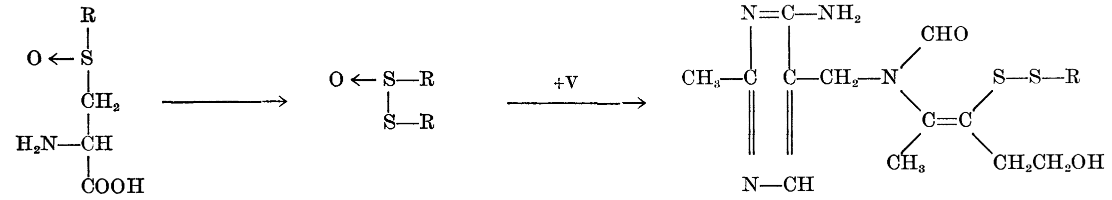

IX $R = -CH_2-CH=CH_2$
X $R = -CH_3$
XI $R = -CH_2-CH_2-CH_3$

XII $R = -CH_2-CH=CH_2$

I $R = -CH_2-CH=CH_2$
II $R = -CH_3$
III $R = -CH_2-CH_2-CH_3$

The present authors have already established that allithiamine (I) is formed by the reaction between the thiol form thiamine (V) and allicin (XII) (*7*), a secondary ingredient of the garlic produced by the enzymatic decomposition of alliin (*8*).

On the other hand, it was found that, when the plants other than the garlic given in Table 1 were treated beforehand with boiling water to inactivate the enzyme, they lost the ability to form allithiamine or its homologs. This fact shows that in the reactions of thiamine and these plants, the secondary ingredients produced by the enzymatic decomposition of the original ingredients take part in the reactions.

From these facts it is presumed that the plants which produce (II) and (III) would then contain new alliin-like ingredients having methyl (X) and propyl (XI) groups respectively, instead of the allyl group of alliin (IX) and that the methyl homolog (X) exists in the plants of *Allium* genus more extensively than alliin (IX).

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The Iron(III)-Phenol Complex in Aqueous Solution

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The nature of purple complex produced by the reaction of phenol with iron(III) chloride in aqueous solution still remains in some question in spite of the many studies made upon the system. The composition $[Fe(OC_6H_5)_3]$ was perhaps first suggested by Raschig's early observations (*1*), using a substituted phenol, and was apparently confirmed by the colorimetric studies of Claasz (*2*). On the other hand, reaction in a 4:1 mole ratio to give an acidic species, $H[Fe(OC_6H_5)_4]$, was indicated by the work of Weinland and Binder (*3*). In a comprehensive study of a large number of systems derived from various phenols and iron(III) chloride, Wesp and Brode (*4*) obtained a single broad band in the absorption spectrum of each system, the position of the band depending upon the phenol used. With phenol itself, this absorption band centered at 558 mμ, the intensity of the absorption at this wavelength being increased by either added iron(III) or phenol, and obeying Beer's law in moderate concentrations. Wesp and Brode reported further that the colored species is destroyed by either acid or alkali and concluded on the basis of ion migration behavior that the composition of the species is $[Fe(OC_6H_5)_6]^{-3}$. Babko (*5*), on the other hand, suggested the presence of the cation $[Fe(OC_6H_5)]^{+2}$ and found its complete formation to be impossible.

On the basis of thermometric and conductimetric titration data, Banerjee and Haldar (*6*) reported reaction of phenol with iron(III) chloride in both 3:1 and 6:1 mole ratios. Inasmuch as Job's method of continuous variations (*7, 8*) showed reaction in only the 3:1 ratio, no partition between aqueous and organic phases could be detected, and ion migration indicated the presence of anionic iron, it was proposed that the colored species has the composition $Fe[Fe(OC_6H_5)_6]$. More recently, however, it has been shown that *m*-cresol gives a neutral 3:1 species with iron (III) and no anionic $[Fe(OAr)_6]^{-3}$ species (*9*). On the other hand, spectrophotometric data have also indicated formation of a number of species of the type $[Fe(OAr)]^{+2}$ with phenols and naphthols (*10*), although the phenol complex itself was not studied because of its instability.

