Anal. Calcd. for $(C_{13}H_{21}O_4N_3)_2$: C, 55.11; H, 7.47; N, 14.8. Found: C, 55.02; H, 7.39; N, 14.4.

Semicarbazone of Monomeric *n*-Butyl Mesityl Oxide Oxalate (Indalone).—The semicarbazone of the monomer was recrystallized from very dilute alcohol as white crystals which turned a bright yellow on exposure to daylight, m. p. 159.5–160° (cor.), sintering at 154°. Both white and yellow forms of the semicarbazone were very soluble in alcohol, the latter forming a colorless solution and recrystallizing, in the absence of light, as the white form.

Anal. Calcd. for $C_{13}H_{21}O_4N_3$: C, 55.11; H, 7.47; N, 14.8. Found: C, 55.02; H, 7.64; N, 15.0.

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Reversible Effect of Stannic Chloride on the Rotation of Starch Dispersions[1]

BY CARROLL L. HOFFPAUIR AND JOHN D. GUTHRIE

The optical rotation of a dispersion of starch in calcium chloride solution is appreciably reduced by the addition of stannic chloride. This effect is reversible inasmuch as the original rotation may be restored by the addition of sodium acetate or uranyl acetate. A similar result is obtained with a dispersion of glycogen while the levorotation of inulin is increased by the addition of stannic chloride. Since stannic chloride is used as a protein precipitant in the determination of starch by a method in general use,[1a] these observations may be of practical as well as of theoretical interest.

Experimental.—A description and analysis of the samples of starch used in this work may be found in a previous communication from this Laboratory.[2]

In a typical experiment four 10-g. portions of laboratory-prepared sweet potato starch were weighed into 400-ml. beakers and mixed thoroughly with 15 ml. of water so that a smooth paste was obtained. To each beaker were added 150 ml. of neutral calcium chloride solution, sp. gr. 1.30, and 5 ml. of 0.8% acetic acid. The mixtures were brought to the boiling point within five minutes, boiled for fifteen minutes, cooled, combined and made to a volume of one liter with the calcium chloride solution. Aliquots of this solution were transferred to 100-ml. volumetric flasks and the indicated amounts of stannic chloride pentahydrate dissolved in the calcium chloride solution were added. Sodium acetate, 2 ml. of a 4 *N* aqueous solution, was added to one series, while 2 ml. of water was added to the other series. The flasks were made to volume with the calcium chloride solution and mixed thoroughly. The optical rotations of the solutions were read in a 20-cm. tube at 25° using a sodium vapor lamp as the source of illumination. Results of this experiment and similar experiments with corn starch and wheat starch are given in Table I. White potato starch exhibited the same behavior.

TABLE I

ROTATIONS OF STARCH DISPERSIONS, 20-CM. TUBE

$SnCl_4 \cdot 5H_2O$ added, g.	25-ml. starch dispersion in 100 ml. total volume Sodium acetate added None	2 ml. 4 *N*	50-ml. starch dispersion in 100 ml. total volume Sodium acetate added None	2 ml. 4 *N*
Sweet potato starch 35.3[a] mg. per ml.				
0.0	3.55	3.55	7.09	7.09
0.2	3.45	3.55	6.87	7.09
0.5	3.30	3.55	6.62	7.09
1.0	3.23	3.50	6.45	6.90
1.5	3.15	3.30	6.31	6.64
2.5	3.09	3.19	6.15	6.35
Corn starch 34.8[a] mg. per ml.				
0.0	3.52	3.51	7.03	7.03
0.5	3.27	3.46	6.60	[b]
1.0	3.18	3.43	6.40	6.90
Wheat starch 34.7[a] mg. per ml.				
0.0	3.48	3.46	6.99	7.00
0.5	3.25	3.45	6.60	[b]
1.0	3.09	3.36	6.43	6.74

[a] Corrected for moisture, ash, protein, and extractives. Solution too cloudy to obtain optical rotation.

