aluminum hydride gave *trans-p*-menthane[3] and since we had found that *l*-menthyl chloride was inert to this reagent.

In Chart 1 are summarized the experiments which were carried out. It is evident that the

CHART I

l-Menthyl *p*-Toluenesulfonate

[$[\alpha]^{28}\mathrm{D}$ $-67.8 \pm 2.8°$ ($c = 0.7$, $l = 2$, chloroform)]

$\downarrow$ LiAlH$_4$ (in ether)	$\downarrow$ LiAlD$_4$ (in ether)
trans-p-menthane	3-deutero-*trans-p*-menthane
$\alpha^{25}\mathrm{D} = 0.00 \pm 0.02°$	$\alpha^{25}\mathrm{D} = -0.14 \pm 0.02°$
($l = 2$, no solvent)	($l = 2$, no solvent)

(No change in properties after A and B)

A. Catalytic hydrogenation over platinum
B. 1. Treatment with alkaline potassium permanganate
 2. Nitric–sulfuric acid wash
 3. Distillation over sodium

reduction of *l*-menthyl *p*-toluenesulfonate with lithium aluminum deuteride gives a deutero-hydrocarbon whose optical rotation is far beyond the limits of experimental error. It is unlikely that optical activity is caused by the presence of impurities. In support of this conclusion it should be observed that: (1) Reduction of the same batch of *l*-menthyl *p*-toluenesulfonate with lithium aluminum hydride resulted in an optically inactive hydrocarbon. (2) Treatment of the 3-deutero-*trans-p*-menthane with such reagents as hydrogen and platinum, alkaline potassium permanganate, sulfuric acid, a mixture of nitric and sulfuric acids, and metallic sodium changed none of the physical properties of the material.

Experimental[4]

***trans-p*-Menthane.**[3]—*l*-Menthyl *p*-toluenesulfonate[1] (14.0 g., 0.0452 mole) was added portionwise to a solution of 90 ml. of dry ether and 2.45 g. (0.0645 mole) of lithium aluminum hydride contained in a clean dry three necked flask fitted with a mechanical stirrer, a reflux condenser carrying a calcium chloride tube, and a glass stopper. After each addition some frothing occurred but the reaction did not appear to be exothermic. The transformation was completed by stirring and heating the reaction mixture overnight under gentle reflux. During this time a granular white solid separated.

Decomposition of the metal complexes was carried out by the cautious addition of a solution of 10 ml. of water and 40 ml. of dioxane followed in turn by 100 ml. of water and enough concentrated hydrochloric acid (about 75 ml.) to dissolve completely the flocculent aluminum salts which were formed. The layers were then separated. The aqueous layer was extracted twice with 10-ml. portions of ether and the combined ether extracts were dried over anhydrous magnesium sulfate. After removing as much ether as possible on a water-bath, 100 ml. of low boiling petroleum ether was added to the residue and the petroleum ether solution was washed successively with three 25-ml. portions of water, six 75-ml. portions of concd. sulfuric acid and four 50-ml. portions of water. The solution was then dried over anhydrous potassium carbonate, filtered into a modified Claisen flask and the petroleum ether was removed on a water-bath. Distillation of the residue gave fractions 1 (0.2 g., $n^{20}\mathrm{D}$ 1.4367) and 2 (3.5 g., $n^{20}\mathrm{D}$ 1.4374), both of which boiled at 57° (17 mm.). Fraction 2 was optically inactive, $\alpha^{25}\mathrm{D} = 0.00 \pm 0.02°$ ($l = 2$, no solvent), d^{20}_{20} 0.7920, d^{20}_{4} 0.7906 and represents a yield of 55% based upon *l*-menthyl *p*-toluenesulfonate. Its infrared absorption curve[5] was identical with that of the *trans-p*-menthane prepared by the catalytic hydrogenation of *trans*-2-*p*-menthene.[1]

3-Deutero-*trans-p*-menthane.—Following exactly the same procedure as described above the reaction was carried out with 22.2 g. (0.0717 mole) of *l*-menthyl *p*-toluenesulfonate, 200 ml. of dry ether and 3.0 g. (0.0717 mole) of lithium aluminum deuteride.[6] Distillation gave fractions 1 (0.3 g., $n^{20}\mathrm{D}$ 1.4365) and 2 (4.6 g., $n^{20}\mathrm{D}$ 1.4372) both of which boiled at 55° (17 mm.). Fraction 2, which amounted to a yield of 46%, had the following additional physical properties: d^{20}_{20} 0.7971, d^{20}_{4} 0.7956,[7] $\alpha^{25}\mathrm{D} = -0.07 \pm 0.01°$ ($l = 1$, no solvent), $\alpha^{25}\mathrm{D} = -0.14 \pm 0.02°$ ($l = 2$, no solvent), $[\alpha]^{25}\mathrm{D}$ $0.09 \pm 0.01°$ ($l = 2$, no solvent).[8] Its infrared absorption curve[5] showed no absorption in the alcohol (3300–3700 cm.$^{-1}$) or olefin (1650 cm.$^{-1}$) regions but there was strong absorption in the region 2133 cm.$^{-1}$ which is characteristic of the C-D stretching frequency.

