

that the study of yeast nutrilites and attempts to isolate them are not interesting alone from the standpoint of the yeast itself but also from the standpoint of higher organisms, since substances which stimulate yeast growth are present in practically all plant and animal tissues and may be presumed to have some function in these tissues.

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### Summary

1. Experiments with Wildiers' original yeast culture shows that his "bios" is not readily absorbed by fuller's earth and appears to be the same as the nutrilitite which stimulates the growth of Gebrüde Mayer yeast. No conclusive evidence of its multiple nature is available.

2. The yeast nutrilitites studied by W. L. Miller and his associates are shown to be distinct from the "bios" of Wildiers. The Toronto workers should be credited with the discovery of a new series of yeast nutrilitites.

3. Yeast No. 578 of the American Type Culture Collection and old process baker's yeast appear to have more complex requirements than Wildiers' yeast. Evidence is presented for the existence of a fourth distinct nutrilitite concerned in the growth stimulation of yeast No. 578. It seems reasonable to suspect that several of the nutrilitites for this yeast may be components of "vitamin B," since the antineuritic vitamin has previously been shown to affect its growth very strikingly.

EUGENE, OREGON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

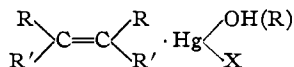
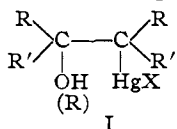
## THE STRUCTURE OF THE COMPOUNDS PRODUCED BY THE ADDITION OF MERCURIC SALTS TO OLEFINS. II

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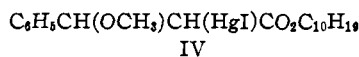
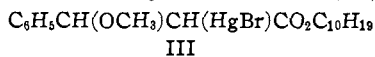
Some time ago a communication<sup>1</sup> from this Laboratory described optically active isomers of an addition product of an olefin of the type  $RR'C=CR'R'$  with a mercuric salt. The conclusion was drawn that the existence of these isomers furnished evidence for believing that such addition products should be represented by ordinary structural formulas (I) rather than as molecular addition products (II).



II

<sup>1</sup> Sandborn with Marvel, THIS JOURNAL, 48, 1409 (1926).

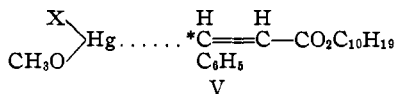
The particular products which have been described previously are two optically active isomers of *l*-menthyl  $\beta$ -methoxy- $\alpha$ -bromomercuri-hydrocinnamate (III) and two optically active isomers of *l*-menthyl  $\beta$ -methoxy- $\alpha$ -iodomercuri-hydrocinnamate (IV).



These products were prepared by adding mercuric acetate to *l*-menthyl cinnamate in methyl alcohol solution and converting the acetoxymercuri derivative thus obtained to the corresponding halide. Since there are two asymmetric carbons produced by the addition of the methoxy and acetoxymercuri groups to the cinnamic ester, it is theoretically possible for four optically active forms of each of these addition products to exist. However, as is often the case in such addition reactions, all of these theoretically possible isomers were not obtained.

Although the isolation of two active isomers of each compound seemed sufficient to establish the fact that these substances were compounds whose structures could be represented best by ordinary valence bonds, it has seemed worth while to attempt to prepare other addition products which might yield the theoretical number of isomers. In the work described in this communication the unsaturated compounds studied were the *l*-menthylamide of cinnamic acid, *d*- and *l*-*sec.*-octyl cinnamates and *d*-bornyl cinnamate. Only the last of these gave stable crystalline derivatives useful for the separation of isomers. However, here, as in the case of the *l*-menthyl cinnamate, only two optically active isomers were obtained.

Reference should be made to a suggestion by Piccard<sup>2</sup> in which he has pointed out that another assumption can be made which will account for two optically active isomers of such addition products without assuming that the mercury derivatives are of the ordinary valence type. This unusual assumption is that the addition product is represented by formula V.



The carbon marked with the asterisk is a coördination center of a molecular addition product and may be optically active.

The work in this paper does not support or detract from this last suggestion but is further evidence of the fact that the addition products of mercuric salts and olefins are capable of optical isomerism.

