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 INSTITUTE
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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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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).