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Mechanism of the Color Reaction of Pyruvic Acid with *p*-Dimethylaminobenzaldehyde. I. On the Reaction Products of Pyruvic Acid and *p*-Dimethylaminobenzaldehyde[1]

Mitsuyoshi Kageura, Yosuke Ohkura, and Tsutomu Momose

Faculty of Pharmaceutical Sciences, Kyushu University[2]

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Four reaction products (I, II, III and IV) were separated in the color reaction of pyruvic acid with *p*-dimethylaminobenzaldehyde in an aqueous sodium hydroxide-dimethylsulfoxide solution at the reaction temperature of 40° or 60°, and their structures and roles in the colorimetric method of pyruvic acid determination previously presented were investigated.

I was obtained from the reaction mixture resulted at the reaction temperature of 40° and determined as the trans form of *p*-dimethylaminobenzalpyruvic acid. The absorption spectral data showed that I was the sole coloring matter in the method of pyruvic acid determination.

II, III and IV were produced in the reaction at 60°, and II and IV were purified as their methyl esters. They were characterized as 5-(*p*-dimethylaminophenyl)-isophthalic acid derivatives as shown in Chart 1, and proved not to be related to the coloration. The reaction pathways to form those products were also discussed.

In the previous paper,[3] a selective colorimetric method for the determination of pyruvic acid was presented on the basis of a new color reaction of the acid with *p*-dimethylaminobenzaldehyde (*p*-DBA) in aqueous dimethylsulfoxide (DMSO) in the presence of alkali hydroxide.

This paper describes the separation and the structures of some reaction products formed in the color reaction and discusses their formation mechanisms and roles in the practical method of pyruvic acid determination.

Isolation of Reaction Products

A DMSO solution of *p*-DBA was mixed with sodium pyruvate dissolved in the equal volume of 10% sodium hydroxide solution and warmed for appropriate time. Each equimolar amounts of *p*-DBA and the pyruvate was employed in the reaction, otherwise a large amount of unreacted reagent might interfere the separation of reaction products.

The color intensity of pyruvic acid was largely affected by the reaction temperature in the practical method of determination, and rather strongly developed at a lower temperature (37°) for the prescribed reaction time (45 min).[3] This fact suggested that the coloring matter formed in an early stage of the reaction might decompose with rising reaction temperature during the reaction time. Therefore, the isolation of reaction products was separately carried out at the reaction temperatures of 40° and 60° to clarify the relationship between the reaction time and the resultant products.

The mixture resulted from the reaction at 40° for 45 min was made slightly acidic with hydrochloric acid and extracted with ethyl acetate. The extract left violet red needles (I), mp 144°, in a relatively high yield. I was also obtained from the pyruvate and *p*-DBA similarly treated for the reaction time of 120 min in the presence of ethanol in stead of DMSO.[4]

1) This forms "Organic Analysis LXXXI." Part LXXX: Y. Ohkura, Y. Watanabe, and T. Momose, *Anal. Biochem.*, in press.
2) Location: *Katakasu, Fukuoka.*
3) M. Kageura, Y. Ohkura, and T. Momose, *Chem. Pharm. Bull.* (Tokyo), **19**, 2241 (1971).
4) Ethanol was already shown to give the selectivity for pyruvic acid as well as DMSO in the method of determination.[3]

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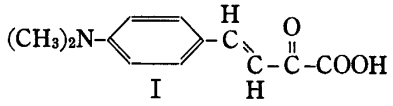
In the reaction at 60° for 60 min, the resulting reaction mixture was acidified with acetic acid and concentrated. The substance thus separated in high yield was filtered and dissolved in water, and then re-precipitated by adding ethanol to be yellowish powder (II). This compound was also yielded in the reaction for 180 min using methanol in stead of DMSO in a higher yield. II was suggested to have carboxyl group in the molecule by the characteristic infrared (IR) absorption band at 1718 cm^{-1} (C=O) and the several ones around 2600 cm^{-1} (OH). II was so acidic and sparingly soluble in usual solvents, that could not be successfully purified by recrystallization and alumina or silica gel column-chromatographic technics. Therefore, II was methylated with diazomethane to give yellow brown prisms (II-methyl ester), mp 205°. On the other hand, the filtrate gave yellow leaflets (III), mp 268°, in rather good yield when diluted with water.

