compounds and no evidence was found for Fe(OR)$_6^{---}$. It is possible that other maxima might be observed at different concentrations and wave lengths. For ethyl acetoacetate, the ferric chloride is believed to react with the cis enol form.[5] Letellier[6] has reported that the maximum of color exists at the ratio of 1 ferric chloride:2 ester in water. The existence of other complex ions has been demonstrated.[7]

The concentration of OR ions may be an important factor in determining which particular complex is formed.[1] It is of interest, therefore, to compare the ionization constants of the organic compounds used. The classical dissociation constants in water at 25° for salicylaldehyde and *m*-cresol are 1.53×10^{-5} [8] and 0.98×10^{-10},[9] respectively. Using the relationship[10]

$$K_a = K_g(1 + K_E)/K_E \qquad (1)$$

where K_a is the classical dissociation constant of the enol form, K_g is the classical dissociation constant, and K_E is the enol–keto equilibrium constant results in a value of 2.9×10^{-10} for K_a for ethyl acetoacetate in water at 25°. Values of 2.09×10^{-11} [10] for K_g and 0.078[5] for K_E were used. Thus it is the more acidic compound, salicylaldehyde, which forms the 1:1 complex. This may be due to steric influences between the ortho CHO group and the hydrated ferric ion.

In regard to electrolysis experiments, Wesp and Brode[1] reported that the phenol complex migrates toward the cathode, while Bent and French[2] claim the color migrates toward the anode. Our results show that the complexes for *m*-cresol and ethyl acetoacetate are neutral; the salicylaldehyde complex should migrate toward the cathode. The observed disappearance of color may be due to the instability of the complex. Due to the neutral nature of the *m*-cresol and ethyl acetoacetate complexes it is essential to establish the existence of the RO$^-$ complex rather than a possible ROH complex. A determination of the *p*H of the solutions as the complexes are formed may prove fruitful in establishing this fact.

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Cevine, a Correction

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In a previous study of the infrared absorption spectra of a number of alkaloids[1] we reported the presence of a carbonyl absorption band in the infrared spectrum of cevine and concluded that this alkaloid contained a carbonyl group. At the suggestion of Dr. H. L. Holmes we re-examined the base on which our observation had been made and found that it consisted not of cevine but of one of the minor alkaloids occurring with it. This alkaloid which is obtained like cevine by saponification of crude veratrine, crystallizes in short prismatic needles melting at 266–270.5° whereas cevine melts at 164–174°. The infrared absorption spectrum of an authentic sample of cevine *does not* contain a carbonyl absorption band.

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Additional Studies on the Intramolecular Hydrogen Bonding in Acetylglycine N-Methylamide

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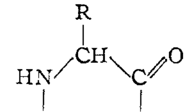
In a previous paper[1] we reported our experimental results of near infrared absorption observed for $CH_3CONHCHRCONHCH_3$ and $CH_3CONHCHRCONHC_6H_5$ (R = H or C_4H_9) in dilute carbon tetrachloride solutions. All these compounds show two NH bands at about 2.9 μ and 3.0 μ of which the former is assigned to the vibrations of the NH group in the free state and the latter to that involved in the ***intramolecular*** hydrogen bonding of the structure



which corresponds to "B form" (one of the two unit structures of a polypeptide chain) proposed by us in 1947.[2] In view of the importance of proving the existence of B form in the structural chemistry of proteins we have recently made additional measurements of the near infrared absorption, the results of which will be reported in the present note.

In order to obtain further information concerning the relation between molar absorption coefficient κ and concentration c for these two NH bands measurements were made at 60° on carbon tetrachloride solutions of acetylglycine N-methylamide $CH_3CONHCH_2CONHCH_3$ of different concentrations c and absorption path-lengths l, keeping the product $c \times l$ constant. The results are shown in Fig. 1. If these two NH bands arise solely from single molecules and not from associated molecules (*intermolecular* hydrogen bonding), all the curves (1), (2) and (3) of Fig. 1 must be of the same form. Actually they are found almost of the same form, but differ slightly from one another.

Let us now consider to what extent these three absorption curves should differ from one another, if the 2.98 μ band were to be assigned solely to the *intermolecularly* hydrogen-bonded NH vibration (*i.e.*, solely to the NH association band). Since

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