Attempted Hydrogenation of 3-Deutero-*trans-p*-menthane.—To a solution of 2.0 ml. (1.6 g., 0.0113 mole) 3-deutero-*trans-p*-menthane in 50 ml. of ether was added 0.1 g. of Adams platinum oxide catalyst and the mixture was hydrogenated at 45 pounds per square in. pressure for four hours. No hydrogen appeared to be absorbed. The solution was filtered, the ether was removed on a water-bath and the residue was distilled under reduced pressure from a modified Claisen flask. Fractions 1 (0.1 g.) and 2 (1.3 g.) both boiled at 54° (17 mm.) and had the same refractive index, $n^{20}\mathrm{D}$ 1.4371. The optical rotation of fraction 2 had not changed, $\alpha^{25}\mathrm{D} = -0.07 \pm 0.01°$ ($l = 1$, no solvent) and no change was found in its infrared absorption curve. Fractions 1 and 2 weighed 1.4 g., which represents an 87% recovery.

Attempted Oxidation of 3-Deutero-*trans-p*-menthane.—Another 2.0-ml. sample was withdrawn from fraction 2 of 3-deutero-*trans-p*-menthane and oxidized with alkaline potassium permanganate by the procedure already described for 2,3-dideuteromenthane.[1] After two drops of fore-run, 1.2 g. (75%) of 3-deutero-*trans-p*-menthane was recovered, b. p. 57° (18 mm.), $n^{20}\mathrm{D}$ 1.4371, $\alpha^{25}\mathrm{D} = 0.07 \pm 0.01°$ ($l = 1$, no solvent). The infrared absorption curve of this material was the same as those which had been obtained previously.

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[3] Schmid and Karrer, *Helv. Chim. Acta*, **32**, 1371 (1949).

[4] All melting points and boiling points are uncorrected.

[5] We are indebted to Miss Elizabeth Petersen and Dr. H. S Gutowsky for the determination and interpretation of the infrared data mentioned in this paper.

[6] Obtained from Metal Hydrides, Inc., Beverly, Massachusetts, on allocation from the United States Atomic Energy Commission. The isotopic purity of this material was 96 atom per cent. deuterium.

[7] This value is in agreement with the formula of McLean and Adams [THIS JOURNAL, **58**, 804 (1936)] for calculating the density of a deuterium compound from the density of its hydrogen analog. The calculated value is 0.7958.

[8] $[\alpha]^{25}\mathrm{D} = \alpha^{25}\mathrm{D}/(l)$ (density).

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The Preparation of 4,4'-Dihydroxyhydrobenzoin by Electrolytic Reduction at Constant Cathode Potential

BY MILTON J. ALLEN

Biedermann[1] and Hertzfeld[2] both prepared 4,4'-dihydroxyhydrobenzoin by reduction of *p*-hydroxybenzaldehyde with sodium amalgam. This method yielded both the alcohol and the

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[1] Biedermann, *Ber.*, **19**, 2374 (1886).

[2] Hertzfeld, *ibid.*, **10**, 1267 (1877).

pinacol. Neither of these workers mentioned the yields obtained.

Takaki[3] treated *p*-hydroxybenzaldehyde with ammonium amalgam and from the mixture of products obtained a very small yield of the hydrobenzoin.

The preparation of 4,4′-dihydroxyhydrobenzoin was carried out by electrolytic reduction at controlled cathode potential with resultant high yield of the desired hydrobenzoin. The tetraacetate was also prepared and characterized.

Experimental[4]

4,4-Dihydroxyhydrobenzoin.—The apparatus used in this preparation is the same as that previously described.[5,6] Twelve grams of *p*-hydroxybenzaldehyde dissolved in 100 ml. of 2 *N* sodium hydroxide was placed in the cathode chamber. A 2*N* sodium hydroxide solution was introduced into the anode chamber. At a cathode potential of −2.0 volts and a temperature of 30° the initial current was 4.1 amperes. After thirty-four minutes of electrolysis a current plateau of 0.5 ampere was reached which indicated the completion of the reaction. The catholyte was filtered and acidified. The precipitate was washed lightly with cold water and cold ethanol, yield 11.5 g. (95.2%), m. p. 214.5°. Recrystallization from methanol gave white prisms, m. p. 215.5°.