The reaction mixture described above was acidified with phosphoric acid and extracted with ethyl acetate. The dried extract obtained in high yield was recrystallized from acetone to brownish crystalline powder (IV), which could not be further purified as II. Thus, IV was methylated with diazomethane to colorless needles (IV-methyl ester), mp 177°.

It was of much interest to note that I could not be separated from the reaction mixture at 60° and that the kind of products depended on the reaction temperature.

Structures of the Reaction Products

From the data of elemental analysis of I and its molecular ion (M^+) in the mass spectrum, I was determined to have the molecular formula of $C_{12}H_{13}O_3N$, which corresponded to that of a possible reaction product, *p*-dimethylaminobenzalpyruvic acid. The existence of an oxalo-group in the molecule was first suggested by characteristic IR absorption bands at 3000—2500, 1760 and 1710 cm^{-1} (Table I), and then confirmed by the strong fragment ions of M^+ -COOH and M^+ -COCOOH in the mass spectrum, though carboxyl proton could not be proved by the nuclear magnetic resonance (NMR) spectrum. The IR spectrum also indicated the presence of double bond and adjacent two aromatic hydrogens by the bands at 1660 and 820 cm^{-1}, respectively. The NMR spectrum showed the signals due to the protons on *p*-dimethylaminophenyl group and the vinyl protons as shown in Table I, and confirmed that the structure of I was nothing else than *p*-dimethylaminobenzalpyruvic acid. Furthermore, the large value of coupling constant of the vinyl protons supported that I might exist as the trans form.



I

The molecular formula of II-methyl ester was established from the elemental analysis and M^+ in the mass spectrum as $C_{21}H_{21}O_7N$, whose composition supported that the compound might be trimethyl ester of a compound drived from the reaction of one mole of *p*-DBA and three moles of pyruvic acid. The IR spectrum (Table I) showed the presence of two different types of ester. Namely, the bands at 1710 and 1755 cm^{-1} might be assigned to the two carbonyls of methoxalyl group similarly to those of I, and the band at 1730 cm^{-1} to that of methoxy carbonyl group. The presence of one methoxalyl and two methoxy carbonyl groups were clarified by the integral intensities of two signals due to methyl protons at δ 3.95 and 3.90 in the NMR spectrum (Table I) and the strong fragment ions of M^+ -$COOCH_3$, M^+ -$COOCH_3$-CH_3 and M^+ -2$COOCH_3$-$COCOOCH_3$+H in the mass spectrum of the compound.

The NMR spectrum also had a singlet ascribable to two isolated aromatic protons at δ 8.34 besides the signals caused by the *p*-dimethylaminophenyl moiety, indicating that the compound had another benzene ring and the two protons were magnetically equivalent on the ring.

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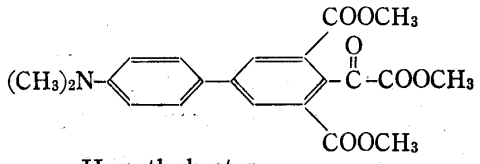
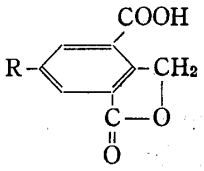
Those data supported that *p*-dimethylaminophenyl and methoxalyl groups were located at 1 and 4 positions of the benzene ring, respectively, and two methoxy carbonyl groups at 3 and 5 or 2 and 6 positions. The positions of methoxy carbonyl groups might be 3 and 5 by the facts that 5-phenyl-2-oxalo-isophthalic acid was postulated as a possible intermediate to form 5-phenyl-isophthalic acid in the reaction between three moles of pyruvic acid and one mole of benzaldehyde[5] and that IV might be formed through II as described later. Therefore, II-methyl ester might be trimethyl ester of 5-(*p*-dimethylaminophenyl)-2-oxalo-isophthalic acid.

