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Structures of Acid B and Related Compounds, Oxidation Products of Lycoramine

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The structures of "acid B" and its monoethyl ester, which are stepwise oxidation products of lycoramine (2), an Amaryllidaceae alkaloid, and the structure of a nitro derivative of acid B, an oxidation product of oxolycoramine (5) with nitric acid, were established as 6, 10 and 12, respectively, on the basis of spectral and chemical evidence.

Keywords—lycoramine; Amaryllidaceae; oxolycoramine; oxolycoraminone; acid A; acid B; nitro acid B; permanganate oxidation; nitric acid oxidation

We previously reported²⁾ the structural elucidation of "acid A" (1) (named by Ishiwata³⁾), which was obtained by stepwise oxidation of the Amaryllidaceae alkaloid lycoramine (2), on the basis of spectral and chemical studies, and synthesis of its racemic methyl ester (3). In further studies on the permanganate oxidation of oxolycoraminone (4),²⁾ two acids, compounds 1 and 2, were obtained in addition to acid A (1). Furthermore, oxidation of oxolycoramine (5)²⁾ with nitric acid in the presence of ammonium metavanadate gave compound 3 with a nitro group. This paper deals with the structural determinations of compounds 1—3 on the basis of chemical correlations and analyses of the infrared (IR), ultraviolet (UV), and ¹H-nuclear magnetic resonance (¹H-NMR) spectra, as well as mass spectra (MS).

Compound 1 (6), mp 265—267 °C (dec.), C₁₇H₁₉NO₇, showed absorption maxima at 258 (log ε 4.05) and 297 nm (log ε 3.75) in its UV spectrum and absorption bands at 1750 and 1740 (C=O) and 1620 (N—C=O) cm⁻¹ in its IR spectrum. The ¹H-NMR spectrum showed signals of an *N*-methylactam ring at δ 3.12 (NMe) and 7.70 (10-H) and a methine proton at δ 5.32 (s)

Chart 1

Chart 2

characteristic of 14-H, in addition to that of an *O*-methyl proton at δ 3.76. Esterification of compound 1 with diazomethane and with anhydrous ethanol–hydrogen chloride gave a dimethyl ester (7), mp 165–167 °C, $C_{19}H_{23}NO_7$, $[\alpha]_D + 12.6^\circ$ and a diethyl ester (8), mp 149–151 °C, $C_{21}H_{27}NO_7$, $[\alpha]_D + 30.3^\circ$, respectively. The former ester (7) was found to be identical with a sample of the dimethyl ester (mp 152–153 °C, $C_{15}H_{17}NO_6$)³⁾ of “acid B” (named by Ishiwata³⁾) by the mixed melting point test. The IR spectrum of the methyl ester (7) showed absorption bands at 1745 and 1725 (C=O) cm^{-1} and at 1630 (NC=O) cm^{-1} . The 1H -NMR spectrum of 7 showed signals of two methoxycarbonyl groups at δ 3.53 and 3.86, and a methine proton at δ 4.97, in addition to those of an amido *N*-methyl group, an aromatic *O*-methyl group, and two aromatic vicinal protons (see Table I). The 1H -NMR spectral data for the diethyl ester (8) were similar to those for 7, except for the presence of the ethyl groups, as shown in Table I. From these findings and those described below, the dimethyl and diethyl esters of compound 1 were concluded to be 7 and 8, respectively. Of the two possible structures, I-type and II-type shown in Chart 2, the II-type structure was excluded for the following reasons: i) the singlets at δ 4.97 and 4.93 due to 14-H in 7 and 8, respectively, showed the presence of a hydrogen atom attached to an oxygen-bearing carbon atom; ii) the chemical shifts of 13-OMe protons (δ 3.53) in 7 and of 13-OEt protons (δ 3.96 and 1.16) in 8 are very similar to the corresponding chemical shifts of the methyl ester (3) (δ 3.55) and ethyl ester (9) (δ 4.00 and 1.19) of acid A (1), as shown in Table I; iii) the MS of 7 and 8 showed the fragment patterns (a)–(d) in Table II, namely $(M-31)^+$, $(M-59)^+$, $(M-73)^+$ and $(M-87)^+$, and $(M-45)^+$, $(M-73)^+$, $(M-87)^+$ and $(M-101)^+$, respectively. Hence, from these results and by consideration of the stereochemistry of lycoramine (2) compound 1 (acid B) was concluded to be 6.

