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The Rotation of Polyols in Ammonium Molybdate Solutions

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In 1891 Gernez discovered that the small rotation of D-mannitol in water is augmented greatly by the addition of an alkali molybdate to the solution. Studies of the enhanced rotations of a number of representative optically active polyols in 5% ammonium molybdate and particularly in acidified molybdate solutions have now demonstrated that such measurements can be of great usefulness, not only in deciding whether a new polyol is an optically active or *meso* form, but also in characterizing and identifying polyols, and in testing the purity of polyols, particularly for biochemical studies.

The optically active polyhydric alcohols, or polyols, have relatively low rotations in water and their $[\alpha]_D$ values, with few exceptions, are less than 5° in magnitude. In order to enhance these rotations, the better to characterize the polyols, a saturated solution of borax is often used as the solvent; the resulting values are usually larger, but may not be sufficient even then to prove conclusively that a substance is optically active and not a *meso* form. Thus, D-gala-L-*gala*-octitol has a specific rotation that is not detectable in water, and is only −0.5° in saturated borax solution.[1]

Gernez,[2] in 1891, incidental to a study of the rotations of tartaric and malic acids, in various molybdate and tungstate solutions, found that the rotation of D-mannitol was considerably exalted by the addition of an alkali molybdate; the specific rotation, however, varied as the relative proportions of the two components were changed. Thirty years later Georges Tanret[3] demonstrated that the maximal specific rotation was reached when his test solution contained two grams of ammonium molybdate for each gram of mannitol. Upon standing, such a solution deposited crystals of a complex salt whose analysis corresponded to the composition $[(13MoO_3{\cdot}7NH_3{\cdot}7C_6H_{14}O_6) - 6H_2O]{\cdot}3H_2O$. Subsequent studies by Honnelaitre[4] led to a simpler formulation of the complex as $2MoO_3{\cdot}C_6H_{14}O_6{\cdot}NH_3$. Honnelaitre observed also that the rotation varied with the *p*H of the solution and Frèrejacque,[5a] by dissolving mannitol in ammonium molybdate containing an excess of sulfuric acid, found that in the acidified molybdate solution the specific rotation was constant when the molar ratio of MoO_3 to $C_6H_{14}O_6$ was varied between 2.8/1 and 12.8/1.

In the accompanying tables are listed the specific rotations that we have measured on a number of representative polyols both in ammonium molybdate and in acidified ammonium molybdate solutions. It will be seen that the rotations in the first solvent change markedly with increasing concentration of polyol, whereas the rotations in the acidified mixture are nearly constant. In order to establish some standard system of measuring these rotations and to catalog the specific rotations thus observed for the benefit of other investigators, we propose to make all future measurements at 20° with sodium light, first at a level of 0.1 g. of polyol in 25 ml. of 5% aqueous ammonium molybdate tetrahydrate, and second after diluting 20 ml. of this solution with 5 ml. of *N* sulfuric acid. Details are given in the experimental section. The specific rotations obtained from the first solution may show some variation from one worker to another, yet when taken in the manner described should furnish a fairly well reproducible value. The specific rotations obtained from the second solution, with all but one of the substances so far studied, are considerably larger in magnitude and should serve as particularly valuable optical constants for the polyols. For many purposes it might be simpler to omit the first measurement and to observe the rotation only in the acidified molybdate solution; here the amount of polyol is not critical, as the tables show, and the use of 20 ml. of 5% ammonium molybdate diluted to 25 ml. with *N* sulfuric acid furnishes enough MoO_3 to give a molar ratio of 8.6/1 with 0.1 g. of a pentitol and 12/1 with 0.1 g. of a heptitol. In the two cases examined (see Tables I and IV) there was no significant change of rotation with ordinary changes of temperature. Readings with a polarimeter and with a quartz-wedge saccharimeter were found to result in identical specific rotations. Also, the specific rotation was found to be constant when the acid strength was varied (see Table II).

The final table (VI) summarizes the best values recorded for eight polyols; additional compounds will be reported subsequently.

When an optically active polyol has a very small rotation its enantiomorph will also have the same small rotation of opposite sign, and a distinction between the enantiomorphs will be greatly aided if the rotations can be magnified in some way. One example already reported from this Laboratory[6] is that of β-sedoheptitol, whose optical activity was early in doubt. The recent $[\alpha]^{20}_D$ measurements of −0.75° in water and +4.3° in saturated borax solution were increased to +49.6° in ammonium molybdate solution (*c*, 0.42); the enantiomorphous D-gluco-L-*talo*-heptitol showed values of +0.95° in water, −4.6° in saturated borax solution, and −49.7° in molybdate solution (*c*, 0.42).

