by the National Formulary[5] is 181–185° although Smith and Nelson[6] reported 185.1° for a carefully sublimed and purified sample.

Purification has usually been carried out by recrystallization from organic solvents.[7] Britton and Eiseman[8] treated the crude molten phenothiazine with a powdered metal melting in the range 200–1100° followed by vacuum distillation. We have found that distillation with superheated steam can replace the vacuum distillation and that iron powder (m. p. 1530°) can be substituted for the metals recommended by them. The method is both simple and rapid and avoids the mechanical difficulties such as bumping and clogging which we encountered with the vacuum distillation.

Experimental

The crude phenothiazine (100 g.) was placed in a distilling flask and heated to 300° by means of a sodium nitrate–potassium nitrate bath. Iron powder (2 g.) was stirred into the molten phenothiazine and after a few minutes, superheated steam was passed through the mixture at the rate of 6 g. a minute. The steam was kept at 300° using the apparatus described by Morton.[9] The receiver was a large round-bottomed flask cooled by means of cold running water. The phenothiazine sublimed into the receiver in the form of a pale yellow snow. The distillation required twenty-five to thirty minutes. The product weighed 91 g. and melted at 178–180°. The melting point could be raised to 181–183° by redistilling the product with superheated steam or by washing with carbon tetrachloride in which the phenothiazine is practically insoluble. Washing the twice-distilled product with carbon tetrachloride gave phenothiazine melting at 183–185°.

We wish to thank the Mallinckrodt Chemical Works, Ltd., for permission to publish this work.

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[5] United States National Formulary, Ed. VII, 1942, p. 323.

[6] Smith and Nelson, This Journal, **64**, 461 (1942).

[7] Belokrinitskii, *J. Applied Chem.* (U. S. S. R.), **14**, 187 (1941); Lannung, *Arch. Pharm. Chem.*, **48**, 141 (1941).

[8] Britton and Eiseman, U. S. Patent 2,295,074.

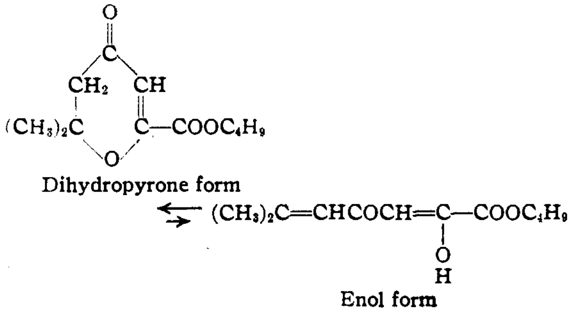
[9] Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1938, p. 144.

RESEARCH LABORATORIES OF THE
MALLINCKRODT CHEMICAL WORKS, LTD.
LASALLE, QUEBEC, CANADA
RECEIVED MARCH 26, 1945

Photochemical Dimerization of *n*-Butyl Mesityl Oxide Oxalate[1]

BY S. A. HALL, R. K. ADAMS, JR., AND H. L. HALLER

The *n*-butyl ester of mesityl oxide oxalic acid, patented under the trade name "Indalone,"[2] is used as an insect repellent to protect against the bites of mosquitoes and flies. The commercial product is a yellow to reddish-brown, high-boiling liquid of characteristic odor. It exists largely as the butyl ester of 2,2-dimethyl-6-carboxydihydro-4-pyrone in equilibrium with the open-chain enol form.



Dihydropyrone form

$$\rightleftarrows (CH_3)_2C{=}CHCOCH{=}\underset{\underset{H}{|}}{\underset{O}{\underset{|}{C}}}{-}COOC_4H_9$$

Enol form

We have found that exposure to ultraviolet light of a thin film of Indalone causes irreversible and quantitative polymerization of the liquid ester to a crystalline solid, m. p. 106–107°, which we have identified as a dimer of Indalone. That this dimerization will take place completely in three and one-half hours on exposure of a thin layer to March sunlight, or in one hour on exposure to an ultraviolet lamp, is of especial interest because of the loss in insect-repellent properties involved after dimerization. Federlin[3] has described dimers of the methyl, ethyl, propyl and amyl esters of mesityl oxide oxalic acid which he obtained by exposure of 20% solutions of the respective esters in methanol to diffuse daylight from eight days to five months. His attempts to saponify the dimeric ethyl ester to the dimeric acid were unsuccessful. This and other aspects of the reaction are being further investigated.