Compound 2 (10), mp 224–227 °C, $C_{19}H_{23}NO_7$, was obtained by extraction with anhydrous ethanol of the residue of the aqueous acidic solution which was separated from the chloroform solution (containing acid A) (see Experimental). Spectral examination of compound 2 revealed the presence of *N*-methylactam [ν_{max} 1640 cm^{-1} (NC=O); δ_H 3.15 (NMe) and 7.45 (10-H)], a methine proton [δ_H 4.97 (14-H)] and an ethyl propionate group [ν_{max} 1750 cm^{-1} (CO₂Et); for MS fragments (a)–(d), see Table II; δ_H 3.98 (13-OCH₂CH₃) and 1.16 (13-CH₂CH₃) (compared with the signals of 15-OEt protons of 8 shown in Table I)]. From these findings, compound 2 was concluded to be a monoethyl ester (10) of acid B (6). The ethoxy group in 10 was assigned to C-13 for the following reasons: methylation of 10 with diazomethane gave a methyl ester (11), mp 144–146 °C, $C_{20}H_{25}NO_7$, $[\alpha]_D - 16.3^\circ$. The 1H -NMR spectrum showed signals of *O*-methyl (δ 3.86) and *O*-ethyl (δ 1.16 and 3.97) protons, which were very similar to the signal of 15-OMe protons in 7 and those of 13-OEt protons in 8, respectively, as shown in Table I. In the MS of 11 the fragment patterns (a)–(d) (see Table II) were the same as those of the diethyl ester (8), but different from those of the dimethyl ester (7). Final evidence of the stereochemistry of compound 2 was obtained by conversion of 10 to the esters 8 and 7 as follows. Esterification of compound 2 with anhydrous ethanol and hydrogen chloride gave the diethyl ester (8), mp 150–151 °C. Hydrolysis of compound 2 with potassium hydroxide–ethanol followed by methylation with diazomethane gave the dimethyl ester (7), mp 164–167 °C. Thus, compound 2 was established as the 13-ethyl ester (10) of acid

TABLE I. ^1H -NMR Data for Esters of Acids A and B (CDCl_3 , δ^a)

	Esters of acid A				Esters of acid B				
	3	9	14	15	7	8	10	11	13
2-CH ₃	3.14	3.16	3.18	3.16	3.14	3.13	3.15	3.14	3.16
8-OCH ₃	3.97	3.98	4.02	4.20	3.92	3.92	3.91	3.92	3.99
9-H	7.00	7.01	7.51		6.90	6.89	6.94	6.89	7.43
	d	d			d	d	d	d	
	(8.0)	(8.0)			(8.0)	(8.0)	(8.0)	(8.0)	
10-H	7.60	7.60		7.96	7.48	7.47	7.54	7.48	
	d	d			d	d	d	d	
	(8.0)	(8.0)			(8.0)	(8.0)	(8.0)	(8.0)	
13-OCH ₃	3.55		3.56	3.56	3.53				3.58
13-OCH ₂ CH ₃		4.00				3.96	3.98	3.97	
		q				q	q	q	
		(7.0)				(7.0)	(7.0)	(7.0)	
13-OCH ₂ CH ₃		1.19				1.16	1.16	1.16	
		t				t	t	t	
		(7.0)				(7.0)	(7.0)	(7.0)	
14-H					4.97	4.93	4.97	4.96	5.05
15-OCH ₃					3.86			3.86	3.91
15-OCH ₂ CH ₃						4.37			
						q			
						(7.0)			
15-OCH ₂ CH ₃						1.35			
						t			
						(7.0)			

^a) Numbers in parentheses are coupling constants J (Hz). Multiplicity: d, doublet; t, triplet; q, quartet; unmarked signal, singlet.

B (6) and oxidation of 4 with permanganate by method (b) (see Experimental) gave the ester (10) instead of acid B (6).

