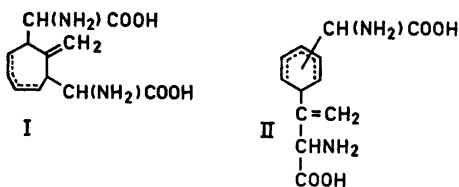


was obtained in much better yield. This saturated dialdehyde gave with silver oxide a dicarboxylic acid $C_{10}H_{16}O_4$ (Found: C 60.34; H 8.10. Calc. for $C_{10}H_{16}O_4$: C 59.98; H 8.05.), from which the corresponding dimethyl ester (mol. wt. 228. Found: C 63.35; H 8.73. Calc. for $C_{12}H_{20}O_4$: C 63.13; H 8.83.) was obtained with diazomethane.

On the basis of these results the true formula of the original amino acid A_1 must be $C_{12}H_{18}N_2O_4$. In addition the molecule must contain a ring, since only two double bonds are present.

The nuclear magnetic resonance studies of the original amino acid A_1 , its diethyl ester and that of the dimethyl ester $C_{12}H_{20}O_4$ lead to the following possibilities (I and II) for the structure of the amino acid A_1 :



The structure II would give on ninhydrin oxidation an α,β -unsaturated aldehyde. This is, however, not in agreement with the experimental results. This being the case the structure I, 2-methylenecyclohept-(4,5 or 6)-ene-1,3-diglycine, corresponds best with the before-mentioned facts. The position of the second double bond remains still in doubt.

Full details of these investigations will be published later.

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The Near IR Absorption of Metal Complexes with Flavin Free Radicals

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It has been demonstrated by Hemmerich¹ and coworkers that flavin free radicals are rather good chelating agents. The affinity of d-metal ions towards the radical is much higher than towards the oxidized and reduced forms of flavin. The importance of these complexes for the catalytic action of metalloflavoproteins is obvious.

We are since some time concerned with the study of the details of the electron distribution within these radicals and their complexes, e.g. with metal ions. A special object of interest in this research is the relationship between ESR (electron spin resonance) and light absorption.

When investigating the metal radical chelates, chloroform solutions of tetraacetyl riboflavin have been used in order to obtain sufficient solubility and to avoid precipitation, which occurs with FMN and FAD, when also the phosphate coordinates to the metal ion. Excess of triethyl-

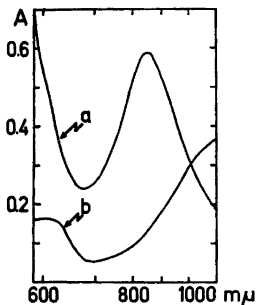


Fig. 1. Light absorption of tetraacetyl riboflavin (7 mM) in the near IR region dissolved in $CHCl_3$, 14 mM $(C_2H_5)_3N$, 5.5 M CH_3CN : (a) with 1.8 mM $Cd(NO_3)_2$ added; (b) with no metal ion added. Samples half reduced with dithionite.

amine was added in order to bind protons liberated during metal chelation. It was found that the metal chelates of the flavin radicals possess an intense absorption in the near infrared with maximum in the region 810 to 840 $m\mu$ (Fig. 1.) in the case of valence-stable transition metal ions Zn^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} and Mn^{2+} . It has been ascertained that this absorption band is due to the complex between the metal ion and the flavin free radicals by establishing for a diamagnetic metal ion (Zn^{2+}) that there is a linear relationship between the ESR and light absorptions (Fig. 2).

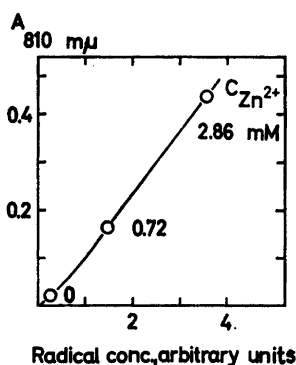


Fig. 2. Comparison of light absorption at 810 $m\mu$ and the integrated ESR absorption for different concentrations of added Zn^{2+} ions. Conditions as in Fig. 1.

The observed sharp absorption band of the radical chelated is easily distinguished from the broader bands of the dimolecular flavin complexes.^{2,3}

The absorption band has not been observed with reducing metal ions (Fe^{2+} , Cu^+ , MoO^{3+}),⁴ nor has it been observed in partially reduced xanthine oxidase,⁵ a metalloflavoprotein containing Fe and Mo.

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Formation of Stable Free Radicals in Alkaline Solutions of Some Monosaccharides

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With the technique of electron spin resonance (ESR) it has been found that free radicals are produced in a comparatively high yield when heating solutions of monosaccharides in a strongly alkaline medium. Radicals were obtained from D-glucose, D-fructose, D-mannose, D-galactose, D-glucuronic acid, D-glucosamine, L-fucose, and D-xylose. Most of the experiments were performed with 6 N KOH in H_2O (non-degassed), and with a molar concentration of the substances between 0.5 and 1.0. After heating on a boiling water bath for 1 to 1½ min the reaction mixtures were chilled to room temperature and filled into the sample tubes. The results obtained with D-glucose are shown in Fig. 1. Immediately after filling into the sample tube, the ESR-spectrum exhibited a complicated hyperfine structure (Fig. 1a), very probably due to the presence of more than one radical species. This pattern changed with time, and after about 20 min the spectrum was dominated by a triplet with a splitting constant of 0.81 gauss, and an intensity ratio of 1:2:1, indicating an interaction of the unpaired electron with two equivalent protons (Fig. 1b). The radical species giving rise to the triplet was rather stable, and the spectrum persisted without any decrease of the intensity for more than a week when the reaction mixture was kept in a stoppered sample tube.

Most of the substances considered exhibited radical spectra similar to those de-