methanol as the milieu, gave the pure amine in yields of 80–86%. 5-Fluoro-2-toluidine was a colorless liquid, b. p. 100–101° (16 mm.),[3] n^{25}_D 1.5379.

Anal. Calcd. for C_7H_8FN: N, 11.21. Found: N, 11.15.[6]

The amino compound was interacted with acetic anhydride to give 5-fluoro-2-acetotoluidide in 96% yield. It separated from aqueous alcohol in the form of white prismatic needles, m. p. 133.5–134°.

Anal. Calcd. for $C_9H_{10}FNO$: N, 8.38. Found: N, 8.54.

4-Fluoranthranilic Acid.—Five and three-tenths grams (0.0317 mole) 5-fluoro-2-acetotoluidide was added to a solution (at 75–80°) containing 10.3 g. of magnesium sulfate heptahydrate and 14.5 g. of potassium permanganate in 750 cc. of water. The mixture was stirred at 75–80° for two hours, then filtered and the filtrates acidified with dilute sulfuric acid. When crystallized from aqueous ethanol, 4.95 g. (79%) of 4-fluoroacetylanthranilic acid was obtained; the white platelets melted 209–209.5°.

Anal. Calcd. for $C_9H_8FNO_3$: N, 7.10. Found: N, 7.04.

Hydrolysis of the acetyl compound with boiling 6 *N* hydrochloric acid or 6 *N* sodium hydroxide gave 78–85% yields of 4-fluoroanthranilic acid. The compound crystallized from water as white needles of melting point 192.5–193°.

Anal. Calcd. for $C_7H_6FNO_2$: C, 54.19; H. 3.90; N, 9.03. Found: C, 54.07; H, 3.65; N, 9.11.

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(6) All analyses were carried out under the direction of Mr. M. E. Auerbach in the analytical laboratories of this Institute.

THE STERLING-WINTHROP RESEARCH
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RECEIVED SEPTEMBER 13, 1947

Ethyl α-Ethoxalylvalerate

The Claisen reaction of diethyl oxalate with ethyl valerate[1] was carried out in dry benzene using commercial sodium methoxide in essentially the manner described for ethyl α-ethoxalylpropionate.[2] An excess of ethyl valerate was used. The crude ester was difficult to distil satisfactorily, and the pure ethyl α-ethoxalylvalerate was obtained in yields of 20–24.5%, based upon diethyl oxalate employed; a 25-cm. vacuum-jacketed Vigreux column was required in the distillation, b. p. 78–80° (0.2 mm.), n^{25}_D 1.4319. This compound was prepared, but not obtained in a pure condition, by Adickes and Andresen.[3]

Anal. Calcd. for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found[4]: C, 57.18; H, 7.66.

To determine the position of entrance of the ethoxalyl group, a sample of the ester was heated at 165–175° with powdered glass during three hours. Decarbonylation led to a 53% yield of diethyl propylmalonate, b. p. 78–80° (2 mm.), n^{25}_D 1.4201. An authentic sample of the malonic ester boiled at 79–81° (2 mm.), n^{25}_D 1.4206.

The **2,4-dinitrophenylhydrazone**, prepared in the customary fashion, separated from 80% alcohol in the form of golden leaflets, m. p. 87–87.5° (lit.[3] value, 85–86°—only this derivative was prepared, using crude ester).

Anal. Calcd. for $C_{17}H_{22}N_4O_8$: N, 13.65. Found: N, 13.80.

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(1) Purchased from Northeastern Chemical Co., Wauwatosa, Wis.

(2) Steck, Hallock and Holland, THIS JOURNAL, **68**, 131 (1946).

(3) Adickes and Andresen, *Ann.*, **555**, 55 (1943).

(4) All analyses were carried out under the direction of Mr. M. E. Auerbach in the analytical laboratories of this Institute.

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RECEIVED SEPTEMBER 13, 1947

COMMUNICATIONS TO THE EDITOR

THE STRUCTURE OF CITRININ

Sir:

Hetherington and Raistrick[1] degraded citrinin (I, $C_{13}H_{14}O_5$) with dilute acid to II ($C_{11}H_{16}O_3$), which was fused with alkali to give III ($C_9H_{12}O_2$), which in turn was methylated and oxidized to two carboxylic acids IV ($C_{11}H_{14}O_4$) and V ($C_{10}H_{12}O_4$). The compound 4-methyl-5-ethylresorcinol has now been synthesized by two methods, and a comparison of this substance with III (prepared from citrinin) shows that they have the same structure. Two acids, 2-ethyl-4,6-dimethoxybenzoic acid and 2-methyl-3,5-dimethoxybenzoic acid have also been synthesized, and their properties correspond to those reported for IV and V, respectively. No degradation products of citrinin have been previously synthesized.

Formylation of 5-ethylresorcinol[2] with zinc cyanide and hydrogen chloride produced 2-ethyl-4,6-dihydroxybenzaldehyde[3]; the two phenolic hydroxyl groups were methylated to give 2-ethyl-4,6-dimethoxybenzaldehyde, which was in turn oxidized to 2-ethyl-4,6-dimethoxybenzoic acid, m. p. 99–100° (Hetherington, *et al.*,[1] reported a melting point of 98–99° for IV).

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.76; H, 6.71.

Reduction of 2-ethyl-4,6-dimethoxybenzaldehyde to 2-methyl-3,5-dimethoxyethylbenzene, followed by demethylation of the two methoxyl groups produced 4-methyl-5-ethylresorcinol, m. p. 67–69°. A mixed melting point of this compound

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(1) Hetherington and Raistrick, *Trans. Roy. Soc.* (London), **B220**, 1–10 (1931).

(2) This compound was prepared by the procedure of Asahina and Ihara, *J. Pharm. Soc. Japan*, **48**, 28 (1928).