Thus the observation of rotations of polyols in ammonium molybdate and particularly in acidified molybdate solutions can be very useful in determining if the substance is optically active, in characterizing and identifying polyols, and in testing the purity of polyols, particularly for biochemical studies. Among the other substances besides

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[1] W. D. Maclay, R. M. Hann and C. S. Hudson, THIS JOURNAL, **60**, 1035 (1938).

[2] D. Gernez, *Compt. rend.*, **112**, 1360 (1891).

[3] G. Tanret, *ibid.*, **172**, 1500 (1921).

[4] A. Honnelaitre, *Ann. chim.*, [10] **3**, 5 (1925).

[5] M. Frèrejacque, (a) *Compt. rend.*, **200**, 1410 (1935); (b) *ibid.*, **208**, 1123 (1939).

[6] A. T. Merrill, W. T. Haskins, R. M. Hann and C. S. Hudson, THIS JOURNAL, **69**, 70 (1947).

TABLE I

L-ARABITOL

c, (g./100 ml.)	$[\alpha]^{20}\mathrm{D}$ in 5% molybdate	c, (g./100 ml.)	$[\alpha]^{20}\mathrm{D}$ in acidified molybdate
0.20	$-29.0 \pm 2.2^{\circ a}$	0.16	$-130.4 \pm 2.7^{\circ a}$
.40	32.1 ± 1.1	.32	130.0 ± 1.4^{b}
.80	34.7 ± 0.5	.64	127.9 ± 0.7
1.20	40.4 ± 0.4	.96	128.3 ± 0.5
1.60	47.6 ± 0.3	1.28	126.4 ± 0.3^{c}
2.00	53.7 ± 0.2	1.60	125.1 ± 0.3
	$[\alpha]^{27}\mathrm{D}$		$[\alpha]^{27}\mathrm{D}$
0.40	34.4 ± 1.1	0.32	130.9 ± 1.4

[a] The statements of probable accuracy refer to the accuracy of the polarimetric readings. They apply also to the other tables but have been omitted for the sake of simplicity. [b] The $[\alpha]^{19}\mathrm{D}$ values of −130° and +131° for L- and D-arabitol, respectively, in the presence of excess molybdic acid, have been reported by Frèrejacque (ref. 5b). [c] The ratio of MoO_3 to $C_5H_{12}O_5$ has dropped at this point to 2.7/1, which apparently is not enough to maintain the constancy of rotation.

TABLE II

D-MANNITOL

c, (g./100 ml.)	$[\alpha]^{20}\mathrm{D}$ in 5% molybdate	c, (g./100 ml.)	$[\alpha]^{20}\mathrm{D}$ in acidified molybdate
0.20	+11.7°	0.16	+140.1°
.40	14.9^{a}	.32	$140.3^{a,b}$
.80	17.0	.64	141.2
1.20	22.8	.96	140.9
1.60	29.4	1.28	139.8
2.00	36.9	1.60	139.2

[a] The corresponding values for a sample of L-mannitol were found to be −14.9° and −140.4°. [b] The $[\alpha]^{20}\mathrm{D}$ values obtained with 0.1 g. of D-mannitol and 20 ml. of 5% molybdate acidified in one case with 4 ml. of *N* sulfuric acid and in the other with 3 ml. of 2 *N* sulfuric acid, in a total volume of 25 ml., were +140.9° and +140.2°, respectively.

TABLE III

6-DESOXY-D-ALTRITOL[a]

c, (g./100 ml.)	$[\alpha]^{20}\mathrm{D}$ in 5% molybdate	c, (g./100 ml.)	$[\alpha]^{20}\mathrm{D}$ in acidified molybdate
0.40	+113.5°	0.32	−43.2°
.80	110.7	.64	42.7
1.20	105.7	.96	41.7
1.60	93.7	1.28	41.9
2.00	78.6	1.60	41.1

[a] N. K. Richtmyer, L. C. Stewart and C. S. Hudson, THIS JOURNAL, **72**, 4934 (1950).

