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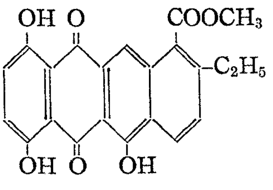
104. Zen-ichi Horii, Takefumi Momose, and Yasumitsu Tamura :

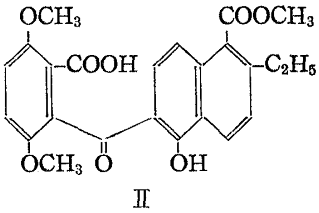
Synthetic Studies on η-Pyrromycinone. V.[*1]
Total Synthesis of η-Pyrromycinone.

(*Faculty of Pharmaceutical Sciences, Osaka University*[*2])

η-Pyrromycinone,[*3] a metabolite of the Streptomyces, was shown in 1960 by Brockmann, Prelog, Ollis, *et al.*1) to be methyl 2-ethyl-6,11-dioxo-5,7,10-trihydroxy-6,11-dihydro-1-naphthacenecarboxylate (I). In recent short communications2,3) have been reported the synthesis of compound (I) and its identification with η-pyrromycinone. The present paper describes a full account of the experiments for the synthesis of I from methyl 2-ethyl-5-hydroxy-6-(2-carboxy-3,6-dimethoxy-benzoyl)-1-naphthoate (II) prepared by the condensation4) of methyl 2-ethyl-5-hydroxy-1-naphthoate5) and 3,6-dimethoxy phthalic anhydride.



I



II

An initial attempt to cyclize II directly to the methyl ether of I by means of sulfuric acid or polyphosphoric acid failed because of the simultaneous elimination of methoxycarbonyl group on cyclization. Therefore, our endeavors were directed to explore alternative routes to I from II. The successful route was *via* methyl 2-ethyl-5-methoxy-6-(6-methoxycarbonyl-2,5-dimethoxybenzyl)-1-naphthoate (VI), 2-ethyl-11-oxo-5,7,10-trimethoxy-6,11-dihydro-1-naphthacenecarboxylic acid (VII) and methyl 2-ethyl-6,11-dioxo-5,7,10-trimethoxy-6,11-dihydro-1-naphthacenecarboxylate (IX), which was carried out according to the model procedures[*2] established preliminarily for 1,4,6-trimethoxynaphthacenequinone. The reactions employed are summarized by the equations shown in Chart 1.

Methylation of II with dimethyl sulfate and anhydrous potassium carbonate in dry acetone gave methyl 2-ethyl-5-methoxy-6-(6-methoxy carbonyl-2,5-dimethoxybenzoyl)-1-naphthoate (III) in 91% yield. Reduction of III by means of zinc powder and boiling aqueous sodium hydroxide was accompanied with partial hydrolysis[*2] to give 2-ethyl-5-methoxy-6-(6-methoxycarbonyl-2,5-dimethoxybenzyl)-1-naphthoic acid (IV) in 95% yield. The half ester (IV) was also obtained by reduction of II with zinc powder in boilling aqueous sodium hydroxide, followed by methylation of resulted 2-ethyl-5-hydroxy-6-(2-carboxy-3,6-dimethoxybenzyl)-1-naphthoic acid (V) with dimethyl sulfate and aqueous potassium hydroxide.

[*1] Part IV. Z. Horii, T. Momose, Y. Tamura : This Bulletin, **13**, 740 (1965).

[*2] Toneyama, Toyonaka, Osaka-fu (堀井善一, 百瀬雄章, 田村恭光).

[*3] For recent review on this subject, see H. Brockmann : Fortschr. Chem. org. Naturstoffe, **21**, 121 (1963).

1) H. Brockmann, V. Prelog, W. D. Ollis, *et al.* : Tetrahedron Letters, No. 8, 25 (1960).

2) Z. Horii, T. Momose, Y. Tamura : This Bulletin, **12**, 1262 (1964).

3) *Idem* : *Ibid.*, **13**, 635 (1965).

4) *Idem* : *Ibid.*, **13**, 737 (1965).

5) *Idem* : *Ibid.*, **13**, 651 (1965).