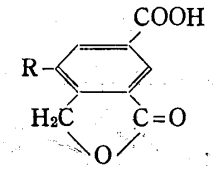
The data of the elemental analysis of III and its M^+ in the mass spectrum well agreed with the molecular formula of $C_{17}H_{15}O_4N$, suggesting that III might be yielded by the reaction of one mole of *p*-DBA and three moles of pyruvic acid as in II. The IR spectrum (Table I) indicated the existence of carboxyl group and ester moiety by the characteristic bands at 3100—2500 and 1710, and 1740, 1230 and 1095 cm^{-1}, respectively. This was also supported by the intense fragment ions of M^+-COOH and M^+-$COOCH_2$+H in the mass spectrum, though signal to be ascribed to the carboxyl proton was not observed in the NMR spectrum.



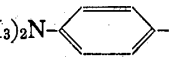
II-methyl ester



IIIa



IIIb

R: $(CH_3)_2N$- 

The NMR spectrum had two doublets at δ 8.16 and 8.36 with small coupling constants due to aromatic hydrogens (Table I), which showed that a benzene ring other than *p*-dimethylaminophenyl moiety was present in the molecule and two hydrogens were located at *m*-positions of the ring each other. A singlet at δ 5.59 was assigned to *o*-methylene protons of the ester moiety, and showed that any proton did not exist on the carbon atom adjacent to the methylene group. And, other signals to be ascribed to protons related to the ester moiety were not observed in the spectrum. These facts and the elemental composition of the compound meant that the ester moiety might be a butyrolactone, in which the carbon atoms at 2- and 3-positions were included in the benzene ring.

The data and consideration described above indicated that the structure of III might be a lactone of 2- or 4-hydroxymethyl-5-(*p*-dimethylaminophenyl)-isophthalic acid (IIIa or IIIb).

Methylation of III with diazomethane gave a methyl ester as yellow needles, mp 156°. The molecular formula, mass spectrum (described in experimental) IR and NMR spectral data (Table I) showed no discrepancy for the consideration of the monomethyl ester of IIIa and IIIb.

The molecular formula of IV-methyl ester was determined by the elemental analysis and M^+ in the mass spectrum as $C_{18}H_{19}O_4N$. This formula directly showed that the compound might be dimethyl ester of an acid formed by eliminating the oxalo-group from II. The IR spectrum of the compound (Table I) proved the presence of ester carbonyl group by the bands at 1730 and 1250 cm^{-1}. The strong fragment ions of M^+-$COOCH_3$ and M^+-$2COOCH_3$ in the mass spectrum indicated that the molecule had two methoxy carbonyl groups, both of which were suggested to be present in the same environment by the integral intensity of singlet at δ 3.97 in the NMR spectrum (Table I). A doublet due to two aromatic hydrogens and a triplet due to one aromatic hydrogen were observed at δ 8.42 and 8.54 with small coupling constants, respectively, besides the signals of *p*-dimethylaminophenyl group

5) O. Doebner, *Chem. Ber.*, **23**, 2377 (1890).

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as shown in Table I. These signals explained that one of three hydrogens was located at an environment different from those of the remaining two which were magnetically equivalent, and therefore the three hydrogens were located at *m*-positions with each other.

