hours. It partially melted, turned dark colored and hydrogen sulfide was evolved copiously. In order to separate any thiohydantoin the reaction-product was triturated with water, as described in the previous experiment, and the insoluble thiohydantoin separated by filtration. This was then purified by digestion with bone-coal and crystallization from boiling water. It separated in prismatic crystals, melting at 225–227°. The yield was about 0.6–0.7 gram.

We obtained no evidence of the formation of 2-thiohydantoin when ethyl thiohydantoate was warmed with dilute hydrochloric acid. Hydrogen sulfide was evolved and the only crystallin substances identified were ammonium chloride and the hydrochloric acid salt of glycocoll.

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MANNITE ESTERS OF SULFURIC ACID.

BY W. R. BLOOR.

Received March 31, 1913.

In the course of the preparation of some esters of mannite with the higher fatty acids for a biochemical investigation,[1] it was found that the yield was unsatisfactory—less than 50% of the theoretical. The method of synthesis employed involved the heating of the two substances in solution in concentrated sulfuric acid to a temperature of 70° for four hours and it was suspected that the reason for the low yield was the destructive action of the strong acid on the mannite at this temperature. Accordingly, the synthesis was carried out at a lower temperature (38°–40°) with the result of a much improved yield. The esters obtained, however, were not the same as at the higher temperature. At 70° the main product was the iso-mannid ester, with small amounts of the mannitan ester, while at 40° only the mannitan ester was recovered. (The opinion was expressed at the time[2] that the reason for the different compound may have been the different method of separation. The mannid compound was extracted directly from the sulfuric acid with ether, while the mannitan compound was separated by pouring the sulfuric acid digestion mixture into excess of water and salting out. The opportunities for hydration were much greater in the second case and the mannitan ester was probably formed at the expense of the mannid ester.) In order to find an explanation for these phenomena the following study of the action of concentrated sulfuric acid on mannite was undertaken.

The literature on the subject[3] states merely that the action of con-

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[1] Bloor, *Biol. Chem.*, 2, 427 (1910); 11, 141, 421 (1912).

[2] *Loc. cit.*

[3] Favre, *Ann. chim. phys.*, 11, 77; Knop and Schnedermann, *Ann.*, 51, 132.

centrated sulfuric acid on mannite is to form the mannite disulfuric acid ester.

The work is divided into two parts—first, a series of determinations to find out the amount of sulfuric acid held in combination by the mannite from time to time at different temperatures, and second, a separation of the mannite-sulfuric acid esters as their barium salts.

In the first part of the work it was found that when mannite is dissolved in concentrated sulfuric acid at temperatures of from 39° to 64° it combines with the acid in the proportion of one molecule of mannite to two molecules of sulfuric acid. The results also showed that at the higher temperatures another reaction took place, the result of which was a progressive decrease in the amount of sulfuric acid held in combination by the mannite. It is probable that the concentrated sulfuric acid acts on the polyatomic alcohol, mannite, at the higher temperatures in a way analogous to its action on simple alcohols like ethyl alcohol, *i. e.*, as a dehydrating agent with the production of substances like ether, ethylene and other anhydride combinations which have less power of combining with acid groups than the alcohol itself. In this fact probably lies the reason for the lower yield of mannite-fatty acid esters when the synthesis is carried out at the higher temperature.

In the second division of the paper the crystallizable barium salts of the compounds resulting from the action of concentrated sulfuric acid on mannite at different temperatures were separated out. Three well defined salts were obtained. The analyses show that they are compounds not of mannite but of anhydrides of mannite, two of them probably unsaturated. The compounds are as follows:

Compound I:

Analyses for the formula $C_6H_6O(SO_4)_2Ba$. Levorotatory.

Specific rotation—17.1°. It is the main compound formed by the action of sulfuric acid on mannite in the cold.

Compound II:

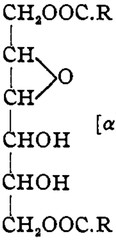
Analyses for the same formula as above—$C_6H_6O(SO_4)_2Ba$, but it is dextrorotatory with a specific rotation +9.1°. It is formed at all temperatures investigated.