Experimental

***n*-Butyl Mesityl Oxide Oxalate Dimer.**—Redistilled commercial **Indalone** (1.2 g.) was placed in a 9-cm. Petri dish and covered tightly with a cellophane cover. The dish was placed upon a sheet of polished aluminum and irradiated with ultraviolet light from a 100-watt mercury-vapor spotlight, type CH-4. After forty-five minutes crystallization of the dimer had spread through two-thirds of the liquid film. Further exposure for fifteen minutes produced complete solidification to the dimer. There was no loss in weight.

A similar experiment was conducted outdoors on March 13 in midday sunlight except that no aluminum reflector was placed under the Petri dish. At a temperature of 13–14° in the sun, the film of **Indalone** was about half solidified after two and one-fourth hours and completely solidified to the dimer after three and one-half hours. The dimer recrystallized from dilute alcohol in prisms, m. p. 106–107° (cor.), which sublimed without decomposition at 0.4 mm. pressure at an oil-bath temperature of 155–180°. The sublimed crystals melted at 106.5–107.5° (cor.).

Anal. Calcd. for $(C_{12}H_{18}O_4)_2$: C, 63.70; H, 8.02; neut. equiv. (4 equivs. per mole), 113; mol. wt., 452. Found: C, 63.59; H, 8.07; neut. equiv., 108; mol. wt., 445 (in benzene), 443 (in camphor).

No color was obtained with alcoholic ferric chloride reagent which indicates that the dimer is not enolized. The monomeric ester with this reagent gives a deep red color which is attributed to the presence of the enol form. With tetranitromethane reagent the dimer gave a negative test for unsaturation; the monomer gave a positive test.

Semicarbazone of Dimeric *n*-Butyl Mesityl Oxide Oxalate.—The semicarbazone crystallized from methanol as very fine white crystals, m. p. 233.0–233.5° (dec.) (cor.).

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[1] This work was done under a transfer of funds, recommended by the Committee on Medical Research, from the Office of Scientific Research and Development to the Bureau of Entomology and Plant Quarantine.

[2] U. S. Patent 2,138,540, issued Nov. 29, 1938; assigned to Ford, Kilgore Development Corp.

[3] Federlin, *Ann.*, **356**, 261 (1907).

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.

U. S. DEPARTMENT OF AGRICULTURE
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BELTSVILLE, MD.

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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.

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.

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		50-ml. starch dispersion in 100 ml. total volume Sodium acetate added None	
	None	2 ml. 4 *N*	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.

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

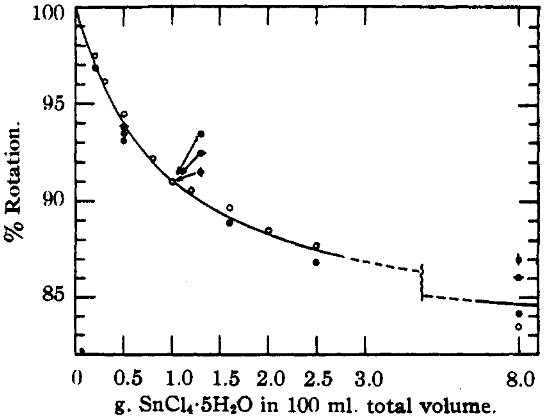

Fig. 1.—Rotation of dispersions of several starches in the presence of different concentrations of stannic chloride: ●, sweet potato; ○, white potato; -ϴ-, corn; ⦶, wheat.

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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).