### Experimental Part

*l*-Menthylamide of Cinnamic Acid.—A solution of 16 g. of cinnamoyl chloride in 50 cc. of dry benzene was added slowly and with shaking to a solution of 31 g. of *l*-menthyl-

<sup>2</sup> Piccard, private communication. See also Pfeiffer, *Naturwissenschaften*, **14**, 1100 (1926).

amine in 100 cc. of dry benzene. The rate of addition was regulated so as to avoid marked increase in temperature. *l*-Menthylamine hydrochloride separated from the solution. When the reaction was complete the mixture was filtered with suction and the precipitate of amine hydrochloride was washed with a little dry benzene. The benzene was evaporated from the filtrate and the amide was recrystallized from methyl alcohol. The yield was 13 g. (47% of the theoretical amount) of a product which melted at 158–159°.

*Anal.* Subs., 1.0010, 1.0010: 47.35, 47.2 cc. of *N*/14 HCl. Calcd. for  $C_{10}H_{27}ON$ : N, 4.9. Found: N, 4.73, 4.7.

*Specific rotation.* Solvent, methyl alcohol; subs., 0.5380, 0.5579; volume of solution, 15 cc.; length of tube, 1 dm.; temperature, 25°;  $\alpha$ ,  $-2.96^\circ$ ,  $-3.09^\circ$ ;  $[\alpha]_D^{25}$   $-82.3^\circ$ ,  $-82.9^\circ$ .

When the amide in methyl alcohol solution was treated with mercuric acetate, a compound containing mercury was obtained, but its instability rendered it unsuitable for fractional crystallization.

*d*- and *l*-2-Octyl Cinnamates.—A mixture of 11 g. of *d*-octanol-2 and 14 g. of cinnamoyl chloride was heated for two hours over a low flame. The resulting brown liquid was distilled under reduced pressure. There was thus obtained 16 g. (73% of the theoretical amount) of a product which boiled at 174–177° (5 mm.). In the same way 13 g. of *l*-octanol-2 and 18 g. of cinnamoyl chloride gave 12 g. (50% of the theoretical amount) of the levo isomer, b. p. 175–180° (6 mm.).

*Analysis* of the dextro isomer. Subs., 0.1611;  $CO_2$ , 0.4626;  $H_2O$ , 0.1337. Calcd. for  $C_{17}H_{24}O_2$ : C, 78.40; H, 9.29. Found: C, 78.31; H, 9.28.

The specific rotations were determined in ethyl acetate solution. *d*-Ester. Subs., 0.5645; volume of solution, 15 cc.; length of tube, 1 dm.; temperature, 30°;  $\alpha$ ,  $+1.6^\circ$ ;  $[\alpha]_D^{30}$   $+42.4^\circ$ . *l*-Ester. Subs., 0.5164; volume of solution, 15 cc.; length of tube, 1 dm.; temperature, 27°;  $\alpha$ ,  $-1.49^\circ$ ;  $[\alpha]_D^{27}$   $-43.3^\circ$ .

When either of the esters was treated with a methyl alcohol solution of mercuric acetate, reaction occurred, as shown by the absence of mercuric ions at the end of nine days. The addition products proved to be very low melting and were not isolated and purified as they were unsuited for extensive fractional crystallization. The addition products were treated with alcoholic sodium bromide but the bromo compounds were also too low melting to be satisfactory for fractional crystallization.

*d*-Bornyl Cinnamate.—This ester was prepared in 85% yields from *d*-borneol and cinnamoyl chloride. The product thus obtained boiled at 200–202° at 6–7 mm. Minguin and Bollemont,<sup>3</sup> described the product as a solid melting at 33°. Hilditch<sup>4</sup> described it as a yellow liquid boiling at 226–230° at 27 mm. with a specific rotation of  $+29.05^\circ$  in chloroform solution and  $+29.10^\circ$  in acetone solution.

*Specific Rotation.* Solvent, methyl alcohol; subs., 1.4252, 1.3383; volume of solution, 15 cc., 20 cc.; length of tube, 1 dm., 2 dm.; temperature, 27°;  $\alpha$ ,  $+3.13^\circ$ ,  $+4.4^\circ$ ;  $[\alpha]_D^{27}$   $+32.8^\circ$ ,  $+32.9^\circ$ . Solvent, ethyl acetate; subs., 2.2256; volume of solution, 20 cc.; length of tube, 2 dm.; temperature, 27°;  $\alpha$ ,  $+7.18$ ;  $[\alpha]_D^{27}$   $+32.3^\circ$ .

