was heated finally at 55° for five hours, cooled and filtered. Recrystallization from ethanol and ethyl acetate resulted in 1.21 g. of orange needles, a yield of 77%. On slow heating these needles sinter at 220°, then show no further change until they melt at 247–248° (corr.). When the crystals are placed in a bath at a temperature slightly below 220°, they melt at 220–221° (corr.), resolidify and melt again at 247–248° (corr.). The azo compound is soluble in concd. hydrochloric acid to form a deep red solution and in alkali to yield a bright orange solution. Also, it is slightly soluble in ethanol and in ethyl acetate, but insoluble in water.

Anal. Calcd. for $C_{21}H_{19}N_5O_2$: C, 67.55; H, 5.13; N, 18.76. Found: C, 67.48; H, 5.33; N, 18.80.

Preparation of 5-Dimethylaniline-*m*-azophenyl-5-ethylhydantoin.—One gram (0.004 mole) of 5-*m*-aminophenyl-5-ethylhydantoin was diazotized as before, with addition to the solution of diazonium salt derived from 0.56 g. (0.46 mole) of dimethylaniline dissolved in 1 cc. of concd. hydrochloric acid and 20 cc. of water. An orange precipitate formed on the addition of 10 g. of hydrated sodium acetate. The mixture was allowed to warm to room temperature, was filtered and the solid crystallized from ethanol and then from ethyl acetate. One and eleven-hundredths grams of light orange needles melting at 233–235° was obtained, or 75% of the theoretical yield. The azo dye is soluble in dilute hydrochloric acid, somewhat less soluble in dilute alkali, slightly soluble in ethanol and ethyl acetate and insoluble in water.

Anal. Calcd. for $C_{19}H_{21}N_5O_2$: C, 64.93; H, 6.02; N, 19.93. Found: C, 64.94; H, 5.92; N, 19.89.

Preparation of 5-[2-Naphthol-6,8-disulfonic acid-*m*-azophenyl]-5-ethylhydantoin.—Three grams (0.013 mole) of 5-*m*-aminophenyl-5-ethylhydantoin was diazotized using 1 g. of sodium nitrite and to the solution was added 7 g. of G Salt dissolved in 50 cc. of water. No appreciable color change was noted until the solution was made alkaline with sodium hydroxide, after which it gradually became deep red in color. The reaction mixture was allowed to stand for twenty-four hours at 0°, when an unsuccessful attempt was made to salt-out the sodium salt through addition of sodium chloride. Six grams of barium chloride dissolved in 20 cc. of water was added and the solution allowed to stand for twenty-four hours, during which time orange material separated from solution. The solid was filtered and recrystallized from water, 4.15 g. of product being obtained. Analysis of this material, dried at room temperature, indicated it to be the octahydrated barium salt; on this basis the yield represented 40% of the theoretical.

Anal. Calcd. for $C_{21}H_{16}N_4O_9S_2Ba.8H_2O$: Ba, 16.88; S, 7.88; N, 6.89. Found: Ba, 16.91; S, 8.13; N, 7.76.

The free sulfonic acid, obtained by decomposing the barium salt with the calculated amount of sulfuric acid, is very soluble in water; the aqueous solution is colored deep red by alkali and orange by acid. Because of its extremely hygroscopic nature it was not possible to prepare the disulfonic acid in a state of analytical purity.

Summary

Colored meta-azo derivatives of nirvanol have been synthesized.

AUSTIN, TEXAS RECEIVED AUGUST 5, 1938

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Mutarotation of *d*-Galactose[1]

BY B. CLIFFORD HENDRICKS AND ROBERT E. RUNDLE

The mutarotation of *d*-galactose has received more attention than other sugars in recent years[2–6] due to its reaction being other than the traditional first order type.

Two groups[4,6] of investigators have developed independently what might be termed a three-sugar postulate. In the language of one group[7] "our method of analysis enables us to calculate: (1) the proportions of these sugars in the final equilibrium mixture; (2) the velocity coefficients of the four unimolecular actions by which they are converted into one another; and (3) the approximate rotatory power of the unknown intermediate sugar." The constants thus deduced by these two groups, however, do not agree. Riiber and co-workers made their deductions from dilatometer studies of *d*-galactose mutarotations while Lowry and his assistants derived theirs from polarimetric data.

One of the authors[8] has shown that the constants reported by Lowry can be used to compute the rotations of "thermal-mutarotations" and of predetermined proportions of α-*d*-galactose and β-*d*-galactose mixtures. The computed data are shown to agree with the observed values made by Isbell and Pigman[9] in a very satisfactory way while calculations made for the same conditions

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(1) Presented at the Joint Program of the Division of Organic Chemistry and the Division of Sugar Chemistry and Technology at the ninety-sixth meeting of The American Chemical Society, Milwaukee, Wisconsin, September 8, 1938.