Compound III:

The analytical results agree with the formula $C_6H_{12}O_4(SO_4)_2Ba$, or $C_6H_8O_2(SO_4)_2Ba.2H_2O$. Preference is given to the latter, since the optical properties of this compound (specific rotation +68.7°) are similar to those of the mannid esters of the fatty acids to which the corresponding formula has already been assigned (see below). This compound is formed only at the higher temperatures.

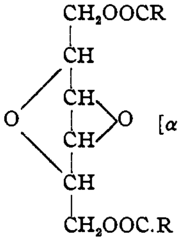
All three compounds are very sensitive to dry heat, decomposing quickly at the temperature of the boiling water bath. Dilute acids hydrolyze them slowly with the production of one molecule of barium sulfate and one molecule of sulfuric acid for each molecule of the salt. None of the compounds reduce Fehling's solution.

The types of mannite compounds which have previously been prepared[1] and to which formulae have been tentatively assigned are as follows:



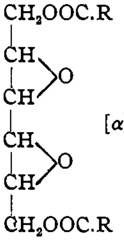
$[\alpha]^{50}_D = +8.0°$.[2]

Mannitan ester



$[\alpha]^{20}_D = +64.90°$.[2]

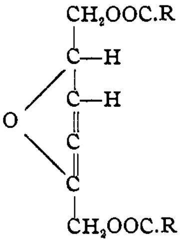
Mannid ester



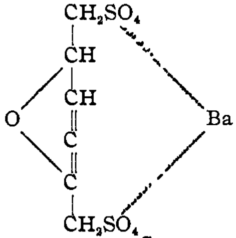
$[\alpha]^{20}_D = +93.6°$.[2]

Iso-mannid ester

They may all be regarded as derivatives by hydration of the hypothetical compound

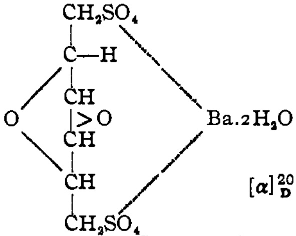


The compounds described in this paper may be represented as follows:



$[\alpha]^{20}_D = +9.1°$.

Compound II.



$[\alpha]^{20}_D = +68.6°$

Compound III.

Compound I, $[\alpha]^{22}_D = -17.10$, is isomeric with Compound II.

The above assignment of formulae is freely acknowledged to be quite arbitrary and is subject to change as new facts become available.

Experimental.

PART I.

The Amount of Sulfuric Acid Bound by Mannite at Different Temperatures.

The temperatures selected were 39°, 49°, 56°, 65°.

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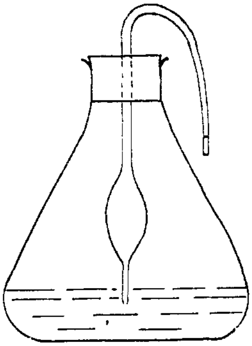
[1] Bloor, *loc. cit.*

[2] These figures are for the esters of stearic acid.

About 50 grams of concentrated sulfuric acid (94.8%) were weighed into a 100 cc. Erlenmeyer flask provided with a stopper through which passed the stem of a small (2 cc.) pipet over whose upper end was slipped a length of fine rubber tubing closed by a glass plug for convenience in taking samples. The arrangement of the apparatus was as follows: The sulfuric acid was warmed to the temperature of the experiment and then about 2.5 grams of *d*-mannite (Kahlbaum's K) introduced. The flask was tightly stoppered and placed in a water-jacketed hot air oven provided with a Bunsen gas regulator which had been adjusted to the desired temperature. Samples of 0.5–2 grams were taken from time to time by means of the pipet, and blown out as quickly as possible into about 35 cc. of water in another 100 cc. Erlenmeyer flask, which with contents had previously been weighed. These flasks were stoppered, put aside to come again to room temperature and weighed, the difference in weight being the weight of the mannite sulfuric acid mixture added. The first sample was generally taken as soon as the solution of the mannite in the sulfuric acid was complete, the other samples at convenient times afterwards. After all the necessary samples had been taken the solutions were titrated with standard alkali, using phenolphthalein as indicator. From the titration figures was calculated the amount of sulfuric acid in combination with mannite in the mixtures at the times of sampling, from which was deduced the rate and extent of combination. The results of the experiments are expressed in the tables following:



Temperature 39°.
Weight of mannite 2.5516 grams.
Weight of sulfuric acid 53.874 grams.

