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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SOUTHERN REGIONAL RESEARCH LABORATORY
NEW ORLEANS, LA.
RECEIVED APRIL 14, 1945

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 $[\alpha]^{20}\text{D}$ −2.9° (water) in agreement with those (m. p. 86°, $[\alpha]^{18}\text{D}$ +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°, $[\alpha]^{20}\text{D}$ −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°.

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(2) The Ohio State University.

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(4) Director of Organic Research, Atlas Powder Company, Wilmington, Delaware.

(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.

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RECEIVED APRIL 30, 1945

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).