(2) Lowry, *J. Chem. Soc.*, **85**, 1570 (1904).

(3) Hudson and Yanovsky, THIS JOURNAL, **39**, 1013 (1917).

(4) Riiber and Minsaas, *Ber.*, **59**, 2266 (1926).

(5) Worley and Andrews, *J. Phys. Chem.*, **32**, 307 (1928).

(6) Smith and Lowry, *J. Chem. Soc.*, 666 (1928).

(7) Lowry and Smith, *J. Phys. Chem.*, **33**, 7–21 (1929).

(8) Rundle, Thesis, University of Nebraska, 1938.

(9) Isbell and Pigman, *Bur. Standards J. Research*, **18**, 141 (1937).

using the Riiber constants do not at all follow the observed data. Neither of the two groups referred to presumes to state the nature of the third or "labile" sugar of the system.

A recent paper[10] proposes a pyranose–furanose interconversion as a part of the mechanism of the complex mutarotation of sugars. If such a transformation were essential in the rotations of a greater complexity than first order changes it would follow that tetramethyl hexoses would never show other than first order mutarotation. This paper reports a study of the mutarotation of tetramethyl α-*d*-galactopyranose.

The tetramethyl α-*d*-galactopyranose was prepared as indicated in another communication.[11] The constants of the sugar were: initial rotation $[\alpha]^{25}\text{D}$ 146.0, $[\alpha]^{0}\text{D}$ 150.5; equilibrium rotation $[\alpha]^{25}\text{D}$ 112.1°, $[\alpha]\text{D}$ 119.9°; and melting point 70.5–71.5°.

The polarimetric measurements were made with a Goerz instrument, which could be read to 0.01°, using a two-decimeter glass metal-jacketed tube. The light was from a General Electric sodium arc lamp. The temperature was controlled by pumping water from a bath maintained to a ±0.1° constancy at the higher temperature. The lower temperature was controlled by a water–alcohol mixture circulated through the tube jacket and a salt–ice bath with a temperature constancy of ±0.2°. The usual method of preparing the sugar solutions was used, care being exercised that volumetric flasks, water and tubes were at correct temperature during the time for dissolving the sugar. The "thermal mutarotation" procedure of Isbell and Pigman[12] was modified. The equilibrium solution was poured into a pre-cooled flask, placed in an ice-bath and shaken until the solution reached 0.0°, after which it was placed in a cold tube. This operation never took more than five minutes.

The authors consider the rotation velocity constant, $k_1 + k_2$, calculated as indicated elsewhere,[9] a means of recognizing departure from the first order type of mutarotation, hence its inclusion in the tables which follow.

Results listed in Tables I, II and III are representative samples of several runs for each type of experiment. Data from other experiments were consistent with those given above. The deviations of these values from the first order rate are smaller than for the unmethylated α-*d*-galactose and for the 25° temperature the deviations practically disappear. The suggested deviations of the rotation–time observations at 0.0° are supported by the "thermal mutarotation" measurements, though, unfortunately, in that study the change of rotation is so small that the experimental error is magnified in the calculated velocity constants. Even so it is relatively less

TABLE I

MUTAROTATION OF TETRAMETHYL α-*d*-GALACTOSE AT 25°

0.8033 g. of sugar in 25 ml. of water

Time, min. and sec.	Rotation obsd.	$(k_1 + k_2) \times 10^4$ calcd.
6′15″	11.28	
7′15″	11.23	
8′15″	11.16	138
9′10″	11.11	125
10′15″	11.06	115
12′30″	10.93	119
14′0″	10.86	117
17′20″	10.70	117
18′50″	10.64	116
22′55″	10.46	117
25′0″	10.39	121
32′15″	10.13	117
39′55″	9.91	120
49′20″	9.70	120
57′30″	9.56	119
78′30″	9.26	126
91′15″	9.20	125
97′30″	9.19	126
117′5″	9.09	126
141′0″	9.04	Av. 121
180′0″	9.01	
∞	9.00	

TABLE II

MUTAROTATION OF TETRAMETHYL α-*d*-GALACTOSE AT 0.0°

1.0007 g. of sugar in 25 ml. of water

Time, min. and sec.	Rotation obsd.	$(k_1 + k_2) \times 10^6$ calcd.
8′15″	12.03	
9′35″	12.01	
22′40″	11.93	1114
40′10″	11.84	1043
41′30″	11.80	1239
56′50″	11.73	1133
78′10″	11.64	1057
112′10″	11.56	875
162′30″	11.35	909
212′0″	11.13	972
244′0″	11.06	926
357′0″	10.82	850
521′0″	10.37	961
581′0″	10.32	917
1426′0″	9.74	867
∞	9.60	

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[10] Isbell and Pigman, *Bur. Standards J. Research*, **20**, 775 (1938).

