

Curator, Anthropology Section for their keen interest in the work.

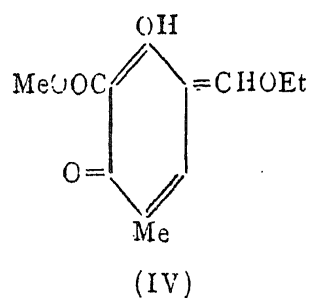
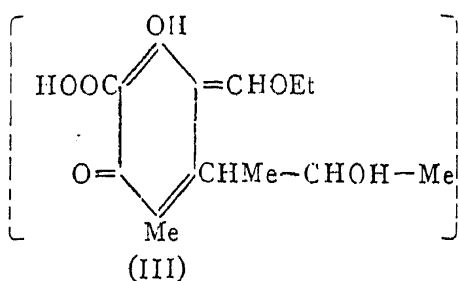
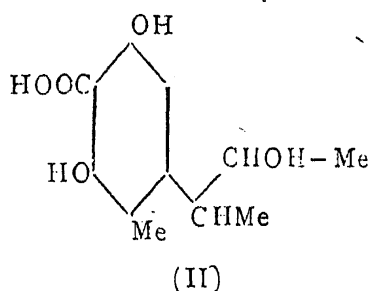
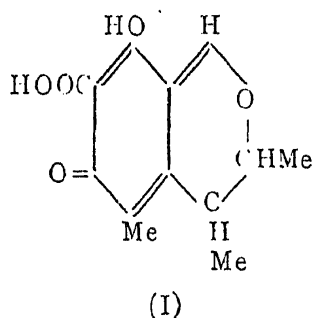
Chemical Laboratory, R. SUBRAMANIAN,  
Govt. Museum, Madras,  
December 31, 1949.

\* Manganese is reported as MnO; it need not necessarily be in that form.

1. Wheeler, R. E. M., *et al.*, *Ancient India* (Bull. of the Arch. Survey of India), July 1946, **2**, 17-124. 2. Farnsworth, M., and Ritchie, P. D., *Technical Studies*, (Harvard University), 1937-38 **6**, 157. 3. Lucas, A., *Ancient Egyptian Materials and Industries*, 1934, London: Arnold, p. 122; Farnsworth and Ritchie, *loc. cit.*, p. 164, footnote 37; Partington, J. R., *Origins and Development of Applied Chemistry*, 1935, Longmans, Green & Co., p. 130. 4. Jackson, Sir H., *Nature*, 1927, **119**, 401; 1927, **120**, 264 and 301. 5. *J. Physical Chemistry*, 1930, **34**, 1-40.

#### A NEW PARTIAL SYNTHESIS OF CITRININ

Two partial syntheses of citrinin (I) and its methyl ester, starting from "Product A" (the phenol produced by acid or alkaline hydrolysis of citrinin), have been described so far.<sup>1,2</sup> In one, due to Robertson, *et al.*,<sup>1</sup> the acid (II; prepared by carboxylation of Product A) or its methyl ester is submitted



to the Gattermann aldehyde synthesis and then, in a second step, cyclized with sulphuric acid; a yield of 33% is claimed.<sup>1</sup> Warren, *et al.*, heat (II) with methylal and benzene saturated with dry hydrogen chloride in a sealed tube at 60° for six hours; dihydrocitrinin is thus obtained and is oxidized to citrinin by bromine in chloroform.<sup>2</sup> A much simpler synthesis, which has interesting possibilities for synthesis in the isochromane series, has now been achieved. When (II) is treated at room temperature (28-30° C.) with about ten times its weight of ethyl orthoformate, a crystalline precipitate of citrinin separates rapidly from the yellow solution. After thirty minutes, crushed ice is added and the yellow needles of citrinin filtered, washed and dried. The m.p. (171.5°, dec.) is undepressed by admixture with natural citrinin, and the yield is nearly quantitative. The reaction apparently proceeds through the ethoxymethylene derivative (III), since a compound (IV) of this type is formed by the action of ethyl orthoformate, acetic anhydride and zinc chloride on the methyl ester of 4-methylresorcinol-2-carboxylic acid.

The behaviour of citrinin towards diazonium salts has now been completely elucidated.<sup>3</sup> In referring to our earlier note on the subject<sup>4</sup> and their own failure to isolate and characterize the products of the interaction of citrinin with diazonium salts, Robertson, *et al.*, have misrepresented the evidence on which we demonstrated the incorrectness of the structure assigned to citrinin by Coyne, Raistrick and Robinson;<sup>5</sup> the fact that Product A, as well as the methylethylresorcinol produced by alkali fusion of Product A, gave disazo dyes proved conclusively that the alkyl groups could not be in the 2:4-positions of resorcinol, and citrinin therefore could not possess the constitution which was accepted for many years.<sup>6</sup>