By using larger amounts of sodium acetate than used in the experiments reported in Table I, it was possible to eliminate the change in rotation produced by as much as 2.5 g. of stannic chloride. For example, using 25- and 50-ml. aliquots of the same sweet potato starch dispersion used for Table I, and 2.5 g. of stannic chloride pentahydrate, the rotations after treatment with 5 ml. of 4 *N* sodium acetate were 3.57 and 7.09°, respectively. Starch dispersions that had stood overnight with added stannic chloride could be restored to their original rotational values by addition of sodium acetate. Uranyl acetate was also effective in eliminating the change in rotation produced by stannic chloride.

Reduction of the rotation of starch was not produced by dilute hydrochloric acid, boric acid, thorium nitrate or antimony trichloride. A very small reduction in rotation was noted when starch dispersions were treated with stannous chloride, but this effect may have been due to the oxidation of a small amount of the tin to the stannic form.

Glycogen dispersed in calcium chloride solution gave a lower rotation on the addition of stannic chloride, but the dispersions became too cloudy to read when sodium acetate was added. The levorotation of inulin dispersed in calcium chloride solution was increased by stannic chloride and the original rotation was restored when sodium acetate was added. Stannic chloride did not alter the rotation of dextrose dissolved in calcium chloride solution.

When the concentration of starch was varied while holding the concentration of stannic chloride constant, a

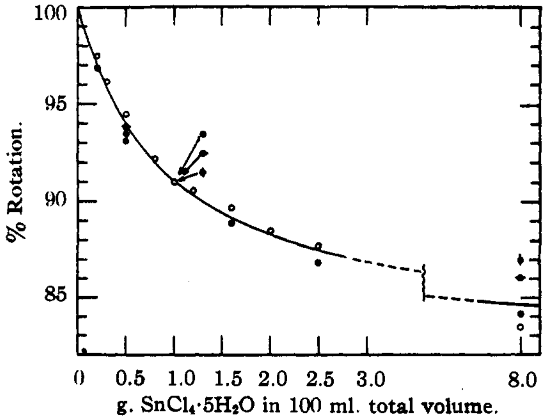

Fig. 1.—Rotation of dispersions of several starches in the presence of different concentrations of stannic chloride: ●, sweet potato; ○, white potato; -ⴱ-, corn; ⏀, wheat.

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(1) Article not copyrighted.

(1a) Clendenning, *Can. J. Research*, **20**, C, 403 (1942).

(2) Steiner and Guthrie, *Ind. Eng. Chem., Anal. Ed.*, **16**, 736 (1944).

straight line was obtained when rotation was plotted against concentration of starch. When the starch concentration was held constant and the concentration of stannic chloride was varied, a curve was obtained when the rotation was plotted against the concentration of stannic chloride. Since the behavior of all of the starches tested was practically identical, the results of the experiments with each starch could be reduced to a comparable basis by expressing the rotations in terms of the original rotation prior to the addition of stannic chloride. This has been done and the values plotted in Fig. 1. The curve was calculated from the equation

$$(0.9 + \text{g. } SnCl_4 \cdot 5H_2O)(\%\text{ change in rotation}) = 17\ (\text{g. } SnCl_4 \cdot 5H_2O)$$

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L-Talitol

BY F. L. HUMOLLER,[1] M. L. WOLFROM,[2] B. W. LEW[3] AND R. MAX GOEPP, JR.[4]

All of the isomeric hexitols have been reported in crystalline form except L-talitol. The synthesis of crystalline β-L-altrose from L-ribose by Austin and Humoller[5] makes this very rare sugar available for the synthesis of its reduction product L-talitol. This step has now been accomplished and L-talitol has been obtained in crystalline form, with melting point 87–88° and rotation $[\alpha]^{20}D$ −2.9° (water) in agreement with those (m. p. 86°, $[\alpha]^{18}D$ +3.0° in water) recorded by Bertrand and Bruneau[6] for crystalline D-talitol, which had been reported previously as a sirup by Fischer.[7]

Fischer[7] had also subjected dulcitol to oxidation with lead peroxide and hydrochloric acid followed by reduction with sodium amalgam. After separation of a considerable amount of dulcitol, Fischer obtained a crystalline tribenzylidene derivative which yielded a crystalline product of melting point 66–67° after hydrolysis of the benzylidene groups. Fischer considered that this substance was D,L-talitol. An authentic sample of D,L-talitol has now been prepared in crystalline form from its pure components and found to melt at 95–96°. Thus the original product of Fischer must have been either an impure preparation or a lower-melting polymorph.