[11] Hendricks and Rundle, THIS JOURNAL, **60**, 2563 (1938).

[12] Isbell and Pigman, *Bur. Standards J. Research*, **16**, 553 (1936).

TABLE III

THERMAL MUTAROTATION OF TETRAMETHYL α-d-GALACTOSE FROM 25 TO 0.0°

0.7514 g. of sugar in 20 ml. of water

Time, min. and sec.	Rotation obsd.	$(k_1 + k_2) \times 10^6$ calcd.
9′15″	8.73	
10′15″	8.74	
37′40″	8.78	2040
74′0″	8.81	1622
157′0″	8.88	1631
397′0″	8.92	866
638′0″	8.97	826
1406′0″	9.05	872
1408′0″	9.04	745
∞	9.07	

than the difference between the velocity constants of the first and second parts of the reaction and the consistent nature of this difference of the various determinations is such that the authors consider it a real difference.

The tetramethyl α-d-galactopyranose cannot have a furanose ring since the fourth carbon is methylated. In consequence if the differences in the mutarotation velocity constants of Tables II and III are real, then the complex mutarotation of tetramethyl α-d-galactose cannot require a galactofuranose as one of the sugars in the interconversion. This does not imply, however, that galactofuranose may not be involved in the complex mutarotation of unmethylated d-galactose.[13]

Summary

The mutarotations of solutions of tetramethyl α-d-galactopyranose have been studied for 25 and 0°. Velocity constants for the first part of the mutarotation at 0.0° show slightly but consistently higher values than for changes nearer the equilibrium.

"Thermal mutarotation" for tetramethyl α-d-galactopyranose for a 25 to 0° change has been investigated. The rotation constant, $k_1 + k_2$, is consistently larger at the first than at the last of the change by an amount which is considered in excess of the experimental error.

It is suggested that the assumed pyranose–furanose interconversion as a part of the mechanism of complex mutarotation can hardly be perfectly general.

[13] Diacetone mannose has been reported by Irvine and Skinner [*J. Chem. Soc.*, 1095 (1926)] as having a complex mutarotation. The authors repeated their work at 17° and found agreement with that report. The changes in specific rotation go from 9 to −3° back to 1°. This change hardly could be attributed to a pyranose–furanose interconversion.

LINCOLN, NEBRASKA RECEIVED SEPTEMBER 6, 1938

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

Studies of Cellulose Hydrolysis by Means of Ethyl Mercaptan. III[1]

BY M. L. WOLFROM AND JOHN C. SOWDEN[2]

Previous publications[3] from this Laboratory have described a study of the course of hydrolysis of the cellulose molecule. The method consisted of allowing a solution of high viscosity cotton linters in fuming hydrochloric acid to hydrolyze at 16° and following the course of hydrolysis by mercaptalation with ethyl mercaptan at various time intervals. Sulfur analyses on the resulting mercaptalated hydrolyzed celluloses then gave an estimate of their average molecular size. Cuprammonium viscosity measurements on the non-mercaptalated hydrolyzed products, isolated after corresponding periods of hydrolysis in the fuming hydrochloric acid, were also employed to estimate the average chain lengths by application of the formula of Kraemer and Lansing.[4] A comparison of the average molecular sizes as determined by the two methods was thus available.

The studies at 16° indicated that the sulfur analytical method gave appreciably lower values for the chain lengths than those calculated from cuprammonium viscosity data, for hydrolyzed products of above 100 glucose units in size. Thus, it is of interest to study further the earlier stages of the hydrolysis, in order to determine the nature of this difference in chain lengths as calculated by the two methods for products having degrees of polymerization greater than 100 glucose units.

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[1] Presented before the Division of Organic Chemistry at the 96th meeting of The American Chemical Society, Milwaukee, Wisconsin, September 8, 1938.

[2] Du Pont Cellulose Research Fellow.

[3] M. L. Wolfrom and Louis W. Georges, THIS JOURNAL, **59**, 282 (1937); M. L. Wolfrom, Louis W. Georges and John C. Sowden, *ibid.*, **60**, 1026 (1938).

[4] E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 164 (1935).