Compound 3 (12), mp 265–269 °C (dec.), $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_9$, $[\alpha]_{\text{D}} -602.4^\circ$. The IR spectrum showed absorption bands at 1725 (C=O), 1625 (NC=O), and 1530 and 1350 (NO_2) cm^{-1} . Methylation of compound 3 with diazomethane gave a dimethyl ester (13), mp 168–170 °C, $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_9$. The IR spectrum showed absorption bands at 1720 (C=O), 1620 (NC=O), and 1520 and 1320 (NO_2) cm^{-1} . As shown in Table I, the ^1H -NMR spectrum indicated the presence of six singlets due to *N*- and *O*-methyl groups, two methoxycarbonyl groups, a methine proton and an aromatic proton. These chemical shifts were very similar to those of acid B dimethyl ester (7), except for the aromatic proton. The chemical correlation between compound 3 (12) or its dimethyl ester (13) and acid B (6) was achieved as follows. Treatment of 6 with 100% nitric acid at 0 °C gave a nitro compound (12), $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_9$, mp 265–269 °C (dec.), which was found to be identical with a sample of compound 3 by the mixed melting point test. Furthermore, nitration of the dimethyl ester (7) with 69% nitric acid gave the same nitro ester (13). From these findings, the nitro ester was established to be a nitro derivative (13) of acid B dimethyl ester (7). The assignment of the nitro group at C-10 in 13 was achieved by nuclear magnetic double resonance (NMDR) analysis: monitoring the line of 8-OMe gave an intramolecular nuclear Overhauser effect (NOE) increment (28%) in the signal of 9-H (δ 7.43). Furthermore, the chemical shift (δ 7.43) of 9-H was similar to that (δ 7.51) of 9-H in the 10-nitro-acid A methyl ester (14) (see Experimental) and different from that (δ 7.96) of 10-H in the 9-nitro ester (15) (see Experimental), as shown in Table I. Hence, compound 3 was established to be the 10-nitro acid B (12).

TABLE II. High-Resolution MS and EI-MS Data for Esters of Acid B (m/z)^{a)}

Fragment	7	8	10	11	13
M^+	377 (52.3) $C_{19}H_{23}NO_7$ C: 377.1473 F: 377.1466	405 (49.0) $C_{21}H_{27}NO_7$ C: 405.1788 F: 405.1804	377 (67.0) $C_{19}H_{23}NO_7$ C: 377.1475 F: 377.1488	391 (55.2) $C_{20}H_{25}NO_7$ C: 391.1630 F: 391.1620	422 (100) $C_{19}H_{22}N_2O_9$ C: 422.1329 F: 422.1349
(a): $[M-OR]^+$	346 (11.0) $C_{18}H_{20}NO_6$ C: 346.1291 F: 346.1258	360 (15.4) $C_{19}H_{22}NO_6$ C: 360.1488 F: 360.1438	332 (27.5) $C_{17}H_{18}NO_6$ C: 332.1131 F: 332.1125	346 (18.7) $C_{18}H_{20}NO_6$ C: 346.1291 F: 346.1303	391 (45.8) $C_{18}H_{19}N_2O_8$ C: 391.1142 F: 391.1126
(b): $[M-CO_2R^1]^+$	318 (10.5) $C_{17}H_{20}NO_5$ C: 318.1340 F: 318.1344	332 (14.0) $C_{18}H_{22}NO_5$ C: 332.1495 F: 332.1459	304 (8.0) $C_{16}H_{18}NO_5$ C: 304.1185 F: 304.1197	318 (8.0) $C_{17}H_{20}NO_5$ C: 318.1340 F: 318.1361	363 (25.0) $C_{17}H_{19}N_2O_7$ C: 363.1161 F: 363.1193
(c): $[M-CH_2CO_2R^1]^+$	304 (41.4) $C_{16}H_{18}NO_5$ C: 304.1185 F: 304.1162	318 (48.4) $C_{17}H_{20}NO_5$ C: 318.1342 F: 318.1320	290 (62.1) $C_{15}H_{16}NO_5$ C: 290.1026 F: 290.1021	304 (60.5) $C_{16}H_{18}NO_5$ C: 304.1185 F: 304.1189	349 (44.2) $C_{16}H_{17}N_2O_7$ C: 349.1036 F: 349.1019
(d): $[M-CH_2CH_2CO_2R^1]^+$	290 (39.0) $C_{15}H_{16}NO_5$ C: 290.1029 F: 290.1002	304 (29.7) $C_{16}H_{18}NO_5$ C: 304.1185 F: 304.1195	276 (27.5) $C_{14}H_{14}NO_5$ C: 276.0872 F: 276.0880	290 (37.2) $C_{15}H_{16}NO_5$ C: 290.1029 F: 290.1037	335 (81.0) $C_{15}H_{15}N_2O_7$ C: 335.0880 F: 335.0827