No. of sample.	Time in minutes.	Weight of sample.	Titration cc. of standard alkali.	H_2SO_4 uncombined in sample.	H_2SO_4 in original sample.	H_2SO_4 combined in sample.	H_2SO_4 combined. Total.	Mannite combined as disulfuric ester. Per cent.
1	*30*	2.0187	13.1	1.753	1.826	0.073	2.04	*74.3*
2	*45*	2.4097	15.45	2.068	2.180	0.112	2.622	*95 5*
3	*60*	2.1376	13.60	1.820	1.934	0.114	3.00	*109.3*
4	*75*	2.1843	13.90	1.860	1.976	0.116	2.997	*109.0*
5	*110*	2.0038	12.80	1.713	1.813	0.100	2.820	*102.0*
6	*140*	2.2796	14.55	1.947	2.064	0.177	2.896	*105.4*
7	*170*	1.9043	12.10	1.619	1.723	0.104	3.08	*112.0*
8	*200*	2.2979	14.65	1.961	2.079	0.118	2.90	*106.0*
9	*260*	1.6901	10.75	1.439	1.529	0.090	3.00	*109.3*

The figures above 100% probably indicate the formation of a small amount of a compound containing more sulfuric acid.

Temperature 49°.
Weight of mannite 2.3394 grams.
Weight of sulfuric acid 48.1938 grams.

No. of sample.	Time in minutes.	Weight of sample taken.	Titration cc. of standard alkali.	H_2SO_4 uncombined in sample.	H_2SO_4 in original sample.	H_2SO_4 combined in sample.	H_2SO_4 combined. Total.	Mannite combined as disulphuric ester. Per cent.
1	*17*	2.1863	14.05	1.880	1.976	0.096	2.218	*88.22*
2	*33*	1.5535	10.00	1.338	1.404	0.066	2.146	*85.34*
3	*49*	2.5865	16.55	2.215	2.338	0.123	2.402	*95.5*
4	*65*	1.9837	12.60	1.686	1.793	0.107	2.724	*108.3*[1]
5	*140*	2.2704	14.45	1.934	2.052	0.118	2.626	*104.4*[1]
6	*170*	1.9442	12.35	1.653	1.757	0.104	2.702	*107.4*[1]
7	*250*	1.4352	9.20	1.231	1.297	0.066	2.323	*92.2*

Temperature 56°.
Weight of mannite 2.2090 grams.
Weight of sulfuric acid 52.6504 grams.

No. of sample.	Time in minutes.	Weight of sample.	Titration cc. of standard alkali.	H_2SO_4 uncombined in sample.	H_2SO_4 in original sample.	H_2SO_4 combined in sample.	H_2SO_4 combined. Total.	Mannite combined as disulphuric ester. Per cent.
1	*10*	1.1417	27.70	1.010	1.060	0.050	2.402	*100.9*
2	*25*	1.2218	29.40	1.075	1.134	0.059	2.64	*109.9*
3	*40*	1.0137	24.60	0.8978	0.9416	0.044	2.38	*100.0*
4	*55*	1.1265	27.30	0.9963	1.046	0.0497	2.419	*101.7*
5	*70*	0.7510	18.09	0.6639	0.6975	0.0336	2.454	*103.1*
6	*100*	0.7694	18.63	0.6799	0.7146	0.0347	2.474	*103.9*
7	*160*	0.7157	17.43	0.6362	0.6648	0.0286	2.191	*92.06*
8	*220*	0.6991	17.04	0.6218	0.6493	0.0275	2.157	*90.36*
9	*340*	1.073	26.25	0.9580	0.9967	0.0387	1.978	*83.11*
10	*24 hrs.*	0.8122	19.95	0.7281	0.7544	0.0263	1.776	*74.62*

Temperature 64–65°.
Weight of mannite 2.5015 grams.
Weight of sulfuric acid 50.108 grams.