From the above evidences, IV-methyl ester was determined as dimethyl ester of 5-(*p*-dimethylaminophenyl)isophthalic acid. This conclusion was supported by the fact that 5-phenyl-isophthalic acid was formed by the condensation of three moles of pyruvic acid and one mole of benzaldehyde in an alkaline solution.[5]

TABLE I. IR and NMR Spectral Data of I,II-methyl Ester, III, III-methyl Ester and IV-methyl Ester

	I	II-methyl ester	III	III-methyl ester	IV-methyl ester
IR ν_{max}^{KBr} cm^{-1}	3000—2500[a] (OH)		3100—2500[a] (OH)		
	1760, 1710 (C=O)	1755, 1730 (C=O)	1740, 1710 (C=O)	1770, 1730 (C=O)	1730 (C=O)
	1660 (C=C)	1710	1230, 1095 (C-O)	1265, 1235, 1075 (C-O)	1250 (C-O)
		1270 (C-O)			
	820 (arom. CH)	910, 825 (arom. CH)	910, 820 (arom. CH)	885, 825 (arom. CH)	875, 820 (arom. CH)
NMR (δ, ppm)[b]	in $(CD_3)_2SO$	in $CDCl_3$	in $(CD_3)_2SO$	in $(CD_3)_2SO$	in $CDCl_3$
$(CH_3)_2N$-	3.01 s (6H)	3.02 s (6H)	2.96 s (6H)	2.97 s (6H)	3.02 s (6H)
Arom. H (adjacent two protons)	6.70 d (2H) $J=9.0$	6.77 d (2H) $J=9.0$	6.80 d (2H) $J=9.0$	6.75 d (2H) $J=9.0$	6.82 d (2H) $J=9.0$
	7.60 d (2H) $J=9.0$	7.55 d (2H) $J=9.0$	7.60 d (2H) $J=9.0$	7.55 d (2H) $J=9.0$	7.58 d (2H) $J=9.0$
-HC=CH-	6.94 d (1H) $J=16.0$				
	7.67 d (1H) $J=16.0$				
Arom. H (isolated)		8.34 s (2H)	8.16 d (1H) $J=1.5$	8.12 d (1H) $J=1.5$	8.42 d (2H) $J=1.5$
			8.36 d (1H) $J=1.5$	8.28 d (1H) $J=1.5$	8.54 t (1H) $J=1.5$
CH_3-O-CO-		3.90 s (6H)		3.90 s (3H)	3.97 s (6H)
		3.95 s (3H)			
>C-CH_2-O-			5.59 s (2H)	5.51 s (2H)	

a) Several poorly resolved bands were observed in this region.
b) J was expressed in cps. abbreviations, s: singlet; d: doublet; t: triplet

Now, the reaction pathways to form II, III and IV may be considered as shown in Chart 1. One mole of *p*-DBA combines with two moles of pyruvic acid and one mole of enolpyruvic acid, yielded under the alkaline conditions of the reaction, by dehydration and dehydrogenation to form II, which may be hydrolyzed to afford IV and oxalic acid.[6] On the other hand, when II liberates carbon dioxide, the resulting aldehyde (V) may be reduced to alcohol (VI) which is converted to IIIa.

If one mole of *p*-DBA condenses with three moles of pyruvic acid in different way to give VII, IIIb may be formed by successive decarboxylation, reduction and dehydration in the same way as in IIIa.

Roles of the Reaction Products in the Practical Method of Pyruvic Acid Determination

The absorption curve of I showed the maximum at 415 mμ when dissolved in an aqueous sodium hydroxide-DMSO solution, whose concentration and composition were adjusted to be identical with those of the final reaction mixture in the practical method (Fig. 1, e). On the other hand, the absorption curve of the reaction mixture of the method measured

6) This acid had already shown to form in the condensation of pyruvic acid and benzaldehyde.[5]