*d*-Bornyl  $\beta$ -Methoxy- $\alpha$ -acetoxymercuri-hydrocinnamate.—A solution of 10 g. of *d*-bornyl cinnamate in 20 cc. of absolute methyl alcohol was added to a solution of 11 g. of mercuric acetate in 100 cc. of absolute methyl alcohol. The reaction was complete after eight days at room temperature. The methyl alcohol was evaporated and the residue was washed with water and dried. The crude product was then analyzed and found to be the desired addition product.

<sup>3</sup> Minguin and Bollemont, *Compt. rend.*, **136**, 238 (1903).

<sup>4</sup> Hilditch, *J. Chem. Soc.*, **93**, 7 (1908).

*Anal.* Subs., 0.1948: Hg, 0.0667. Calcd. for  $C_{22}H_{30}O_5Hg$ : Hg, 34.82. Found: Hg, 34.24.

The product thus obtained behaved like a mixture. After crystallization from methyl alcohol or petroleum ether the product melted over the range 90–100°. When the material was fractionated, samples were obtained which melted at 98–100°, 92–98°, 89–92°. However, these fractions had almost the same specific rotations (+11.3°, +13.4° and 10.8°, respectively), and mixed melting point determinations showed that they were mixtures. Apparently the isomers of the acetate compound were not separated by crystallization.

*d*-Bornyl  $\beta$ -Methoxy- $\alpha$ -bromomercuri-hydrocinnamate.—A solution of 20 g. of *d*-bornyl cinnamate in 50 cc. of absolute methyl alcohol was added to a solution of 22 g. of mercuric acetate in 250 cc. of absolute methyl alcohol. After two weeks the mixture was filtered to remove a small amount of precipitate and the methyl alcohol was evaporated under reduced pressure. The white solid was washed with water to remove acetic acid and mercuric acetate and dried. The yield of crude acetate was 45 g. This product was dissolved in about 200 cc. of absolute methyl alcohol and treated with a solution of 10 g. of sodium bromide in the same solvent. Crystals began to separate in a very short time. The first crop of crystals was filtered after one day. After recrystallization from petroleum ether this product melted at 131–132° (A). The next fraction to be isolated from the methyl alcohol was recrystallized from petroleum ether and it melted at 120–124°. Finally a third fraction (weighing 13 g.) of the addition compound was obtained. After recrystallization from petroleum ether it melted at 147–148° (B). A mixture of the first and third fractions melted at 120–125°. No further material separated from the reaction mixture even after standing for six months. About one centimeter of brown oil remained after the alcohol was evaporated.

The two bromo compounds were analyzed and rotations were determined.

Compound (A), m. p. 131–132°.

*Anal.* Subs., 0.2484: Hg, 0.0832. Calcd. for  $C_{20}H_{27}O_3HgBr$ : Hg, 33.7. Found: 33.5.

*Specific rotation.* Subs., 0.1505; volume of solution, 15 cc.; solvent, ethyl acetate; length of tube, 1 dm.; temperature, 25°;  $\alpha$ , +0.17°;  $[\alpha]_D^{25}$  +17.3°.

Compound (B), m. p. 147–148°.

*Anal.* Subs., 0.2332: Hg, 0.0771. Calcd. for  $C_{20}H_{27}O_3HgBr$ : Hg, 33.7. Found: Hg, 33.1.

*Specific rotation.* Subs., 0.1050; volume of solution, 15 cc.; solvent, ethyl acetate; length of tube, 1 dm.; temperature, 25°;  $\alpha$ , +0.10°;  $[\alpha]_D^{25}$  +14.9°.

### Summary

1. Two optical isomers of *d*-bornyl  $\beta$ -methoxy- $\alpha$ -bromomercuri-hydrocinnamate have been characterized.

2. The *l*-menthylamide of cinnamic acid and the *d*- and *l*-*sec.*-octyl esters of cinnamic acid have been characterized. The mercuric acetate addition products of these compounds were found to have physical properties which made it impractical to attempt to separate them into isomers by crystallization.