Lack of consistency among these reports prompted a further study of the phenol-iron(III) chloride system. In aqueous solutions, the color is destroyed by heat and by alkalies, precipitation of hydrous iron(III) oxide occurring in both instances. The color is stable in the pH range 1.7–3.0 but is destroyed by additional acid. Best results in producing color systems of reasonable stability were obtained at pH 2.2. Even at optimum pH, the color intensity first increases for some 2 hr and then decreases with time until after some 12 hr or more a purple solid is precipitated. Dialysis also yields a purple flocculate. Microanalyses

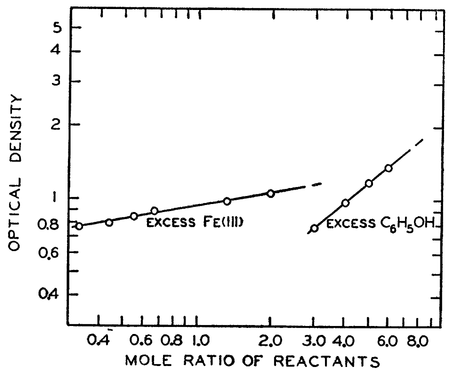

FIG. 1. Effect of excess reagent upon the optical density of the iron(III) chloride-phenol system at 600 mμ.

of these residues gave inconsistent results showing no conceivable phenol-iron(III) ratios, suggesting that the colored solid is not the same as the colored species in solution but is rather an adsorption or hydrolysis product, or both.

Spectrophotometric studies on solutions of phenol to iron(III) mole ratios of 0.5 : 1, 1 : 1, 2 : 1, 4 : 1, 6 : 1, 10 : 1, and 20 : 1 indicated in all instances a single broad absorption band centering at 550–560 mμ, in agreement with the observations of Wesp and Brode (*4*). Similarities existent among all these spectra suggest strongly the presence of but a single colored species. Application of the method of continuous variations (*7, 8, 11*) to systems prepared from 0.079 *M* phenol and iron(III) chloride solutions at wavelengths of 450, 555, 600, and 700 mμ indicated reaction in only the 3 : 1 ratio, in agreement with the results of Banerjee and Haldar (*6*). The formal composition of the colored complex must then be $[\mathrm{Fe(OC_6H_5)_3}]$.

Beer's law is obeyed over the concentration range ca. 0.007–0.02 *M*, but significant deviations are noted at lower concentrations. Addition of either excess phenol or excess iron(III) in these low concentration ranges decreases deviations from Beer's relationship.

These observations are in general agreement with an equilibrium picture of the system as represented by the expression

$$\mathrm{Fe}^{+3} + 3\mathrm{C_6H_5OH} \rightleftharpoons [\mathrm{Fe(OC_6H_5)_3}] + 3\mathrm{H}^+ \qquad (1)$$

This equilibrium apparently is established somewhat slowly, as evidenced by the observed increase in color intensity after mixing the reactants, and is complicated by subsequent reactions leading to precipitation. That the equilibrium involves appreciable quantities of unreacted iron(III) and phenol is evidenced both by the data of the Beer's law studies and by those summarized in Fig. 1. These results on the increases produced in optical density at 600 mμ by additions of phenol and iron(III) chloride beyond a 3 : 1 stoichiometry show clearly how the concentration of the colored species depends upon the quantities of reactants present. Since optical density is a direct measure of the concentration of the species $[\mathrm{Fe(OC_6H_5)_3}]$, comparison of the slopes of the two curves (0.84 for excess phenol and 0.18 for excess iron(III)) indicates that these reagents are effective in increasing the quantity of the complex present at equilibrium roughly in accordance with predictions based upon Eq. 1. Instability of the complex precludes closer agreement.

In an electric field, the purple color does not appear to migrate. Although there are some indications of the presence of both cationic and anionic iron, the presence of unreacted iron(III) chloride in the equilibrium system and the probability of its existing in both cationic and anionic forms render inconclusive any suggestions that these ionic species are phenol complexes. It seems best to conclude that the major, and very probably the only, colored species is molecular $[\mathrm{Fe(OC_6H_5)_3}]$. That this material does not extract into organic solvents is perhaps due to its polar nature or even to excessive agglomeration, as indicated by its failure to pass through a dialyzing membrane.

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