Communication to the Editor

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Mechanism of the Reaction between Fructose and Diphenylamine

Fructose gives a sensitive violet coloration with diphenylamine when heated in a mixture of methanol and hydrochloric acid.¹⁾ This reaction has been widely used In the detection and estimation of the sugar. The mechanism of the reaction was studied by several investigators,^{2~4)} but no satisfactory explanation is found in the literature. The main dye produced in the reaction was isolated in a crystalline form to clarify the mechanism.

The crude dye was extracted with a mixture of hydrous methanol and sulfuric acid to give a crystalline sulfate which was repeatedly recrystallized from 80% methanol in the presence of a small amount of sulfuric acid. The dye formed golden prisms of m.p. 198° (decomp.), gave almost the same visible-light absorption curve as that of the developed color. It has a probable formula of $C_{60}H_{50}O_{11}N_4S_2$ (Calcd.: C, 67.51; H, 4.73; O, 16.50; N, 5.25; S, 6.01. Found: C, 67.46; H, 5.24; O, 16.44; N, 4.96; S, 5.80), and showed neither hydroxyl nor carbonyl absorption band in its infrared spectrum. On the other hand, Thies and Kallinich⁴⁾ gave a molecular weight of about 810 to the free amorphous dye and supposed that it might be a derivative of triphenylmethane dye from its visible absorption spectrum. Therefore, a more probable structure of the crystalline dye might be written as follows:

$$\begin{bmatrix} H \\ -\overset{\cdot}{N} = & H \\ -\overset{\cdot}{N} = & \overset{\cdot}{N} - & \\ -\overset{\cdot}{N} - & & & \\ -\overset{\cdot}{H} & & & & \\ -\overset{\cdot}{H} & & & & \\ -\overset{\cdot}{N} - & & & \\ -\overset{\cdot}{H} & & & & \\ -\overset{\cdot}{N} - & & & \\ -\overset{\cdot}{H} & & & & \\ -\overset{\cdot}{N} - & & & \\ -\overset{\cdot}{H} & & & & \\ -\overset{\cdot}{N} - & & & \\ -\overset{\cdot}{H} & & & & \\ -\overset{\cdot}{N} - & & & \\ -\overset{\cdot}{H} & & & \\ -\overset{\cdot}{N} - & & & \\ -\overset{\cdot}{H} & & & \\ -\overset{\cdot}{N} - & & & \\ -\overset{\cdot}{H} & & & \\ -\overset{\cdot}{N} - & & \\ -\overset{\cdot}{H} & & & \\ -\overset{\cdot}{N} - & & \\ -\overset{\cdot}{H} & & & \\ -\overset{\cdot}{N} - & & \\ -\overset{\cdot}{N} -$$

This assumption might be confirmed by the fact that 5,5'-diformyldifurfuryl ether⁵⁾ gave the same dye in higher yield when heated with diphenylamine in a mixture of methanol and hydrochloric acid. Fructose may first form 5-hydroxymethylfurfural in the color reaction and the dehydration might occur to give the ether which would form the above derivative of triphenylmethane dye with diphenylamine.

Details of these experiments will be published in the near future.

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³⁾ L. Radlberger: Österr.-ung. Z. Zuckerind. u. Landwirtsch., 44, 261(1915)