Experimental

L-Talitol.—A solution of 400 mg. of crystalline β-L-altrose in 30 cc. of water containing a suspension of 150 mg. of a nickel catalyst supported on kieselguhr was treated for twelve hours at 100° with hydrogen under a pressure of 2000 lb. per sq. in. (133 atm.). The cooled reaction mixture (non-reducing toward Fehling solution) was filtered and concentrated to a sirup under reduced pressure; yield 320 mg. Pure material was obtained on crystallization from absolute ethanol, from which L-talitol separated in spherical clusters of colorless, well-defined needles; yield 280 mg., m. p. 87–88°, $[\alpha]^{20}D$ −2.9° (*c* 5, H_2O, 2-dm. tube), taste sweet.

Anal. Calcd. for $C_6H_{14}O_6$: C, 39.55; H, 7.75. Found: C, 39.59; H, 8.06.

D,L-Talitol.—An accurately weighed amount of 6.1 mg. of pure D-talitol[8] was mixed with a like amount of pure L-talitol and the mixture was recrystallized from 95% ethanol, from which D,L-talitol crystallized in clusters of colorless prisms; yield 11.1 mg., m. p. 95–96°.

CHEMICAL LABORATORY
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[5] W. C. Austin and F. L. Humoller, THIS JOURNAL, **56**, 1153 (1934).

[6] G. Bertrand and P. Bruneau, *Bull. soc. chim.*, [4] **3**, 495 (1908).

[7] E. Fischer, *Ber.*, **27**, 1524 (1894).

[8] We are indebted to Professor C. S. Hudson of the National Institute of Health, U. S. Public Health Service, Bethesda, Maryland, for a sample of pure D-talitol.

Studies in the Terpene Series. III.[1] Hydrogen Transfer Reaction During the Dehydration of Terpenic Alcohols

BY V. N. IPATIEFF AND HERMAN PINES

It has been reported[2] that terpenic alcohols undergo dehydration by means of dilute aqueous magnesium chloride solution to form terpenic hydrocarbons; the structure of some of the terpenic hydrocarbons obtained was determined. In view of the recent observation made by the authors and R. C. Olberg[1] that limonene in the presence of halogen-containing catalysts undergoes hydrogen disproportionation resulting in the formation of *p*-cymene, it was decided to reinvestigate some of the higher boiling hydrocarbons resulting from the treatment of terpineol and 1,8-*p*-menthanediol. The experiments were made by treating one mole of the alcohols with 0.03 mole of magnesium chloride dissolved in 5.5 moles of water. The mixture was heated in an autoclave of 850 cc. capacity at 250° for three hours. It was found that the higher boiling fractions of the reaction product contained a large proportion of *p*-cymene. The yield of *p*-cymene produced amounted to about 18–20 mole per cent. based on the alcohols charged.

The presence of *p*-cymene in the mixture of hydrocarbons was demonstrated by means of selective hydrogenation. It was found that only olefinic hydrocarbons underwent hydrogenation when an equimolal mixture of limonene, dihydrolimonene and *p*-cymene, diluted with an equal volume of *n*-pentane, was subjected to treatment with hydrogen under a pressure of 80 atm. at 45° and in the presence of nickel–kieselguhr catalyst, *p*-cymene remains unchanged. The amount of *p*-cymene obtained from the hydrogen transfer reaction was determined by: (1) ultraviolet absorption, (2) extraction of the *p*-cymene, after selective

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[1] For paper II of this series, see V. N. Ipatieff, H. Pines and R. C. Olberg, THIS JOURNAL, **67**, 694 (1945).

[2] V. N. Ipatieff and H. Pines, *ibid.*, **66**, 1120 (1944).