between DHA and hydroxylamine 3-methyl-4-(3-methyl-5-isoxazolyl)-3-isoxazolin-5-one (II) was obtained without 4(1*H*)-pyridones (N), showing the quite different process from that of 2,6-dimethyl-4*H*-4-pyrone with hydroxylamine. In the latter case, 4-hydroxylamino-2,6-dimethylpyridine 1-oxide^{5,6)} was obtained. The details of this work will be reported in the near future.

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5) P. Yates, *et al.* : Can. J. Chem., **40**, 2146 (1962).

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On the Reaction Products between Dehydroacetic Acid and Amino Acids

It was pointed out several times that dehydroacetic acid (DHA) is very reactive with ammonia, primary amines, and some of the compounds possessing amino group, such as sulfanilamides.^{1,2)} In all cases, the primary reaction product is Schiff's base and the final product 2,6-dimethyl-4(1*H*)-pyridone derivative even under a mild condition.

In an extension of this work to amino acids from the biochemical point of view, we noticed that 2,6-dimethyl-4(1*H*)-pyridone derivative was also formed *via* the primary product Schiff's base under the similar condition.

As soon as DHA was treated with the equivalent mole of glycine at room temperature, the formation of the compound (I), m.p. 247~248° (decomp.), which had been identified already as 3-[1-(carboxymethylimino)ethyl]-4-hydroxy-6-methyl-2*H*-2-pyrone,³⁾ was recognized by the paper chromatography (Rf 0.61). When the test solution (1%) was kept at room temperature with an excess of glycine, a new spot appeared in the paper chromatogram (Rf 0.43) after 80 days. It was isolated as white prisms, m.p. 229° (decomp.), and identified as 4-oxo-2,6-dimethyl-1,4-dihydro-1-pyridineacetic acid (II) in consequence of an elemental analysis, infrared and ultraviolet spectra. II was also obtained from the reaction of 2,6-dimethyl-4*H*-4-pyrone with glycine in a small yield.

On the other hand, when DHA reacted with the equivalent mole of a basic amino acid histidine under the similar condition, a new compound (III) was detected by the paper chromatography (Rf 0.33), and after 6 days the formation of another compound (IV) was clearly observed in the test solution (1%) with an excess of histidine (Rf 0.11),

1) S. Iguchi, *et al.* : This Bulletin, **11**, 385 (1963).

2) *Idem* : *Ibid.*, **11**, 390 (1963).

3) *Idem* : *Ibid.*, **7**, 323 (1959).

The former was identified as 3-{1-[1-carboxy-2-(4-imidazolyl)]-ethylimino}ethyl}-4-hydroxy-6-methyl-2*H*-2-pyrone, m.p. 209~210° (decomp.), and the latter α -(4-imidazolyl)-methyl]-4-oxo-2,6-dimethyl-1,4-dihydro-1-pyridineacetic acid, m.p. 170~175° (decomp.), from the data of an elemental analysis and the absorption spectra.

In addition to the fact mentioned above, a primary bioactive amine histamine also reacted with DHA and readily transformed into 2,6-dimethyl-4(1*H*)-pyridone derivative *via* Schiff's base and 2,6-(dihistamyl)-2,5-heptadien-4-one as was expected,

Furthermore, we tried to investigate the reaction of DHA with the other amino acids such as lysine and arginine, and found that the basic amino acid is generally more active than the acidic one; the reactivity depends on the basicity of amino acids.

This experiment has aimed to clear the reactivity of DHA with amino acids, especially the ease which DHA was transformed into 2,6-dimethyl-4(1*H*)-pyridone even under a mild condition. Detail of this work will be reported in the near future.

In the paper chromatography, Dragendorff's reagent was used as a spraying reagent and BuOH-AcOH-H₂O (4:1:5) system as the developing solvent.

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The Polyphosphoric Acid-Catalyzed Ring Opening of 4,5-Epoxy-3-oxo Steroids : The Synthesis of 4-Alkylthio-4-en-3-oxo Steroids and their Analogs

A number of studies¹⁾ on the ring opening or rearrangement of steroidal α -epoxyketones, mainly of 4,5-epoxy-3-oxo and 16,17-epoxy-20-oxo steroids, have so far been accumulated in connection with a view to synthesizing modified steroid hormones. However, the reaction still represents a promising method for the synthesis of potential steroids with desired biological activity separated from other actions of the natural hormones, and also for the exploration of complex stereochemical aspects in steroidal

1) References cited in C. Djerassi : "Steroidal Reactions" (1962). Holden-Day Inc., San Fransisco.