No. of sample.	Time in minutes.	Weight of sample.	Titration cc. of standard alkali.	H_2SO_4 uncombined in sample.	H_2SO_4 in original sample.	H_2SO_4 combined in sample.	H_2SO_4 combined. Total.	Mannite combined as disulphuric ester. Per cent.
1	*16*	1.5672	10.18	1.355	1.414	0.058	1.946	*72.4*
2	*31*	1.7540	11.33	1.516	1.583	0.067	2.009	*74.9*
3	*46*	1.8598	12.05	1.613	1.686	0.073	2.064	*76.91*
4	*62*	1.8712	12.10	1.619	1.689	0.070	1.967	*73.3*
5	*77*	1.4116	9.15	1.224	1.274	0.050	1.862	*69.4*
6	*83*	1.5015	9.70	1.298	1.355	0.057	1.996	*74.2*
7	*97*	1.5885	10.33	1.382	1.434	0.052	1.721	*64.1*
8	*142*	1.3133	8.53	1.141	1.185	0.044	1.762	*65.5*

For more ready comparison the results have been plotted on the accompanying chart.

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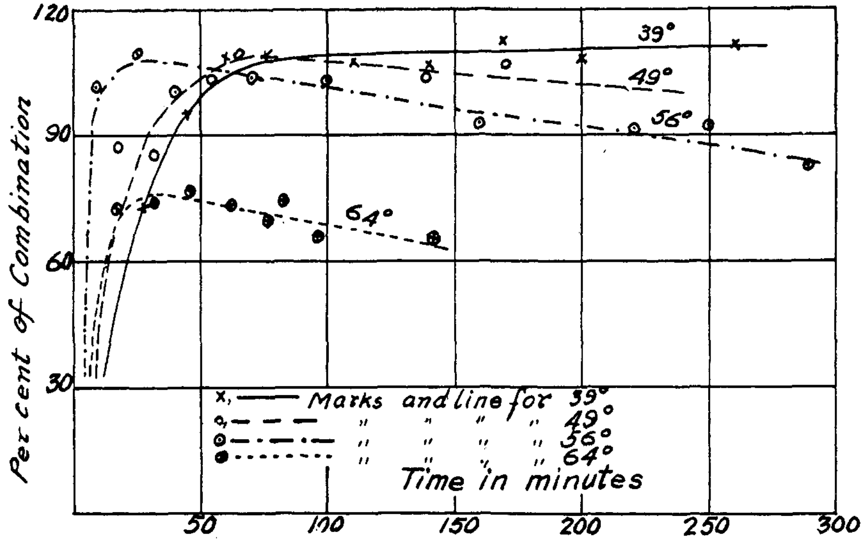
[1] Indicate a slight amount of combination in higher forms.

The inherent error in the determination is too great to permit of any exact interpretation of these curves. However, these facts appear to be clear. When mannite is dissolved in concentrated sulfuric acid the main substance formed is the disulfuric acid ester. Along with the formation of the disulfuric acid ester there occurs another reaction, the result of which is the production of substances with less power to bind sulfuric acid. This second reaction takes place more rapidly the higher the temperature, so that in the case of the highest temperature studied (64°), the amount of mannite disulfuric acid ester in the solution never exceeds 75% and rapidly becomes less. In this fact probably lies the reason for the low yield of fatty acid esters at higher temperatures, to which attention has been directed at the beginning of the paper.



PART II.

Preparation of the Barium Salts of the Mannite-Sulfuric acid Esters.

Preparations were made from the combined residues of the determinations described above and from solutions of mannite in sulfuric acid, each of which had been kept at a definit temperature for a given time. For reasons which will appear the latter preparations will be described first.

Three samples of 25 grams of purest mannite (Kahlbaum's K) were dissolved in 300 cc. of concentrated sulfuric acid and kept, one at room temperature (about 22°) for four days, another at incubator temperature (38°–39°) for twenty hours, and a third at the temperature of the boiling water bath (about 95°) for three hours. At the end of the heating period preparation number one remained clear and almost colorless, number two was yellowish brown, while number three was very dark colored although still clear. The solutions were poured into water and the excess of acid removed with powdered barium carbonate. The neutralization was continued with barium hydroxide solution until the solutions were just alkaline to phenolphthalein. The precipitate was filtered off, boiled out several times with water, filtered and the filtrates added to the main filtrate, which was then evaporated to a small bulk. Care was taken to avoid overheating at the edges of the dishes, since the esters are readily decomposed by dry heat. The syrupy solution was fractionated as follows: about $^1/_3$ its volume of alcohol was added and it was set aside to crystallize. After two or three days the crystallized mass was filtered and alcohol was added to the filtrate to bring the alcohol content up to about 50%. This solution was set aside to crystallize as before, the crystals filtered off and the filtrate diluted with alcohol to bring the alcohol content up to 75%. The substances which now separated were gummy, could not be made to crystallize and were rejected. The first two fractions were recrystallized until the optical rotation was constant, then they were filtered, washed first with dilute alcohol, then with 95% alcohol and finally with ether; after which they were dried to constant weight in a vacuum desiccator over concentrated sulfuric acid. The products obtained were as follows:

Series I. Room Temperature.—Only one compound was obtained in crystallin form from this series.