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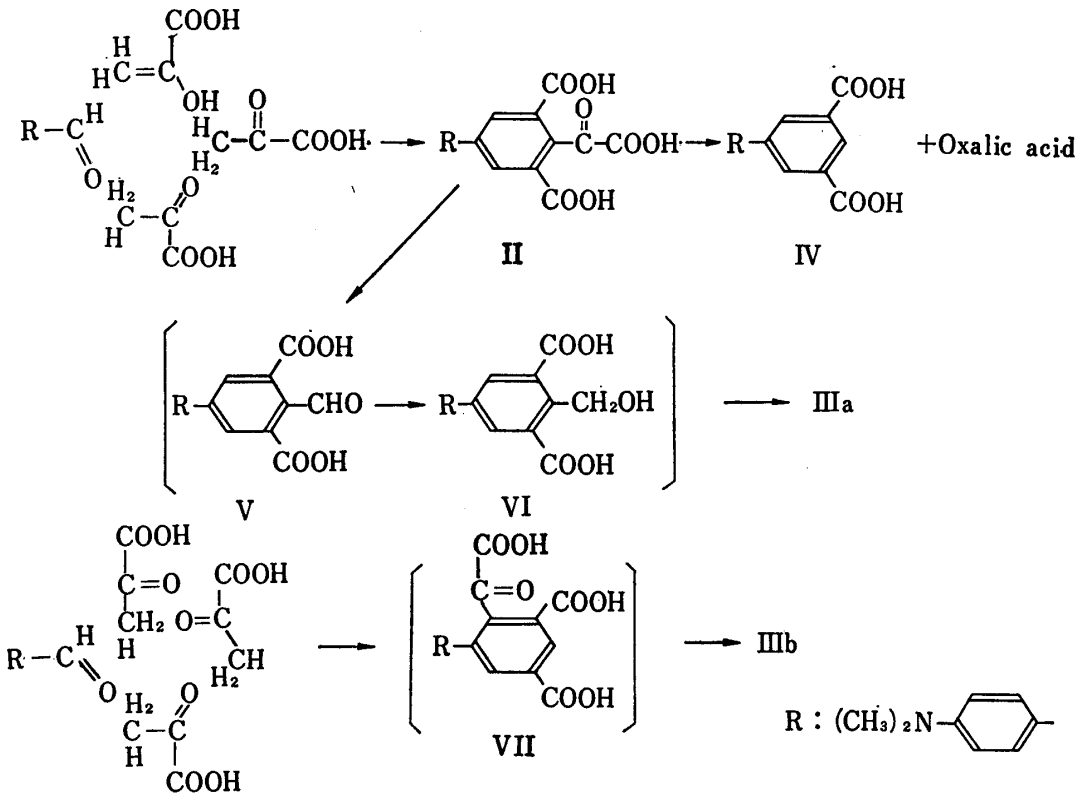

Chart 1. The Reaction Pathways to Form II, III and IV

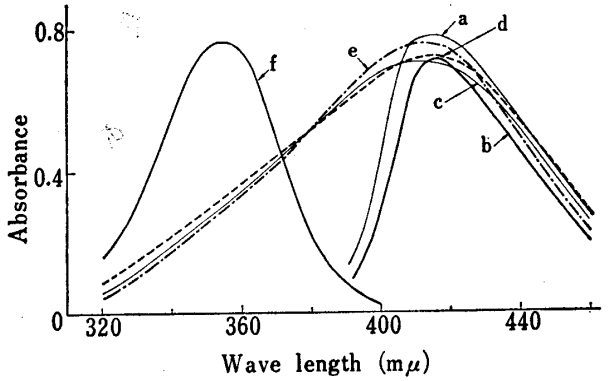

Fig. 1. Absorption Curves of I in Various Media and the Reaction Mixture

a: 1 ml of 1 mM aqueous solution of sodium pyruvate was treated with 3 ml of 0.5% *p*-DBA in 60% (by volume) DMSO solution and 1 ml of 25% NaOH at 37° for 45 min, and then diluted with H_2O to 20 ml. Measured against the reagent blank.

b: 1 ml of 0.56 mM aqueous solution of I was diluted with the 0.5% *p*-DBA solution, 25% NaOH and H_2O to 20 ml as in(a). Measured immediately after preparing the solution against the reagent blank.