a) Numbers in parentheses are intensities (%) of fragment ion peaks. C: Calcd; F: Found.

- 7: $R^1=R^2=Me$, $R^3=H$
 8: $R^1=R^2=Et$, $R^3=H$
 10: $R^1=Et$, $R^2=R^3=H$
 11: $R^1=Et$, $R^2=Me$, $R^3=H$
 13: $R^1=R^2=Me$, $R^3=NO_2$

Experimental

All melting points are uncorrected. The spectrophotometers used were a JEOL model JNM-PS-100 or FX-200 for NMR spectra with tetramethylsilane (TMS) as an internal standard, a JEOL model JMS-D-300 for MS, and a Hitachi model 215 for IR spectra. The plates used for preparative thin-layer chromatography (PLC) were coated with silica gel (Kieselgel, PF₂₅₄, Merck). Aluminum oxide 90 (activity II—III, Merck) was used for column chromatography.

Oxidation of Oxolycoraminone (4) with $KMnO_4$ —(a) As described in a previous paper,²⁾ treatment of 4 (0.2 g) with a mixture of 1% $KMnO_4$ (43 ml) and Na_2CO_3 (0.2 g) in H_2O at 3–4 °C provided acid A²⁾ and acid B.²⁾

(b) An aqueous solution of 1% $KMnO_4$ (210 ml) was added dropwise to a mixture of 4 (0.6 g), Na_2CO_3 (0.6 g), H_2O (140 ml), and acetone (20 ml) at 5–6 °C during 5 h. The reaction mixture was filtered. The filtrate was concentrated, washed with $CHCl_3$, made acidic with 15% HCl, and extracted with $CHCl_3$. The extract was evaporated to give a residue (130 mg), which was triturated with EtOH to give acid A (1)²⁾ (20 mg), mp 218–221 °C. The aqueous acidic solution separated from the $CHCl_3$ layer was evaporated to dryness *in vacuo*. The residue was extracted with anhydrous EtOH. The extract was evaporated to dryness to give a residue, which was extracted with anhydrous EtOH– $CHCl_3$ (30:1). The extract was subjected to acidic aluminum oxide column chromatography with benzene and $CHCl_3$. The eluate with $CHCl_3$ was evaporated and the residue was crystallized from benzene– $CHCl_3$ to give colorless plates (30 mg) of compound 2.

Acid B (6) (Compound 1)—Colorless prisms, mp 265–267 °C (dec.) (from acetone). IR $\nu_{max}^{KBr} cm^{-1}$: 1750

(C=O), 1740 (C=O), 1620 (NC=O). $^1\text{H-NMR}$ (pyridine- d_5) δ : 3.12 (3H, s, NMe), 3.76 (3H, s, 8-OMe), 5.32 (1H, s, 14-H), 6.92 and 7.70 (each 1H, d, $J=8$ Hz, 9-H and 10-H, respectively); (CD_3OD) δ : 3.12 (3H, s, NMe), 3.89 (3H, s, 8-OMe), 5.03 (1H, s, 14-H), 7.00 and 7.32 (each 1H, d, $J=8$ Hz, 9-H and 10-H, respectively). MS m/z (%): 349 (M^+ , 32), 331 (23), 319 (22), 247 (40), 233 (92), 232 (100), 189 (44), 188 (48). Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_7$: C, 55.58; H, 5.76; N, 3.81. Found: C, 55.28; H, 5.72; N, 4.10.