4,4-Dihydroxyhydrobenzoin Tetracetate.—Five grams of the hydrobenzoin was suspended in 75 ml. of acetic anhydride and a few drops of concentrated sulfuric acid added. The mixture was shaken until all the hydrobenzoin was in solution and then poured on ice. The solid was recrystallized from 70% ethanol and dried over phosphorus pentoxide, yield 4.99 g. (78.4%), m. p. 121.5–122.5°.

Anal. Calcd. for $C_{22}H_{22}O_8$: C, 63.76; H, 5.35. Found: C, 63.57; H, 5.52.

A sample of the tetraacetate was saponified and the resulting product gave no depression in melting point when mixed with a sample of 4,4′-dihydroxyhydrobenzoin.

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(3) Takaki, *J. Pharm. Soc. Japan*, **58**, 156 (1938).

(4) All melting points reported are corrected.

(5) Allen, *J. Org. Chem.*, **15**, 435 (1950).

(6) Allen, *Ind. Eng. Chem.*, *Anal. Ed.*, **22**, 804 (1950).

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The Heat Capacity of Sucrose from 25 to 90°[1]

BY G. L. ANDERSON, JR., HOWARD HIGBIE[2] AND GEBHARD STEGEMAN[3]

In recent years this laboratory has been engaged in a program to secure thermal data on biologically active compounds. Measurements are now being made to evaluate the quantities required for a thermal description of the system sucrose–water from 0 to 90°. Heat capacity values for solid sucrose from −179 to 24° are available,[4] and this paper presents the results of measurements covering the temperature range from 24 to 90°.

Experimental

The sucrose was Standard Sample 17 prepared by the National Bureau of Standards.[5] This was received in a highly purified condition and was used without further treatment.

The heat capacity measurements were made in an adiabatic calorimeter of the type described by Southard and Brickwedde.[6] Only the important differences between the Southard and Brickwedde apparatus and that used in this investigation are noted here. In the present case a copper resistance thermometer was wound on the outside of the sample container and was calibrated by comparison with a platinum resistance thermometer bearing a certificate of calibration from the National Bureau of Standards. The heater was centrally located in a re-entrant tube in the sample container. The cable carrying the electrical leads to the calorimeter heater, thermometer and to the difference thermocouples between the shield and sample container was cemented on the outside of the radiation shield heater. The heat capacity values obtained in this investigation along with the values reported by Parks, Huffman and Barmore in the neighboring temperature region are tabulated below. The calculated values were obtained from the equation

$$C_p = A + B(t - 25°) + C(t - 25°)^2$$

where A = 101.7 cal. mole^{-1} degree^{-1}
B = 0.394 cal. mole^{-1} degree^{-2}
C = 5.1 × 10^{-4} cal. mole^{-1} degree^{-3}

Temp., °C.	Heat capacity of solid sucrose (cal. mole^{-1} degree^{-1}) Measured	Calculated
2.6	93.1[a]	93.2
8.9	95.5[a]	95.6
16.7	98.2[a]	98.4
23.2	102.7	101.0
23.8	101.0[a]	101.2
23.9	101.3	101.3
26.4	102.3	102.2
28.2	102.3	103.0
29.8	103.4	103.6
40.0	107.5	107.7
47.3	110.6	110.8
69.4	120.8	120.2
89.7	129.4	129.3
26.8[b]	103.4[b]	102.4

[a] Values reported by Parks, Huffman and Barmore.
[b] Check determination.

The principal source of uncertainty in these measurements was the measurement of the temperature rise of the sample container. From observations of the rate of temperature drift while adiabatic conditions were being maintained as well as possible it was estimated that the uncertainty in the value of heat capacity of sucrose was ±2%.

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(1) This work was supported by a grant to the University of Pittsburgh of The Sugar Research Foundation, Inc., and is a portion of the dissertation presented by Howard Higbie to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) The M. W. Kellogg Co., Jersey City 3, N. J.

(3) Deceased September 5, 1949.

(4) Parks, Huffman and Barmore, THIS JOURNAL, **55**, 2733 (1933).

(5) Circular C 440, U. S. Department of Commerce, National Bureau of Standards, page 392.

(6) Southard and Brickwedde, THIS JOURNAL, **55**, 4378 (1933).