c: 0.028 mM aqueous solution of I

d: 10 ml of 0.28 mM aqueous solution of I was mixed with 20 ml of 25% NaOH, and diluted with H_2O to 100 ml. Measured immediately after preparing the solution.

e: 10 ml of the solution of I in d was mixed with 60 ml of 60% (by volume) DMSO solution and 20 ml of 25% NaOH, and diluted with H_2O to 100 ml. Measured as in d.

f: d and e were left standing at 25° for 1 day.
c, d, e and f were measured against H_2O.

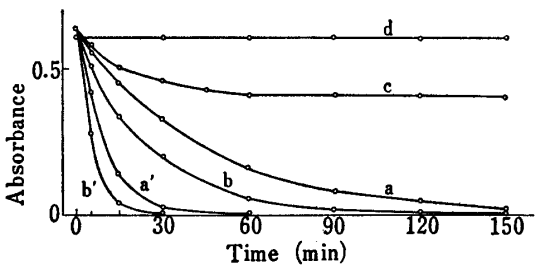

Fig. 2. Stability of I in Various Media

a and a': 1 ml of 0.5 mM aqueous solution of I was mixed with 1.8 ml of DMSO, 1 ml of 25% NaOH and 1.2 ml of H_2O, and left standing at 37° in (a) and 60° in (a'). After each period, the mixture was diluted with H_2O to 20 ml, and the absorbance was immediately measured at 415 mμ against H_2O.

b and b': 1 ml of the solution of I in (a) was mixed with 1 ml of 25% NaOH and 3 ml of H_2O and left standing at 37° in b and 60° in b', and then treated as in(a).

c: 1 ml of the solution of I in (a) was mixed with 3 ml of the 0.5% *p*-DBA solution in Fig. 1, (a) and 1 ml of 25 % NaOH and warmed at 37°. After each period, the mixture was diluted as in (a) and the absorbance was immediately measured at 420 mμ against the reagent blank.

d: 1 ml of the solution of I in (a) was diluted with 4 ml of H_2O, and then treated as in c (measured against H_2O).

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against the reagent blank had the maximum at 415 mμ (Fig. 1, a), and the shape was entirely identical with that of the solution of I in longer wave length region than the maximum. The difference of the shapes in shorter wave length region was caused by the strong light absorption of an excessive *p*-DBA in the reagent blank (Fig. 1, b). The data showed that I was the sole coloring matter of the reaction in the practical method of determination.

The color of I in the aqueous sodium hydroxide-DMSO or an aqueous sodium hydroxide solution (Fig. 1, e and d) faded with time at 37° (Fig. 2, a and b), and finally the absorption curves changed to form a new band with a maximum at 355 mμ (Fig. 1, f). The new band was identical with that of *p*-DBA. This spectral change took place more rapidly at a higher temperature (60°) (Fig. 2, a′ and b′), indicating that I was easily hydrolized to *p*-DBA and pyruvic acid.

The same tendency was rather weakly observed when I was dissolved in the aqueous sodium hydroxide-DMSO solution containing a large amount of *p*-DBA, whose concentrations were identical with those of the reaction mixture in the practical determination method, and allowed to stand at 37° within 60 min. After this period, however, the decomposition and re-formation of I was shown to reach an equilibrium (Fig. 2, c).

A neutral solution of I was found to be quite stable at 37° (Fig. 2, d). Therefore, it is recommended that the reaction mixture is neutralized with an acid at the end of the prescribed reaction time in the procedure for the pyruvic acid determination.

