This technique greatly increases the specificity of the fermentation method and an investigation of the conditions necessary for its application to substances like animal tissue and

excreta is under way.

THE FLEISCHMANN LABORATORIES STANDARD BRANDS INCORPORATED 810 GRAND CONCOURSE NEW YORK, N. Y. RECEIVED SEPTEMBER 16, 1938

# COMMUNICATIONS TO THE EDITOR

#### CRYSTALLINE COPPER-PROTEIN POSSESSING TYROSINASE ACTIVITY

Sir:

A crystalline material has been obtained from the aqueous extract from the wild mushroom, *Lactarius piperatus*, which may be phenol oxidase, or closely related to it. The crystals were six-sided plates and undoubtedly belonged to the hexagonal system. They were insoluble in water, dilute acids and salt solutions, but soluble in an aqueous solution of secondary sodium phosphate. Analysis showed a copper content of 0.25 and 13.6% nitrogen. Their phosphate solution was active in promoting the aerobic oxidation of pcresol and catechol.

The procedure followed in obtaining the crystals can be described briefly as follows. The aqueous extract of the ground mushrooms was precipitated with 0.6 saturated ammonium sulfate, redissolved in water, the latter made 0.2saturated with ammonium sulfate and the precipitate discarded. The filtrate obtained in the last operation was reprecipitated with 0.6 saturated ammonium sulfate, the precipitate formed redissolved in water and the solution treated with three volumes of cold acetone. The precipitate thus obtained was dissolved in water and treated with alumina. The liquid separated from the alumina contained about 50% of the active oxidase. This liquid was treated with boneblack and after filtering the filtrate was again precipitated with 0.6 saturated ammonium sulfate. The precipitate from the last operation was taken up in water and had an activity of 7000 units per cc. when determined according to the Graubard and Nelson method as modified by Adams and Nelson [THIS JOURNAL, 60, 2472 (1938)]. When this liquid was gradually acidified by acetic acid,

changing the pH from 6.5 to 5, and allowed to stand in the ice box, crystals separated.

DEPARTMENT OF CHEMISTRY	HAROLD R. DALTON
Columbia University	J. M. Nelson
New York City	-
RECEIVED NOVEMB	er 25, 1938

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#### TETRAMETHYLPLATINUM AND HEXAMETHYLDI-PLATINUM

Sir:

Tetramethylplatinum has been prepared in 46%yield from trimethylplatinum iodide and methylsodium. It is the most soluble organoplatinum compound so far prepared, being readily soluble in the cold in benzene, acetone, ether and petroleum ether (b. p.  $60-68^{\circ}$ ). The compound crystallizes from petroleum ether as large hexagonal crystals which decompose but do not melt at elevated temperatures. Anal. Pt, 76.84; C, 18.32; H, 4.31. We have found that the compound is one of several by-products of the Pope and Peachey [J. Chem. Soc., 95, 571 (1909)] reaction for the preparation of trimethylplatinum iodide from platinic chloride and methylmagnesium iodide. Hydrogen chloride converts tetramethylplatinum to trimethylplatinum chloride. Anal. Pt, 70.20; Cl, 13.10.

Hexamethyldiplatinum has been synthesized in 60% yield by heating trimethylplatinum iodide with powdered potassium in dry benzene. Anal. Pt, 81.13; C, 14.55; H, 3.92. The compound is very soluble in benzene, acetone and ether, but only slightly soluble in cold petroleum ether. It is best crystallized from a benzene-petroleum ether solution. Molecular weight determinations show that hexamethyldiplatinum is not dissociated at the freezing point of benzene [mol. wt.: calcd., 480.4; found, 482]. Iodine in ether converts the compound to the known trimethylplatinum iodide.

These two organoplatinum compounds are interesting because they demonstrate for the first time that true organoplatinum compounds not having acid radicals can be prepared. A detailed account of these and other organoplatinum compounds will be published shortly.

THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE M. LICHTENWALTER AMES, IOWA

RECEIVED OCTOBER 31, 1938

# THE IDENTIFICATION OF METHYLCHAVICOL IN AMERICAN GUM SPIRITS OF TURPENTINE

Sir:

Recent investigations have shown that gum spirits of turpentine of slash and longleaf pine contain about 95% of pineues [Dupont, Ann. chim., [10] 1, 184 (1924); Aschan, "Naftenföreningar, Terpener och Kamferarter," Helsingfors, 289 (1926); Palkin, Technical Bulletin 596, U. S. Department of Agriculture (1932)]. We have been able to obtain physical and chemical evidence, including the fact that homoanisic acid is obtained on oxidation, that the fractions boiling above those of the pineues contain considerable amounts of methylchavicol (4-methoxyallylbenzene).

This was shown by the isolation of methylchavicol from turpentine by the method described by Balbiano [Ber., 42, 1504 (1909)], for the separation of methylchavicol from anethole. Seventy-five grams of a fraction, b. p. 88-95° at 10 mm., obtained by fractionation of steam-distilled residues of spirits of turpentine was dissolved in 400 cc. of ether and shaken for one hour with a solution of 81 g. of mercuric acetate dissolved in 350 cc. of water. After separating the ether, the aqueous solution was heated for ten hours at 70-80° with 70 g. of sodium hydroxide and 80 g. of granulated zinc. The mixture was then distilled with steam, the distillate extracted with ether and the ether solution dried and distilled, leaving 8 g. of methylchavicol, the main fraction of which boiled at  $213-215^{\circ}$ ;  $d^{25}_{25}$  0.9600;  $n^{22}$ D 1.51372. Physical constants recorded in the literature are: b. p. 214-215° [Klages, Ber., 32, 1439 (1899); d<sup>21</sup> 0.9645; n<sub>D</sub> 1.5236; (Beilstein, "Handbuch der organischen Chemie," fourth edition, 6, 571 (1923)]. Ten grams of this product was oxidized at room temperature with 630 cc. of 4% potassium permanganate solution. After removal of manganese dioxide, the filtrate was evaporated to about one-third of its original volume and acidified with hydrochloric acid. The precipitated anisic acid was recrystallized from water and melted at  $184-185^{\circ}$  (corr.); yield, 2.5 g. Calcd. for C<sub>8</sub>H<sub>8</sub>O<sub>8</sub>: C, 63.18; H, 5.30. Found: C, 63.32; H, 5.46. The acid did not lower the melting point in the mixed melting point test with an authentic sample of this material.

The aqueous filtrate from which the anisic acid had been removed was evaporated to a small volume, extracted with ether and dried. The ether was distilled and about 0.3 g. of a substance, apparently homoanisic acid, was obtained. It was recrystallized from water and melted at 85.5- $86.5^{\circ}$ . Homoanisic acid melts at 85- $86^{\circ}$ [Pschorr, Wolfes and Buckow, *Ber.*, **33**, 172 (1900)]. Calcd. for C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>: C, 65.04; H, 6.07. Found: C, 65.30; H, 6.54.

We assume that the difference in odor between highly purified turpentine and American gum spirits of turpentine can be partly attributed to the presence of phenol ethers.

G. & A. LABORATORIES, INC. SAVANNAH, GEORGIA RECEIVED OCTOBER 28, 1938

## PANTOTHENIC ACID AS A GROWTH FACTOR FOR THE DIPHTHERIA BACILLUS

Sir:

It has been shown in experiments already presented elsewhere that  $\beta$ -alanine and nicotinic acid are essential for the growth of certain strains of the diphtheria bacillus [Mueller, Proc. Am. Exptl. Biol. Med., 36, 706 (1937)].  $\beta$ -Alanine has long been known to be a constituent of meat extract both in the free form and also combined with histidine in the compound carnosine, in which form it has also been shown to be available to the diphtheria bacillus [Mueller, J. Biol. Chem., 123, 421 (1938)]. In a personal communication, we have recently learned from Dr. R. J. Williams that pantothenic acid [Williams, et. al., This JOURNAL, 55, 2912 (1933); 60, 2719 (1938)] also yields  $\beta$ -alanine upon hydrolysis. Dr. Williams suggests, further, that  $\beta$ -alanine may be effective in producing growth with C. Diphtheriae only insofar as it serves as a building stone for the production of pantothenic acid, which may be the material actually required by the organism,