

*Synthetic Resins Catalyzing the Racemization of Amino Acids. III.
Racemization by the Column Procedure*

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In previous papers¹⁻³⁾, the preparation and activity of the resins catalyzing the racemization of amino acids were described. In the present research, it was found that, on the continuous flow of an amino acid solution

containing cupric ion through a column of the resin, racemization of the amino acid was achieved to a degree which was determined by or was dependent on the flow rate. The catalytic resin used was prepared, as has been described in a previous paper²⁾, by chemical modification of *o*-cresol-phenol-formalin resin. Powdered *o*-cresol-phenol-formalin resin was oxidized with chromium trioxide in a mixture of acetic

1) K. Toi, Y. Izumi and S. Akabori, This Bulletin, 35, 1422 (1962).

2) K. Toi, Y. Izumi and S. Akabori, *ibid.*, 36, 734 (1963).

3) K. Toi, *ibid.*, 36, 739 (1963).

anhydride [and acetic acid, and the acetal produced was hydrolyzed with 4 N hydrochloric acid. The aldehyde content of the resin was 0.24 mmol. per gram of dry resin.

A column 30 cm. long and 2 cm. in diameter was made with 40 g. of the resin, which had been previously buffered to pH 10.0~10.5 with a borate buffer. The column was fitted with a glass jacket, through which water at 80°C was circulated, and operated at a constant temperature. An aqueous solution of 1.0 M L-alanine containing 0.1 M cupric acetate monohydrate was adjusted to pH 10.0~10.5 with sodium hydroxide. This solution was run through the column, and the effluent was fractionated every 5 ml. Each fraction of five intervals was diluted with two volumes of 6 N hydrochloric acid, and its optical rotation was measured. The racemization reaction during the passage through the column proceeded well, with the decrease in the flow rate shown in Fig. 1. L-Alanine racemized completely at a flow rate of 5 ml. per 13 min.

The amino acid content in the solution used for the optical rotation measurement was determined by the ninhydrin colorimetric method⁴⁾. The loss of the alanine during the passage through the column was below 10%.

Fractions 80 to 120 were combined and made

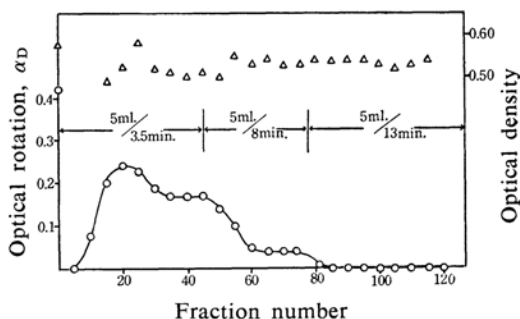


Fig. 1. Racemization of L-alanine by column procedure.

○ Optical rotation of the effluent.
△ Optical density measured by the ninhydrin method.

acidic with hydrochloric acid. The acidic solution was treated with hydrogen sulfide to remove the cupric ion. After subsequent treatment of the solution with ion exchange columns to remove the sodium salt, alanine was obtained in a yield of 14 g., which corresponded to 80% recovery. The alanine which recovered was optically inactive. $[\alpha]_D^{15} 0.00$ (c 3, 6 N hydrochloric acid).

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4) E. W. Yemm and E. C. Cocking, *Analyst*, **80**, 209 (1955).