On the other hand, III and the methyl esters of II and IV dissolved in the aqueous sodium hydroxide-DMSO solution had their absorption maxima at 308, 312 and 306 mμ, respectively and no absorption bands in the visible region (Fig. 3). Furthermore, the absorption curves of the methyl esters did not change even when their solutions were left standing at room temperature for 5 days and then warmed at 60° for 5 hr to hydrolyze them to II and IV, suggesting that the hydrolyzed products showed the identical absorption curves with those of the original esters. Those spectral evidences indicated II, III and IV were not directly concerned with the coloration in the method of pyruvic acid determination.

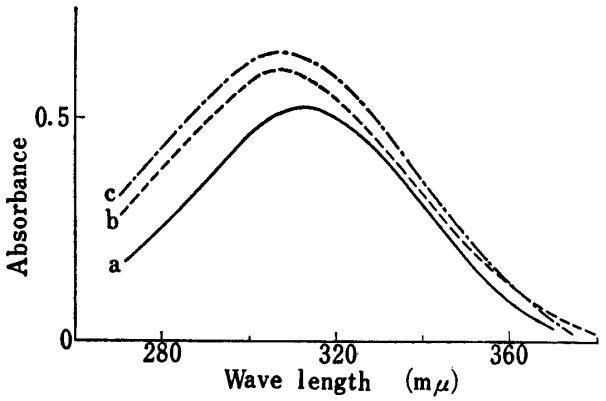

Fig. 3. Absorption Curves of II-methyl Ester, III and IV-methyl Ester

0.03 mM solutions in a mixture of DMSO, 25% NaOH and H_2O in the volume ratio of 18: 10: 22
a: II-methyl ester
b: III
c: IV-methyl ester

Experimental[7]

Reaction of Pyruvic Acid with *p*-DBA——To 3.0 g of *p*-DBA in 50 ml of solvent (DMSO, EtOH or MeOH), 2.4 g of pure sodium pyruvate[8] dissolved in 50 ml of 10% NaOH was added under water cooling and warmed at 40° or 60° for an appropriate time with occasional stirring.

Isolation of I——The reaction mixture resulted for the reaction time of 45 min at 40° using DMSO as the solvent was cooled in an ice-water bath and diluted with 200 ml of H_2O. The mixture was washed with about 100 ml of AcOEt 2 times to remove unreacted *p*-DBA, carefully acidified with 40 ml of 10% HCl under ice-water cooling and then extracted with 100 ml of AcOEt 3 times. The combined extract was

7) All melting points were not corrected. UV spectra were taken on Shimadzu SV-50A Spectrophotometer, absorbances on Beckman DB or Hitachi 139 Spectrophotometer in a cell of 10 mm optical length, IR spectra on Koken DS-301 Spectrometer, NMR spectra on JNM C-60H Spectrometer at 60 Mc with tetramethylsilane as the internal standard, and MS on JMS-01SG Spectrometer.

8) T. Momose, S. Moritani, and Y. Ohkura, *Bunseki Kagaku*, in press.

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dried over Na_2SO_4 and evaporated to almost dryness *in vacuo*. The residue was dissolved in a small amount of H_2O and left standing overnight. The separated crystals (600 mg) were recrystallized from benzene to violet red needles of mp 144° (I). *Anal.* Calcd. for $C_{12}H_{13}O_3N$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.93; H, 6.02; N, 6.37. Mass Spectrum *m/e*: 219 (M^+), 174 (M^+-COOH), 146 (M^+-COCOOH, base peak). UV $\lambda_{max}^{H_2O}$ mμ (ε): 415 (2.56×10^4).

I was also obtained by treating the reaction mixture resulted for the reaction time of 120 min at 40° using EtOH as the solvent. Yield 600 mg.