Fraction 1: Crystallizes from water in glistening sheaf-like aggregate of oblong needles, the single crystals being about 2–3 mm. long.

Solubility—about 1.5% in water at 22°.

Rotation $\left\{ \begin{array}{l} (a)\ 1.23 \text{ grams in 100 cc water in 2 dcm. tube} = -0.42°. \\ (b)\ 1.64 \text{ grams in 100 cc. water in 2 dcm. tube} = -0.56°. \end{array} \right.$

Whence $[\alpha]_D^{22}$ = (a) —17.1°, (b) —17.1°.

Analysis.—These compounds when boiled with dilute acid decompose, yielding one molecule of barium sulfate and one molecule of free sulfuric acid for each molecule of ester. For analysis a weighed amount of material was dissolved in water, made up to volume and an aliquot portion measured into an Erlenmeyer flask. Enough hydrochloric acid was added to make the solution about 10%, and the solutions were heated at low heat on an electrically heated hot plate for several hours. The precipitated barium sulfate was filtered on a prepared Gooch filter, ignited and weighed in the regular way. The filtrate was transferred quantitatively back to the Erlenmeyer flask, 10 cc. of 10% barium chloride added and the solutions, after digesting for a short time on the hot plate, were filtered and the second barium sulfate precipitate weighed as before. The first barium sulfate precipitate carries out all the combined barium and one-half the sulfuric acid. The second precipitate carries down the remaining sulfuric acid.

ANALYSIS.

Weight of substance. Gm.	$BaSO_4$ 1st ppt.	Ba Per cent.	$BaSO_4$ 2nd ppt.	$BaSO_4$ Total.	S Per cent.
0.1886	0.1076	33.56	0.1008	0.2084	15.18
0.1886	0.1070	33.37	0.1008	0.2078	15.13
0.2600	0.1420	32.12	0.1422	0.2842	15.01
	Average	33.01			15.10

which agrees best with the formula $C_6H_6O(SO_4)_2Ba$ (Ba % = 32.29 and S % 15.04).

Series II. Incubator Temperature.

First fraction:

Crystal form—rosets of six-sided plates.

Solubility—about 6.5% at 20°.

Rotation $\begin{cases} (a) \text{ 6.98 grams in 200 cc. water in 2 dcm. tube} = +4.8°. \\ (b) \text{ 8.48 grams in 200 cc. water in 2 dcm. tube} = +5.82°. \end{cases}$

Whence $[\alpha]_D^{22} = (a) + 68.8°, (b) + 68.62°$.

ANALYSES.

Weight of substance. Gm.	$BaSO_4$ 1st ppt.	Ba Per cent.	$BaSO_4$ 2nd ppt.	$BaSO_4$ Total.	S Per cent.
0.1740	0.0840	28.34	0.0852	0.1692	13.33
0.1743	0.0843	28.44	0.0867	0.1710	13.47
	Average	28.39			13.40

which agrees with the formula of the barium salt of mannite disulfuric acid $C_6H_{12}O_4$-$(SO_4)_2Ba$ (Ba % = 28.83, and S % = 13.45), or with that of the barium salt of mannid disulfuric acid with two molecules of water of crystallization. $C_6H_8O_2(SO_4)_2Ba.2H_2O$.

Series II. Incubator Temperature.

Second fraction:

Two preparations:

Crystal form—aggregates of coarse needles.

Solubility—about 20% in water at 22°.

Rotation—Prep. I. (*a*) 2.94 grams in 100 cc. water in 2 dcm. tube at 20° = +0.54.

(*b*) 3.61 grams in 50 cc. water in 2 dcm. tube at 20° = +1.32.

Prep. II. (*c*) 3.97 grams in 100 cc. water in 2 dcm. tube at 20° = +0.72.

(*d*) 4.29 grams in 100 cc. water in 2 dcm. tube at 20° = +0.78.

