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<th><strong>Title</strong></th>
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<tr>
<td><strong>Abstract</strong></td>
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<tr>
<td><strong>Notes</strong></td>
<td>Summaries of Doctor and Master Theses</td>
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</table>

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The Utilization of the Dicarboxylic Acids Containing Ether Linkages

Chihiro KATO (加藤 千 滦)

Very few have been reported about the dicarboxylic acids containing ether linkages. The author synthesized the following three dicarboxylic acids which may be prepared easily from ethylene or propylene. Then their higher alkyl esters and amides were derived to examine their plasticizing activities.

(I) 1,2-bis(carboxymethoxy)-ethane m.p. 75~77°C
(II) 1,2-bis(β-carboxyethoxy)-ethane m.p. 66.5~67°C
(III) 1,2-bis(β-carboxyethoxy)-propane oily

The procedure of synthesis is as follows;

a) \( \text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \)
   \( \xrightarrow{\text{HNO}_3, \text{NH}_4\text{VO}_3} \)
   \( \text{HOOCCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{COOH} \)  (I)

b) \( \text{HOCH}_2\text{CH}_2\text{OH} + 2\text{CH}_2\text{CHCN} \rightarrow \text{NCCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CN} \)
   \( \xrightarrow{\text{HCl}} \)
   \( \text{HOOCCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{COOH} \)  (II)

c) \( \text{HOCH(CH}_3\text{)CH}_2\text{OH} + 2\text{CH}_2\text{CHCN} \)
   \( \xrightarrow{\text{KOH}} \)
   \( \text{NCCH}_2\text{CH}_2\text{OCH(CH}_3\text{)CH}_2\text{OCH}_2\text{CH}_2\text{CN} \)
   \( \xrightarrow{\text{HCl}} \)
   \( \text{HOOCCH}_2\text{CH}_2\text{OCH(CH}_3\text{)CH}_2\text{OCH}_2\text{CH}_2\text{COOH} \)  (III)

As esters, dioctyl-, didecyl- and dibenzyl esters of (I), (II) and (III), then as amides, diamides of octyl-, dodecyl- and benzyl amines were selected.

Moreover, polyamide type polymers which were condensed from those dibasic acids and hexamethylene diamine were tested about the physicochemical characteristics of products.

The Synthesis of Cyclic α-Amino Acids

Eisuke KAJI (梶 英 輔)

It has been previously found in our laboratory that the Diels-Alder reaction between \( \alpha\cdot\beta\)-unsaturated \( \alpha\)-nitroesters and dienes forms cyclic \( \alpha\)-nitroesters, which
can be led to a new kind of cyclic α-amino acids. In all cases, the cyclic α-nitroesters (Diels-Alder adducts) have been obtained as a mixture of diastereomers.

From an adduct, ethyl 2-nitro-3-α-nitro-phenyl-bicyclo[2.2.1]5-heptene-2-carboxylate (I), the author isolated its four diastereomers in crystalline forms by column chromatography and fractional recrystallization. The structural assignments of the four isomers were made by the NMR spectroscopy. The readily available three ones of these isomers were led to corresponding pure isomers of amino acids by reduction followed by hydrolysis. It was found that the crude adduct I was directly subjected without isomeric separation to reduction and hydrolysis to afford a sterically pure amino acid (the main isomer) in a 40% yield. From another adduct, ethyl 2-nitro-3-m-nitro-phenyl-bicyclo[2.2.1]5-heptene-2-carboxylate, two amino acid isomers were obtained in sterically pure state.

On the other hand, the reaction of N-benzyloxy-carbonyldihydroalanine methyl ester with cyclopentadiene produced a new adduct, methyl 2-benzyloxy-carbonylaminobicyclo[2.2.1]5-heptene-2-carboxylate, which have been led to 2-amino-cyclo[2.2.1]heptane-2-carboxylic acid by hydrogenation followed hydrolysis in a good yield.

Total Syntheses of Antibiotic Glucosides

Eiichi KITAZAWA (北沢栄一)

Neamine, one of the antibiotic aminosugars, has been synthesized from paromamine which was synthesized in our laboratory.

A tosyl derivative, which was obtained by the preferential tosylation of tri-N-acetylparomamine with p-toluenesulfonyl chloride, was treated with sodium azide in dry N,N'-dimethylformamide to give an azided erivative. Hydrogenolysis of the azide compound with platinum oxide in methanol, followed by N-acetylation, gave tetra-N-acetyl derivative, which had the same properties as tetra-N-acetylneamine prepared from natural neamine. The absolute structure of the synthetic product and its identity with the tetra-N-acetylneamine were confirmed by the copper complex method. De-N-acetylation of tetra-N-acetyl-neamine with hydrazine hydrate gave an amino derivative, m.p. 233°C (decomp.), [α]D23 +86.8° (c 0.5, H2O), which had the same properties, (m.p., optical rotatory, I.R., etc.) as natural neamine.

Furthermore, a structural isomer of neamine, namely 6-O-(3,6-diamino-3,6-dideoxy-α-D-glucopyranosyl)-deoxystreptamine, was synthesized from 6-O-(3-amino-3-deoxy-α-D-glucopyranosyl)-deoxystreptamine which was obtained from kanamycin by partial hydrolysis. Structural proof was obtained from the nuclear magnetic re-