Monoethyl Ester (10) (Compound 2) of Acid B (6)—Colorless plates, mp 224–227 °C (from benzene– CHCl_3). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3000–2500 (COOH), 1740 (C=O), 1730 (C=O), 1640 (NC=O). For NMR and MS, see Tables I and II, respectively. Anal. Calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_7$: C, 60.47; H, 6.14; N, 3.71. Found: C, 60.80; H, 6.04; N, 3.73.

Dimethyl Ester (7) of Acid B (6)—(a) From Acid B (6): A mixture of **6** (10 mg), MeOH (10 ml), and ethereal diazomethane was left to stand overnight at 0 °C. Work-up in the usual way gave the dimethyl ester (**7**) as colorless prisms, mp 165–168 °C (from benzene). $[\alpha]_D^{13} + 12.6^\circ$ ($c=0.20$, EtOH). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1745 (C=O), 1725 (C=O), 1630 (NC=O). For $^1\text{H-NMR}$ and MS, see Tables I and II, respectively. Anal. Calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_7$: C, 60.47; H, 6.14; N, 3.71. Found: C, 60.54; H, 6.14; N, 3.97. This ester (**7**) was identical with a sample of the dimethyl ester (obtained by Ishiwata³) of acid B by the mixed melting point test.

(b) From the Monoethyl Ester (10): A mixture of **10** (5 mg), 45% KOH (30 ml) and EtOH (30 ml) was refluxed for 3.5 h. The solvent was evaporated off under reduced pressure and the residue was diluted with H_2O . The aqueous solution was washed with CHCl_3 , made acidic with 15% HCl, and then extracted with CHCl_3 (1000 ml). The extract was dried over Na_2SO_4 and evaporated. The yellow residue (30 mg) was treated with ethereal diazomethane to give colorless plates, mp 164–167 °C (from ether); this product was identical with the sample of the ester (**7**) prepared by method (a) as judged from the spectral data and the result of the mixed melting point test.

Diethyl Ester (8) of Acid B (6)—(a) From Acid B (6): A solution of **6** (5 mg) in anhydrous EtOH (10 ml) saturated with dry hydrogen chloride was left to stand overnight at room temperature. Work-up in the usual manner gave the ester (**8**) as colorless plates, mp 149–151 °C (from EtOH). $[\alpha]_D^{13} + 30.3^\circ$ ($c=0.71$, EtOH). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1740 (C=O), 1730 (C=O), 1630 (NC=O). For $^1\text{H-NMR}$ and MS, see Tables I and II, respectively. Anal. Calcd for $\text{C}_{21}\text{H}_{27}\text{NO}_7$: C, 62.21; H, 6.71; N, 3.46. Found: C, 61.84; H, 6.33; N, 3.53.

(b) From the Monoethyl Ester (10): Similar treatment of **10** (5 mg) with anhydrous EtOH (10 ml) saturated with hydrogen chloride gave colorless plates, mp 149–151 °C (from benzene); this product was identical with the sample of **8** prepared by method (a) as judged from the spectral data and the result of the mixed melting point test.

Ethyl Methyl Ester (11) of Acid B (6)—The ester **10** (compound 2) (80 mg) was treated with ethereal diazomethane in MeOH in the usual way to give the ester (**11**) (60 mg), mp 144–146 °C (from benzene–petr. ether). $[\alpha]_D^{13} + 16.3^\circ$ ($c=0.15$, EtOH). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1755 and 1725 (C=O), 1635 (NC=O). For $^1\text{H-NMR}$ and MS, see Tables I and II, respectively. Anal. Calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_7$: C, 61.37; H, 6.44; N, 3.54. Found: C, 61.14; H, 6.24; N, 3.79.