Whence $[\alpha]_D^{20°}$ = (*a*) +9.18°, (*b*) +9.15°, (*c*) +9.07°, (*d*) +9.09°. Average = +9.12°.

Analysis.	Weight of substance.	$BaSO_4$ 1st ppt.	Ba Per cent.	$BaSO_4$ 2nd ppt.	$BaSO_4$ Total.	S Per cent.
I.	0.1469	0.0807	32.30	0.0808	0.1615	15.09
	0.1469	0.0808	32.32	0.0805	0.1613	15.07
II.	0.1984	0.1079	31.98	0.1101	0.2180	15.09
	0.3968	0.2175	32.24	0.2185	0.4360	15.09
		Average	32.21			15.09

Theory for $C_6H_6O(SO_4)_2Ba$ is S = 15.04, Ba = 32.29.

Series III. Boiling Waterbath.

Fraction I. Two preparations:

Crystal form from water—irregular six-sided plates.

Solubility—about 6.5% in water at 22°.

Rotation—(*a*) 3.087 grams in 100 cc. water in 2 dcm. tube at 20° = +4.24°.
(*b*) 6.5 grams in 200 cc. water in 2 dcm. tube at 20° = +4.45°.
(*c*) 5.39 grams in 200 cc. water in 2 dcm. tube at 20° = +3.70°.

Whence $[\alpha]_D^{20°}$ = (*a*) +68.67°, (*b*) +68.5°, (*c*) 68.65°.

ANALYSIS.

	Weight of substance.	$BaSO_4$ 1st ppt.	Ba Per cent.	$BaSO_4$ 2nd ppt.	$BaSO_4$ Total.	S Per cent.
1st. prep.	0.2735	0.1327	28.53	0.1343	0.2670	13.40
	0.2735	0.1326	28.53	0.1344	0.2670	13.40
2nd. prep.	0.2696	0.1307	28.51	0.1321	0.2628	13.38
	0.2696	0.1315	28.68	0.1347	0.2662	13.56
		Average	28.56			13.43

Theory for the barium salt of mannite disulfuric acid $C_6H_{12}O_4(SO_4)_2Ba$ or for $C_6H_8O_2(SO_4)Ba.2H_2O$ is Ba 28.83%, S 13.43%.

Fraction II. Two preparations:

Crystal form—aggregates of microscopic needles.

Solubility—about 20% in water at 20°–22°.

Rotation—(*a*) 0.784 grams in 50 cc. water in 2 dcm. tube at 20° = +0.38°.
Prep. I. (*b*) 0.947 grams in 50 cc. water in 2 dcm. tube at 20° = +0.34°.
Prep. II. (*c*) 1.58 grams in 100 cc. water in 2 dcm. tube at 20° = +0.29°.

$[\alpha]_D^{20}$ = (*a*) +9.18°, (*b*) +8.98°, (*c*) +9.18°.

ANALYSIS.

	Weight of substance.	$BaSO_4$ 1st ppt.	Ba Per cent.	$BaSO_4$ 2nd ppt.	$BaSO_4$ Total.	S Per cent.
I.	0.1568	0.0850	31.88	0.0853	0.1703	14.91
	0.1568	0.0859	32.21	0.0850	0.1709	14.96
II.	0.1578	0.0857	31.93	0.0863	0.1720	14.96
	0.1578	0.0860	32.05	0.0872	0.1732	14.73
		Average	32.02			14.90

Theory for $C_6H_6O(SO_4)_2Ba$ is Ba% 32.29, S %15.04.

Series IV.—The combined residues from the determinations described in the first part of the paper were treated with barium carbonate and hydroxide as above and the barium salts of the esters prepared as described for the other series. The purification in this case was accomplished in a slightly different way. To the hot aqueous solution of the salts was added alcohol until precipitation just began and the solutions were allowed to stand until separation was complete. The process was repeated until a compound of constant rotation was obtained.

Only one preparation was obtained.

Crystal form—from 40% alcohol it crystallizes in globular aggregates of coarse needles.

Optical Activity:

0.8505 gram in 10 cc. water in 1 dcm. tube gives a rotation of +3.24°.
1.00 gram in 10 cc. water in 1 dcm. tube gives a rotation of +3.71°.
0.4328 gram in 10 cc. water in 2 dcm. tube gives a rotation of +3.25.
Specific rotation (1) 38.0°, (2) 37.1°, (3) 37.55°.
Average, $[\alpha]_D^{20°} = +37.55°$.

