ing this period a thin slush formed. The temperature was then raised to 63–66° and maintained for ten minutes. The pale pink slurry was then chilled to 20–25°, 77 cc.[5] of 3 *N* hydrochloric acid added *cautiously* from a dropping funnel (ice-water cooling as required), resulting in a pale slightly cloudy solution.

The charge then was steam-distilled (about 90 cc. distillate) to remove the solvent, digested while hot with 0.3 g. of Norit and 0.2 g. of Filter-Cel and filtered with suction. The colorless filtrate was cooled to 0–5°, 10 cc. of concentrated hydrochloric acid added, then titrated at this temperature with molar sodium nitrite solution to a strong blue streak (ten minutes end-point) on starch-iodide paper. Almost the theoretical amount was required. During the titration pale yellow nitrosamine needles separated. The crystals were filtered with suction, washed with water and dried at 55°; yield 2.66 g., m. p. 134–135°. The filtrate, on extraction with ether, yielded an additional 0.12 g.; total yield 92%.

On recrystallizing the combined crops from 10% ethanol, in the presence of a little Norit, the m. p. was raised to 135.5°, identical with purified N-nitroso-N-methyl-*p*-aminophenol prepared from photographic Metol as shown by mixed m. p.

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[5] The first 20 cc. of 3 *N* hydrochloric acid must be fed very slowly, dropwise. During this period the main heat effect is evident and the bulk of the hydrogen gas evolved (by decomposition of the excess lithium aluminum hydride). Thereafter the balance may be added faster. Prior to the acid addition the calcium chloride tube is removed (*versus* any back pressure) and the flask vented to the hood.

CONTRIBUTION FROM THE
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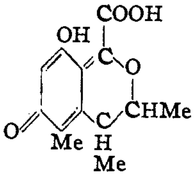
The Constitution of Citrinin

BY T. S. GORE, T. B. PANSE AND K. VENKATARAMAN

The structures originally assigned[1] to citrinin (I) and its degradation products (II) and (III) are untenable in the light of their behavior towards diazonium salts.[2] Cram[3] has now shown by synthesis and direct comparison that (III) is 4-methyl-5-ethylresorcinol, a conclusion at which we had arrived by circumstantial evidence. The 2,4 and 4,6-compounds were ruled out by the ability of (III) to form disazo dyes. Comparison of the absorption spectra and the color reactions of the bis-benzeneazo derivative of (III) with those of 2,4- and 4,6-bis-benzeneazoresorcinol and a series of analogous dyes showed that (III) is 5-methyl-4-ethylresorcinol (IV) or 4-methyl-5-ethylresorcinol (V). The absorption curves for 2,4-bis-benzeneazoresorcinol, 2,6-bis-benzeneazo-5-methyl-4-ethyl resorcinol and the bis-benzeneazo derivative of (III) had a well-defined, high intensity band in the visible region ($\lambda_{\text{max.}} \backsim 415$ mμ; $\epsilon_{\text{max.}} \backsim 60{,}000$). 4,6-bis-Benzeneazoresorcinol and 4,6-bis-benzeneazo-2-ethylresorcinol exhibited a band of relatively low intensity in the visible region ($\lambda_{\text{max.}} \backsim 415$ mμ; $\epsilon_{\text{max.}} \backsim 20{,}000$) and absorption maxima in the near ultraviolet ($\lambda_{\text{max.}} \backsim 340$ mμ; $\epsilon_{\text{max.}}$ 36,000).

Shah and Robinson's synthesis[4] of (IV) was repeated, and it was found to melt at 79–82° (Shah and Robinson, m. p. 75–80°), while (III) as a monohydrate melts at 68–69°, and after dehydration at 98–99°; the m. p. of (III) was considerably depressed by admixture with (IV). Cram[3] has quoted us erroneously as reporting a m. p. of 65–70° for (III). The bis-benzeneazo derivatives of (III) and (IV) melted, respectively, at 171° and 188°, and the mixed m. p. was lower. It followed therefore that (III) is 4-methyl-5-ethylresorcinol. However, this is in conflict with the observation of Hetherington and Raistrick[1] that neither of the acids obtained by oxidation of the dimethyl ether of (III) gave the anthrachrysone reaction. We prepared 3,5-dimethoxy-2-methylbenzoic acid (VII) by the methylation of the corresponding α-resorcylic acid,[5] and found that it readily gave a bordeaux-red color on warming with sulfuric acid (the anthrachrysone reaction); Cram has recorded that the acid (VI) synthesized by him corresponds in its properties to one of Hetherington and Raistrick's acids. The m. p. (157–158°) reported for (VI) by Cram is in agreement with ours, while Hetherington and Raistrick's two acids melted at 142–146° and 98–99°.

From the formulation of (III) as 4-methyl-5-ethylresorcinol, the properties of (II), including the formation of (III) from (II) by alkali fusion, are fully explained by the structure 4-methyl-5-(1-methyl-2-hydroxy)-propyl-resorcinol, proposed



by Cram. The experimental results of Hetherington and Raistrick[1] and the behaviour of citrinin towards diazonium salts[2] would then agree with the above constitution for citrinin.

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[1] Raistrick, Robinson, *et al.*, *Phil. Trans. Roy. Soc.*, **B220**, 269, 297 (1931).

[2] Gore, *et al.*, *Nature*, **157**, 333 (1946).

[3] Cram, THIS JOURNAL, **70**, 440 (1948).

[4] Shah and Robinson, *J. Chem. Soc.*, 1491 (1934).

[5] Woodward and Reed, THIS JOURNAL, **65**, 1569 (1943).

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The Employment of Sodium Hydride as a Condensing Agent

BY NATHAN GREEN AND F. B. LAFORGE

Sodium hydride is now being produced on a large scale, and its advantages as a catalyst in various organic reactions have been indicated by Hansley and Carlisle.[1] Its use in this Laboratory in the preparation of ethyl β-oxocaprylate, ethyl β-carbethoxy-α-oxo-enanthate, and 5-carbethoxydihydrocinerone has been described in previous articles.[2,3] We have since employed this reagent in

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[1] Hansley and Carlisle, *Chem. Eng. News*, **23**, 1332 (1945).

[2] Soloway and LaForge, THIS JOURNAL, **69**, 2677 (1947).

[3] LaForge and Soloway, *ibid.*, **69**, 2932 (1947).