10-Nitro Derivative (12) (Compound 3) of Acid B (6)—(a) From Oxolycoramine (**5**): **5** (100 mg) was added portionwise to a warm solution of ammonium metavanadate (2 mg) in 50% HNO_3 (2 ml). The mixture was stirred at 55 °C for 1.5 h, and then at 100 °C for 0.5 h. The reaction mixture was diluted with H_2O (100 ml) to give yellow crystals, which were recrystallized from EtOH to give compound **3** (**12**) (70 mg) as pale yellow crystals, mp 265–269 °C (dec.). $[\alpha]_D^{22} - 602.4^\circ$ ($c=0.83$, acetone). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3000–2500 (CO_2H), 1725 (C=O), 1625 (NC=O), 1530 and 1350 (NO_2). $^1\text{H-NMR}$ (CD_3OD) δ : 3.15 (3H, s, NMe), 3.98 (3H, s, OMe), 5.18 (1H, s, 14-H), 7.61 (1H, s, 9-H). MS m/z (%): 394 (M^+ , 5), 376 (19), 332 (20), 278 (21), 277 (52), 203 (31). Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_9$: C, 51.78; H, 4.61; N, 7.10. Found: C, 51.92; H, 4.34; N, 6.83.

(b) From Acid B (6): A mixture of **6** (50 mg) and 100% HNO_3 (0.3 ml) was stirred at 5 °C for 0.5 h and then at room temperature for 1 h. The reaction mixture was diluted with H_2O (1.5 ml). The resulting precipitate was separated by centrifugation, washed with H_2O , and dried. The precipitate was recrystallized from acetone to give yellow prisms, mp 265–269 °C (dec.); this product was identical with the sample of **12** prepared by method (a) as judged from the result of the mixed melting point test.

Dimethyl Ester (13) of Compound 3 (12)—(a) From **12**: A mixture of **12** (10 mg), MeOH (10 ml), and ethereal diazomethane was left to stand overnight at 0 °C. Work-up in the usual way gave **13** as pale yellow plates, mp 168–170 °C (from benzene–petr. ether).

(b) From the Diester (**7**): A mixture of **7** (6 mg) and 69% HNO_3 (0.15 ml) was stirred at 0–2 °C for 4 h. The reaction mixture was diluted with H_2O (0.7 ml), made basic with 20% NH_4OH , and extracted with CHCl_3 . The extract was evaporated under reduced pressure. The residue was subjected to PLC using SiO_2 –[benzene–acetone (3:1)] to give two fractions of R_f 0.26–0.34 (**7**, 2 mg) and R_f 0.36–0.45 (crude **13**, 0.7 mg). The crude **13** was recrystallized from petr. ether–ethyl acetate to give **13** as pale yellow plates, mp 164–165 °C. The esters prepared by methods (a) and (b) were identical as judged from the result of the mixed melting point test and comparison of their IR spectra.

Nitration of Methyl Ester (3) of Acid A (1)—A mixture of **3** (26 mg) and 100% HNO_3 (0.2 ml) was stirred at 0 °C for 1 h. The reaction mixture was diluted with H_2O (0.7 ml), made basic with 20% NH_4OH , and extracted with CHCl_3 . The extract was evaporated under reduced pressure. The residue was subjected to PLC using SiO_2 –[benzene–acetone (3:1)] to give two fractions: that of R_f 0.69–0.75 gave **14** as an oil (2 mg) and that of R_f 0.57–0.63 gave **15** as

an oil (4 mg). Compound (**14**): High MS m/z : Found: 378.1076. Calcd for $C_{17}H_{18}N_2O_7$: 378.1064. For 1H -NMR, see Table I. Irradiation at δ 4.02 (8-OMe) resulted in a 31% NOE increment in the signal of 9-H. Compound (**15**): High MS m/z : Found: 378.1047. Calcd for $C_{17}H_{18}N_2O_7$: 378.1062. For 1H -NMR, see Table I. Irradiation at δ 4.20 (8-OMe) resulted in no NOE increment.

References and Notes

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- 2) S. Kobayashi, T. Tokumoto, T. Koike, K. Iizuka, H. Irie, and S. Uyeo, *Chem. Pharm. Bull.*, **34**, 2443 (1986).
- 3) S. Ishiwata, *Yakugaku Zasshi*, **58**, 13 (1938). The formulas $C_{13}H_{13}NO_6$ [mp 261—262 °C (dec.)] and $C_{15}H_{17}NO_6$ (mp 152—153 °C; mp 165—167 °C in our laboratory) reported by Ishiwata for acid B and its dimethyl ester, respectively, were revised to $C_{17}H_{19}NO_7$ and $C_{19}H_{23}NO_7$ by us.