(3) This substance had been prepared previously by Geissman and Tulagin (unpublished work).

with III[4] prepared from citrinin gave no depression. The bis-(*p*-nitrobenzoate) of 4-methyl-5-ethylresorcinol was prepared (m. p. 205–6°) and compared with the bis-(*p*-nitrobenzoate) of III (m. p. 205–6°). A mixed melting point determination gave 205–206°. *Anal.* Calcd. for $C_{23}H_{18}O_8N_2$: C, 61.33; H, 4.03. Found: C, 61.50; H, 4.03.

Methylation of the hydroxyl groups of 2-methyl-3,5-dihydroxybenzoic acid (prepared by the method of Jacobsen and Wierss[5]) gave 2-methyl-3,5-dimethoxybenzoic acid, m. p. 157–158° (Hetherington, *et al.*,[1] reported m. p. 142–146° for V). *Anal.* Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.16; neut. equiv., 196.2. Found: C, 61.35; H, 6.55; neut. equiv., 195. This acid was converted to the amide which was treated with methylmagnesium bromide to give 2-methyl-3,5-dimethoxyacetophenone, m. p. 46–47°. Reduction of this ketone with hydrazine followed by demethylation produced 4-methyl-5-ethylresorcinol, m. p. 67–69°. Admixture of this sample with III or with the sample prepared from 5-ethylresorcinol produced no depression.

The above evidence completely eliminates the formulas advanced by Coyne, Raistrick and Robinson[6] for citrinin, II, III, IV and V.

Terminal-methyl number determinations were run on citrinin (2.68 and 2.76) and on II (2.57 and 2.51). Since II couples with two moles of benzenediazonium chloride in an apparently normal manner (Gore, *et al.*[4]), and since the molecule must have at least three terminal methyl groups, II would appear to be 4-methyl-5-(1-methyl-2-hydroxypropyl)-resorcinol. The synthesis of this substance has been undertaken.

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[4] Hetherington, *et al.*,[1] reported a melting point of 97–99° which changed to 65–70° after the sample stood for some time. Gore, Panse and Venkatarumen [*Nature*, 157, 333 (1946)] reported 65–70° and Spranger and Ruoff [*J. Org. Chem.*, 11, 189 (1946)] 67–70° as the melting point of III.

[5] Jacobson and Wierss, *Ber.*, 16, 1960 (1883).

[6] Coyne, Raistrick and Robinson, *Trans. Roy. Soc.* (London), B220, 297–300 (1931).

DEPARTMENT OF CHEMISTRY
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RECEIVED NOVEMBER 10, 1947

REDUCTION OF CARBON DIOXIDE TO METHANOL BY LITHIUM ALUMINUM HYDRIDE[1]

Sir:

Carbon dioxide is rapidly absorbed by lithium aluminum hydride in ether solution. From such mixtures formaldehyde was isolated, as the dimethone derivative and as hexamethylenetetramine, in yields not over 25%. Schlesinger and Finholt[2] found two moles of carbon dioxide absorbed per mole of hydride, which is consistent with reduction to the formaldehyde stage but does not exclude further reduction followed by partial carbonation of the resultant methoxide.

We then found that, with lithium aluminum hydride in excess, 0.75 mole of hydride is consumed per mole of carbon dioxide and hence that the reduction under these conditions proceeds to the methanol stage.

However, the isolation of methanol proved troublesome. The best of many different procedures for the recovery of small amounts of methanol from ether–water mixtures gave yields, based on carbon dioxide, of less than 50%. The conventional procedure for effecting reductions with lithium aluminum hydride was eventually abandoned in favor of one which is better with respect to yield and better adapted to isotopic synthesis since it involves fewer operations.

A relatively non-volatile solvent, diethyl carbitol, replaces diethyl ether, and a high-boiling alcohol, *n*-butylcarbitol, is used both to decompose the excess hydride and to liberate methanol by alcoholysis. Methanol, the most volatile component of the system, is then obtained in a simple distillation employing an inert entraining gas. The over-all process is shown below:

First Stage

$$4CO_2 + 3LiAlH_4 = LiAl(OCH_3)_4 + 2LiAlO_2$$

Second Stage (R = *n*-butylcarbityl)

$$LiAlH_4 + 4ROH = LiAl(OR)_4 + 4H_2$$

$$LiAl(OCH_3)_4 + 4ROH = LiAl(OR)_4 + 4CH_3OH$$

In a typical experiment, the carbon dioxide generated from 13.0 g. of barium carbonate by the slow addition of 30% perchloric acid, and diluted by a stream of nitrogen, was passed through drierite into a solution of 3.8 g. of lithium aluminum hydride in 500 cc. of diethyl carbitol. Shortly thereafter, 120 g. of *n*-butylcarbitol was added and, with continued flow of nitrogen gas, the mixture was heated. The product, collected in a trap cooled by a Dry Ice freezing mixture,[3] was redistilled to separate a small residue of high-boiling material and there was obtained as distillate 1.71 g. of methanol, $n^{20}\text{D}$ 1.3310, identified further as the N-(α-naphthyl)-carbamate, m. p. 124°. The yield of methanol was thus 81% based on barium carbonate. A small fraction, 1.7%, of unreacted carbon dioxide was collected in an ascarite tube through which the effluent gas passed.

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RECEIVED DECEMBER 16, 1947

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[1] Experimental work started at George Herbert Jones Laboratory, The University of Chicago, and continued at Clinton National Laboratory, Oak Ridge, operating under Contract No. W-35-058-eng-71 with the Atomic Energy Project.

[2] Schlesinger and Finholt, unpublished work.

[3] An improvement in yield might result from liquid nitrogen cooling since methanol is appreciably volatile at Dry Ice temperatures.

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