Barium and sulfur were determined in this compound in the same way as for the compounds of the previous series. The results of the analyses are as follows:

	Weight of substance taken.	Wt. of $BaSO_4$ 1st ppt.	Ba Per cent.	Wt. of $BaSO_4$ 2nd ppt.	Total $BaSO_4$.	Sulphur Per cent.
1	0.2282	0.1167	30.08	0.1182	0.2349	14.14
2	0.2212	0.1128	30.01	0.1153	0.2281	14.17
3	0.3154	0.1622	30.26	0.1636	0.3258	14.19
		Average	30.11			14.16

Decomposes with darkening when heated dry on the water bath.

Concentrated sulfuric acid acting upon mannite yields apparently four di-sulfuric acid esters:

Ester I. Specific rotation —17.1°. Ba content = 33.01%.
S content = 15.10%.

Solubility in water at 22°, 1.5%. Formed only the action of cold sulfuric acid on mannite.

Ester II. Specific rotation +9.1°. Ba content = 32.12 } Average of all
S content = 15.00 } analyses.

Solubility in water at 22°, 22%. Formed at 38° and higher. (A small amount of a compound with properties similar to this one was found as the second fraction in the series of compounds formed by the action of cold sulfuric acid. The amount was, however, too small for accurate identification.) When heated dry on the water bath it quickly darkens with decomposition.

Ester III. Specific rotation 68.7°. Ba content = 28.47 } Average.
S content = 13.41 }

Solubility in water at 22°, 6.5%. Not formed at lower temperatures.

Ester IV. Specific rotation 37.55°. Ba content = 30.11 } Average.
S content = 14.16 }

The first three are probably definit compounds. Number four, from its origin and from the fact that in its rotation and its analysis it is almost exactly the average of two and three, is probably a mixture of equal parts of each. Numbers two and three correspond in optical activity to two of the mannite esters of the fatty acid already described—number two to the mannitan diesters and number three to the mannid forms.

We may summarize the results of the investigations on the mannite esters as follows:

1. When mannite is dissolved in concentrated sulfuric acid it is dehydrated to the form $C_6H_6O(OH)_2$, at the same time combining with the acid as the disulfuric acid ester.

2. At low temperatures there is produced mainly a levorotatory ester. At higher temperatures dextrorotatory compounds are produced together with derivatives which have partly lost their power to combine with acid groups.

3. In the presence of the higher fatty acids, esters are produced presumably with the above anhydride of mannite. During the processes of separation they become hydrated to mannid and mannitan forms.

THE EFFICIENCY OF THE PREPARATION OF ETHER FROM ALCOHOL AND SULFURIC ACID.

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The preparation of ethyl ether from alcohol and sulfuric acid has been the subject of much experiment and theoretical discussion since the discovery of the process in 1544. The generally accepted theory at present is that ethyl sulfuric acid and water are first formed and that the ethyl sulfuric acid then reacts with more alcohol to form ether and sulfuric acid, in accordance with the equations:

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O$$
$$C_2H_5HSO_4 + C_2H_5OH = C_2H_5OC_2H_5 + H_2SO_4.$$

According to this theory the sulfuric acid acts only as a catalyst and a limited quantity should be capable of converting an unlimited amount of alcohol into ether and water. Experience has shown, however, that this is not the case, and various explanations have been offered of the limitations of the process.

It is often stated that the accumulation of the water formed in the first reaction so dilutes the sulfuric acid that it ceases to perform its function as catalyst. It is also considered by some that the sulfuric acid is slowly destroyed by other reactions, the chief of which is said to be its reduction to sulfur dioxide by the organic materials present.

The limit of reasonable efficiency is variously given; some writers state that the sulfuric acid can convert only three times its weight of alcohol into ether, others give somewhat higher figures.

The object of the work here reported was to determin experimentally the efficiency of the method, or the completeness of the reaction, during the progress of the preparation, to find the limit of reasonable efficiency, and to ascertain the cause of the final failure of the reaction.

Experimental.

Efficiency of the Process.—Several preliminary experiments were made in finding a satisfactory method of maintaining a fairly constant tempera-