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 Communications to the Editor
 

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UDC 547.466.2

**Reaction of Hydrazoic Acid with Dialkylmalonic Acids**

Earlier report from this laboratory<sup>1)</sup> showed that amino acids were obtained from monoalkylmalonic acids in a high yield by the Schmidt reaction. The present writer found that an abnormal reaction occurred in using dialkylmalonic acids as the starting material and a mixture of amino acids were obtained, instead of the expected amino acid.

Procedure of this reaction was as follows: A mixture of 1.6 g. of diethylmalonic acid, 5 cc. of 100% H<sub>2</sub>SO<sub>4</sub>, and 10 cc. of CHCl<sub>3</sub> was kept at 50~60°, 8 cc. of 6.5% hydrazoic acid in CHCl<sub>3</sub> was slowly added, and the mixture was maintained at the same temperature for several hours. The reaction mixture was then poured into ice water, the aqueous layer was separated, and carefully adjusted to pH 5 with hot concentrated solution of Ba(OH)<sub>2</sub>. BaSO<sub>4</sub> that precipitated was removed and the filtrate was passed through Amberlite IR-120 column. The amino acid adsorbed was readily eluted from the column with 0.15~0.5N NH<sub>4</sub>OH. Free amino acid was obtained by the concentration of the eluate. Yield, 0.15 g.

The product was easily purified by sublimation, but two spots (Rf 0.37, 0.63: solvent—BuOH: AcOH: H<sub>2</sub>O=4:1:1) were observed on the paper chromatogram. Using paper chromatography, these amino acids were separated and respectively identified as DL-2-amino-butyric acid (Rf 0.37; Yield, 0.07 g. *Anal.* Calcd. for C<sub>4</sub>H<sub>9</sub>O<sub>2</sub>N: C, 46.59; H, 8.80; N, 13.58. Found: C, 46.76; H, 8.96; N, 13.67) and 2-ethyl-2-aminobutyric acid (Rf 0.63; Yield, 0.05 g. *Anal.* Calcd. for C<sub>6</sub>H<sub>13</sub>O<sub>2</sub>N: C, 54.93; H, 9.99; N, 10.68. Found: C, 55.15; H, 10.12; N, 10.90).

In the case of ethylisobutylmalonic acid, the reaction mixture showed three spots on the paper chromatogram.

Further study is being made to find out the mechanism of this abnormal reaction and detailed description on this work will be reported in the near future.

The writer expresses grateful thanks to Prof. T. Suzuki and Prof. T. Uno for their kind advices.

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July 10, 1958

1) Paper read before the General Meeting of the Pharmaceutical Society of Japan, April 8, 1956.

UDC 582.273:581.19

**Constituents of *Chondria armata***

A crystalline acid component was isolated from a seaweed, *Chondria armata* (KÜTZING) OKAMURA (Japanese name "Hanayanagi" or "Dōmoi") (family Rhodomelaceae), and was named domoic acid. It formed colorless needles of m. p. 217° (decomp.);  $[\alpha]_D^{25} -109.6^\circ$  (c=1.314, H<sub>2</sub>O); U. V.  $\lambda_{\text{max}}^{\text{H}_2\text{O}}$ : 242 m $\mu$  (log  $\epsilon$  4.42) (*Anal.* Calcd. for C<sub>15</sub>H<sub>21</sub>O<sub>6</sub>N·2H<sub>2</sub>O: C, 51.86; H, 7.25; N, 4.03; 2C-CH<sub>3</sub>, 8.66; 2H<sub>2</sub>O, 10.37; mol. wt., 347.36. Found; C, 51.60, 51.71, 51.89; H, 7.11, 7.17, 7.16; N, 4.08, 4.08, 4.34; C-CH<sub>3</sub> (Kuhn-Roth method), 7.48, 6.97; H<sub>2</sub>O, 10.13; mol. wt. (modified Akiya method), 366). Domoic acid is soluble in water and AcOH, easily soluble in dil. mineral acids and alkali hydroxide solutions, and soluble in alkali carbonate and NaHCO<sub>3</sub>.