TABLE IV

L-FUCITOL (=6-DESOXY-L-GALACTITOL)

c, (g./100 ml.)	$[\alpha]^{20}\mathrm{D}$ in 5% molybdate	c, (g./100 ml.)	$[\alpha]^{20}\mathrm{D}$ in acidified molybdate
0.20	+44.3°	0.16	+198.8°
.40	47.4^{a}	.32	197.7^{a}
.80	51.9	.64	196.2
1.20	59.1	.96	196.7
1.60	68.2	1.28	197.3
2.00	77.3	1.60	196.2
	$[\alpha]^{26}\mathrm{D}$		$[\alpha]^{26}\mathrm{D}$
0.40	44.6	0.32	195.0

[a] A sample of the antipodal D-fucitol (=6-desoxy-D-galactitol) recently prepared in this Laboratory showed $[\alpha]^{20}\mathrm{D}$ values of −47.4° and −195° (*c*, 0.40) in these solvents, respectively.

TABLE V

PERSEITOL (=D-MANNO-D-*gala*-HEPTITOL)

c, (g./100 ml.)	$[\alpha]^{20}\mathrm{D}$ in 5% molybdate	c, (g./100 ml.)	$[\alpha]^{20}\mathrm{D}$ in acidified molybdate
0.20	+23.4°	0.16	+147.1°
.40	23.6	.32	146.3
.80	24.7	.64	147.4
1.20	26.0	.96	145.9
1.60	29.6	1.28	146.1
2.00	36.8	1.60	145.8

TABLE VI

SUMMARY OF BEST VALUES FOR ROTATIONS OF POLYOLS

Compound	$[\alpha]^{20}\mathrm{D}$ in 5% molybdate (*c*, 0.40)	$[\alpha]^{20}\mathrm{D}$ in excess acidified molybdate (*c*, *ca.* 0.4)
L-Arabitol	−32°	−130°
D-Mannitol[a,b]	+16	+141
D-Rhamnitol[a]	+23	+151
L-Fucitol	+47	+196
6-Desoxy-D-altritol	+113	− 43
Perseitol	+24	+146
Volemitol[c]	+55	+109
7-Desoxy-L-gala-D-*manno*-heptitol[d]	+51	+201

[a] *Cf.* N. K. Richtmyer and C. S. Hudson, THIS JOURNAL, **72**, 3880 (1950). [b] *Cf.* ref. 6. [c] Synonym, D-manno-D-*talo*-heptitol; *cf.* ref. 6. [d] *Cf.* E. Zissis, N. K. Richtmyer and C. S. Hudson, THIS JOURNAL, **72**, 3882 (1950).

borax, boric acid and the molybdates that have been reported to augment the rotation of D-mannitol may be mentioned certain oxides and salts of antimony, arsenic, beryllium, bismuth, copper, tungsten and uranium.[7] None of these seems to have been studied thoroughly or to offer any advantage over the colorless solutions prepared from the readily available commercial ammonium molybdate tetrahydrate.

Experimental

Ammonium Paramolybdate Solution.—The stock solution was prepared by dissolving 25.0 g. of the commercial hydrated salt, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Mallinckrodt analytical grade), in distilled water and diluting to 500 ml. The filtered solution was kept in the polarimeter room at 20 ± 1°. The small amounts of crystalline material that separated on standing were removed by filtration when necessary.

Rotation Measurements.—A sample of polyol weighing 0.100 ± 0.001 g. in a 25-ml. volumetric flask was filled to the mark at 20° with the stock ammonium molybdate solution and the rotation observed in a 4-dm. tube; both a polarimeter and a quartz-wedge saccharimeter gave identical $[\alpha]^{20}\mathrm{D}$ values. Then 20 ml. of the solution of polyol in ammonium molybdate was pipetted into a second 25-ml. flask, the flask was filled to the mark with *N* sulfuric acid, and the rotation of this solution was measured. The acidified molybdate solution was washed from the flask and the polarimeter tube fairly soon afterwards to avoid the deposition of crystalline material in these containers.

The recovery of a rare polyol from the molybdate solutions may be accomplished by removing the inorganic material by passage through a suitable pair of ion-exchange columns and concentrating the deionized solution. In this manner pure 6-desoxy-D-altritol was recovered from the experiments recorded in Table III in nearly quantitative yield.

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[7] For some references, see under "D-mannitol" in "Beilsteins Handbuch der organischen Chemie," Fourth Edition, Volume 1.