III and Figs. 1 and 2, the three rhamnose isomers and the meta isomer of mannose mutarotate. These substances, however, come to equilibrium at a maximum or minimum point and do not pass through such a point as do the simple hydrazones of these sugars. The ortho and para derivatives of mannose were found to have a constant rotation. Rotations were taken in a 1:1 mixture of ethyl alcohol and pyridine. The initial values were obtained ten to fifteen minutes after solution was started.

TABLE III
THE MUTAROTATION OF RHAMNOSE *o*-, *m*- AND *p*-NITROPHENYLHYDRAZONE IN 1:1
PYRIDINE-ALCOHOL MIXTURE

Ortho		Meta		Para	
Time, hours	$[\alpha]_D$	Time, hours	$[\alpha]_D$	Time, hours	$[\alpha]_D$
10 min.	-37.5°	10 min.	-21.0	10 min.	-50.3
1.25	-36.0	30 min.	-21.0	1.25	-49.3
2.25	-35.0	2	-18.5	3.5	-48.0
5.25	-33.5	3	-17.5	6	-45.8
8	-33.5	4	-16.3	22.5	-27.5
24	-33.5	5	-15.0	25	-25.5
		21.5	- 2.3	28	-22.3
		23.5	- 0.8	30	-21.0
		26	+ 0.3	34	-19.0
		28.25	+ 1.8	47	-15.0
		46.5	+11.8	51	-14.0
		48.5	+13.5	54	-12.3
		51	+13.5	72	- 8.5
		53	+13.8	95	- 8.5
		69.5	+17.0	144	- 8.5
		73.5	+17.1		
		76	+16.9		
		95	+18.3		
		141.5	+18.3		

In the case of the simple phenylhydrazones⁵ the mutarotation curves indicated that two or more changes take place in pyridine or pyridine-

⁵ Butler and Cretcher, THIS JOURNAL, 53, 4358 (1931).

alcohol solution. The shape of the curves for the nitrated phenylhydrazones which mutarotated shows that the reaction of these substances under

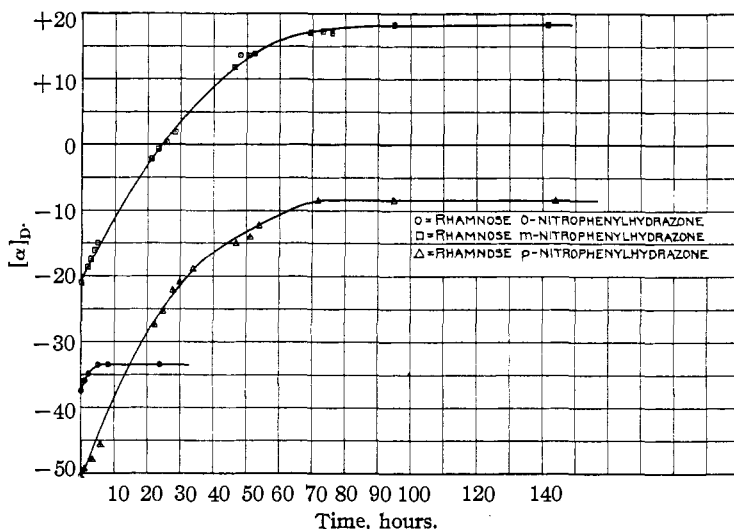


Fig. 1.

similar conditions is of a simpler type since they come to equilibrium at a maximum or minimum point and do not pass through it. No speculations

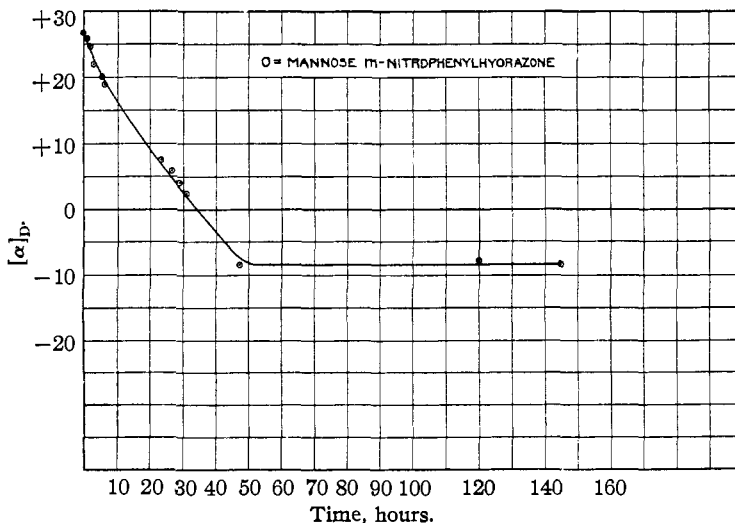


Fig. 2.

regarding the nature of these changes can be made until more work is done in the field. The chemistry of the sugar hydrazones is receiving further attention in this Laboratory.

TABLE IV

THE MUTAROTATION OF MANNOSE *o*-, *m*-, AND *p*-NITROPHENYLHYDRAZONE IN 1:1 PYRIDINE-ALCOHOL MIXTURE

Ortho		Meta			
Time	$[\alpha]_D$	Time, hours	$[\alpha]_D$	Time, hours	$[\alpha]_D$
15 min.	+52.0	10 min.	+26.5	26.5	+6.0
30 hours	+52.0 ^a	1	+26.0	29	+4.0
		2	+24.5	30.75	+2.5
		3	+22.0	47.5	-8.5
Para		5.5	+20.0	120	-7.8
Time	$[\alpha]_D$	6.5	+19.0	144	-8.3
15 min.	+56°	23.5	+7.5		
4 hours	+56° ^{as}				

^a Values obtained at intervals during the thirty-hour period (*o*-nitrophenylhydrazone) and the four-hour period (*p*-nitrophenylhydrazone) did not change from the initial rotations.

The results reported above show clearly the futility of applying rules which have been found to hold for other classes of optically active position isomers, to position isomers in the sugar hydrazone group. This is not surprising in view of the complexity of the reaction between sugars and hydrazines.

Summary

The optical rotations of the three isomeric nitrophenylhydrazones of rhamnose and mannose herein recorded do not agree with those which might be expected on the basis of rules found to hold for other classes of optically active position isomers, but the variations appear less erratic than the variations in the rotations previously recorded.

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ELECTRON SHARING ABILITY OF ORGANIC RADICALS. NITROGEN HETEROCYCLICS

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In a preceding paper by Hixon and Johns¹ it was pointed out that if the electronic concepts of valence are at all correct, there must be a correlation between the affinities of different polar groups attached to identical organic radicals. In support of this generalization a mathematical relationship was demonstrated between the dissociation constants of the five series of compounds, R(NH₂), R(COOH), R(CH₂COOH), R(CH₂CH₂COOH) and R(OH), all data in Landolt-Börnstein being included which permitted at least one comparison of any radical. In a later paper by Johns and Hixon²

¹ Hixon and Johns, *THIS JOURNAL*, **49**, 1786 (1927).

² Johns and Hixon, *J. Phys. Chem.*, **34**, 2226 (1930).