Contribution from the Research Laboratory of Professor N. F. Witt, Retired, Department of Chemistry, University of Colorado, Boulder, CO 80302, U. S. A.

L-Glutamic Acid Crystals Grown from Saturated Aqueous Solutions at $25^\circ$ and $37^\circ$ C

By

G. Goe

With 5 Figures

(Received May 5, 1975)

Introduction

L-Glutamic acid molecules are known to appear in either ring ($\alpha$)- or chain ($\beta$)-like spatial configurations when positioned in a regular crystalline array. The results reported in the present communication indicate that the L($\beta$)-glutamic acid crystals grow from saturated aqueous solutions maintained near room temperature ($25^\circ$). The L($\alpha$)-glutamic acid crystals appear from saturated solutions maintained near body temperature ($37^\circ$).

In 1931, Bernal\textsuperscript{1} determined a ring-like spatial configuration for the L-glutamic acid molecules in crystals. Later, in 1955, Hirokawa\textsuperscript{2} determined a chain-like spatial configuration for L-glutamic acid molecules in crystals. At that time, Hirokawa\textsuperscript{2} referred to the ring configuration as the $\alpha$-form, the chain configuration as the $\beta$-form, and introduced the notation: L($\alpha$)- and L($\beta$)-glutamic acid. These two configurations are shown schematically in Fig. 1.

The preliminary X-ray tests of Hirokawa\textsuperscript{2} revealed the dimensions of the unit cells of the two crystalline forms to be different but further structural determinations showed the dimensions of the unit cells to be at least related. Thus, Hirokawa\textsuperscript{2} appears to have been the first researcher not only to recognize but also to investigate at some length these two crystalline forms of L-glutamic acid. Certainly, Winchel\textsuperscript{3} and other standard references\textsuperscript{4,5} make no suggestion of the two forms.
Studies of the dicarboxyl amino acids, aspartic and glutamic acid and their amide derivatives, started in the laboratory of Prof. N. F. Witt in 1967. Since that time we have been able to study the behavior of the saturated aqueous solutions of the amino acids and to observe their crystal growth under rigidly controlled conditions. To date, we find the appearance of a dual crystalline form to be peculiar only to the laevo isomer of glutamic acid. Neither the dextro isomer, the racemic form nor the amide derivative of glutamic acid show a sensitivity to temperature over the 20\(^\circ\text{C}\)–40\(^\circ\text{C}\) range when maintained in an aqueous environment. Further, aspartic acid, the second dicarboxyl amino acid, produces only single crystalline forms for either of the optical isomers, the racemic mixture or the amide derivative. For that reason we confine our discussions of crystal growth to L-glutamic acid.

In this paper we report an observed temperature dependence for a conformational change in the L-glutamic acid molecules. In the experimental section we describe our water supply, the behavior of the saturated solutions and the characteristics of the crystal growth. We conclude that an aqueous environment maintained near body temperature (37\(^\circ\text{C}\)) favors the formation of the ring molecular configuration for L-glutamic acid. The chain configuration consistently appears near room temperature (25\(^\circ\text{C}\)).

The amino acid crystals we study are grown from saturated aqueous solutions prepared from freshly distilled, de-ionized, pure liquid water. For the practical reason that a sample size of only one drop of liquid is required to make a measurement, we have consistently determined the refractive index as a means of moni-

Fig. 1. Molecular configurations for L-glutamic acid. The chain (\(\beta\))-form is shown in the left; the ring (\(\alpha\))-form is on the right. The OH...N linkage closes the six member ring.