Isolation of II and III, and Methylation of II——The reaction mixture resulted for the reaction time of 60 min at 60° using DMSO as the solvent was diluted with 200 ml of H_2O and washed with 100 ml of ether 2 times to remove *p*-DBA remained unreacted. The mixture was acidified by adding 20 ml of AcOH and concentrated *in vacuo*. The residual substance was dissolved in 20 ml of H_2O and allowed to stand overnight. Yellow powder thus separated (II) (900 mg) could not be purified as described before. Thus, II was suspended in ether and methylated with etherial diazomethane in the usual manner. The product was recrystallized from benzene to yellow brown prisms of mp 205° (II-methyl ester). *Anal.* Calcd. for $C_{21}H_{21}O_7N$: C, 63.15; H, 5.30; N, 3.51. Found: C, 63.38; H, 5.44; N, 3.37. Mass Spectrum *m/e*: 399 (M^+), 340 (M^+-$COOCH_3$, base peak), 325 (M^+-$COOCH_3$-CH_3), 195 (M^+-2$COOCH_3$-$COCOOCH_3$+H). UV λ_{max} (in a mixture of 18 ml of DMSO, 22 ml of H_2O and 10 ml of 25% NaOH) mμ (ε): 312 (1.75×10^4).

II-methyl ester was also obtained by treating the reaction mixture resulted for the reaction time of 180 min at 60° using MeOH as the solvent in the same way as described above. Yield 1300 mg.

The filtrate remained after II was separated was diluted with 200 ml of H_2O and the separated crystals were recrystallized from MeOH to yellow leaflets of mp 268° (III). Yield 900 mg. *Anal.* Calcd. for $C_{17}H_{15}O_4N$: C, 68.67; H, 5.08; N, 4.71. Found: C, 68.93; H, 5.16; N, 4.71. Mass Spectrum *m/e*: 297 (M^+, base peak), 252 (M^+-COOH), 240 (M^+-$COOCH_2$+H). UV λ_{max} (in a mixture of 18 ml of DMSO, 22 ml of H_2O and 10 ml of 25% NaOH) mμ (ε): 308 (2.15×10^4).

Methylation of III——III was suspended in Et_2O and methylated with etherial diazomethane in the usual manner, and recrystallized from benzene to yellow needles of mp 156° (III-methyl ester). *Anal.* Calcd. for $C_{18}H_{17}O_4N$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.55; H, 5.40; N, 5.02. Mass Spectrum *m/e*: 311 (M^+, base peak), 296 (M^+-CH_3), 254 (M^+-$COOCH_2$+H), 252 (M^+-$COOCH_3$). UV λ_{max} (in a mixture of 18 ml of DMSO, 22 ml of H_2O and 10 ml of 25% NaOH) mμ (ε): 308 (1.97×10^4).

Isolation of IV and Its Methylation——The reaction mixture resulted from the reaction time of 60 min at 60° using DMSO as the solvent was diluted with 200 ml of H_2O and washed with 100 ml of ether to remove the remaining *p*-DBA. After adding 20 ml of H_3PO_4 (80%), the mixture was extracted with 100 ml of AcOEt 3 times. The combined extract was dried over Na_2SO_4 and evaporated to dryness *in vacuo*. The residue was recrystallized from acetone to brownish crystalline powder (IV). Yield 1400 mg. IV was not purified by the usual purification technics. IV was methylated with diazomethane in the usual manner and the resulting product was recrystallized from EtOH to colorless needles of mp 177° (IV-methyl ester). *Anal.* Calcd. for $C_{18}H_{19}O_4N$: C, 68.99; H, 6.11; N, 4.47. Found: C, 69.23; H, 6.19; N, 4.42. Mass Spectrum *m/e*: 313 (M^+, base peak), 254 (M^+-$COOCH_3$), 195 (M^+-2$COOCH_3$). UV λ_{max} (in a mixture of 18 ml of DMSO, 22 ml of H_2O and 10 ml of 25% NaOH) mμ (ε): 306 (2.03×10^4).

Acknowledgement We thank Mr. H. Matsui and Miss Y. Soeda for UV and IR spectral measurements, Messrs M. Shido, K. Ishimura and Y. Inoue for elemental analyses, Mr. Y. Tanaka for NMR spectral measurement and Mrs. Y. Muto for mass spectral measurement.

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