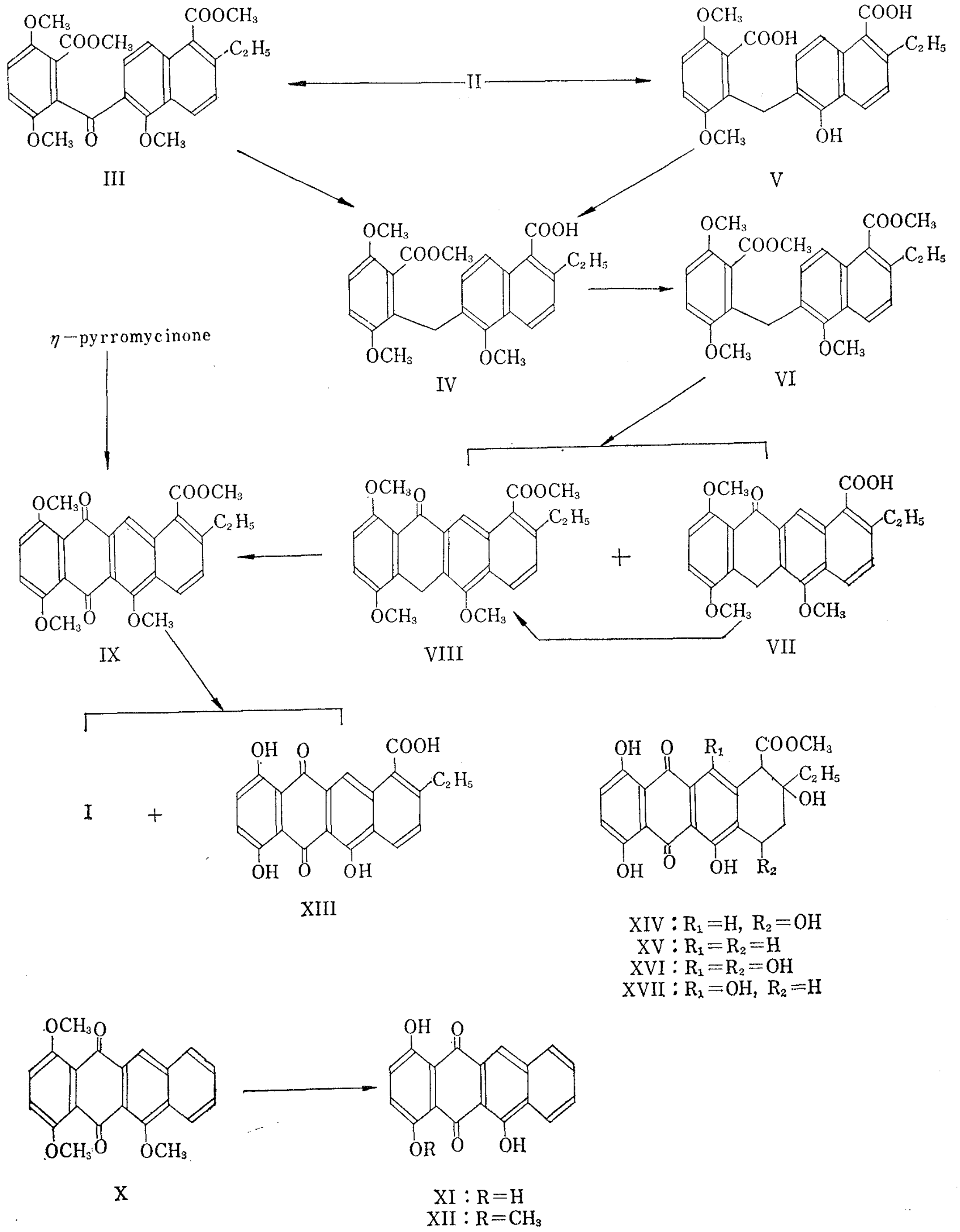
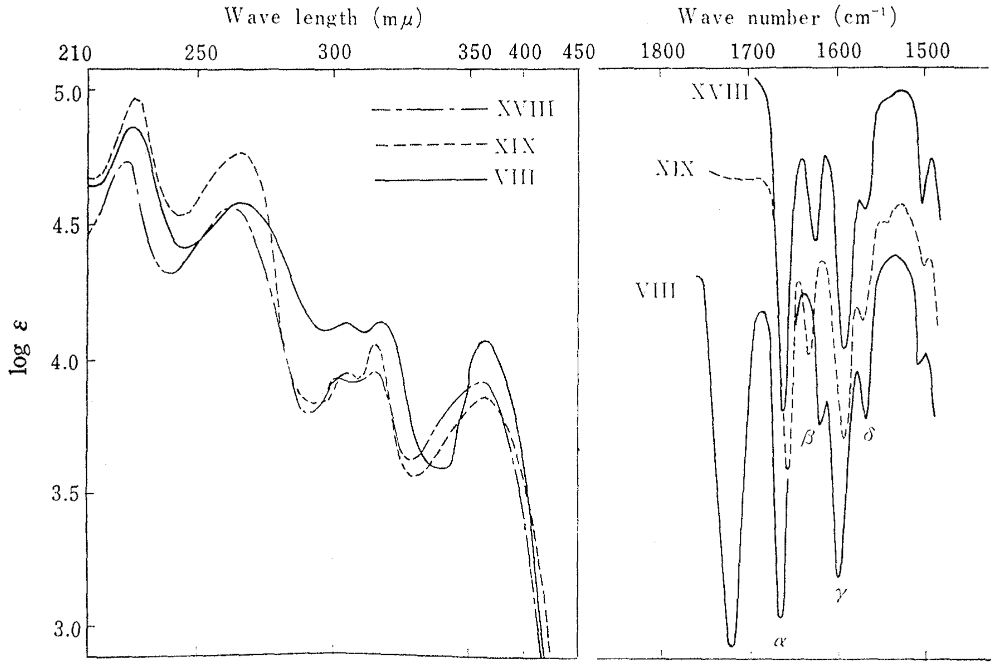


Chart 1.

The diester (VI) was prepared by methylation of IV with methyl iodide (78% yield) or dimethyl sulfate (88% yield) in dry acetone in the presence of anhydrous potassium carbonate. Cyclization of VI by heating with polyphosphoric acid at 100° for 10 minutes gave a mixture of nearly equal amounts of the naphthacenone-carboxylic acid (VII, 30% yield) and its methyl ester (VIII), the latter of which was also obtained by methylation of VII. Oxidation of VIII with 2.5 molar equivalents of chromium trioxide according to the method described in the preceding paper[*2] gave the naphthacenequinone-ester (IX) in 13% yield. The infrared and ultraviolet spectra of VIII, IX and their related compounds are shown in Figs. 1 and 2, which confirmed the structures of VIII and IX.

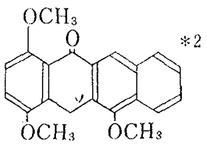


Maximum, mμ (ε × 10^{-4})		
XVIII[a]	XIX[a]	VIII
224.5 (5.48)	228.3 (9.48)	226.5 (7.32)
264 (3.68)	266 (6.06)	266.5 (3.86)
304 (0.88)	303 (0.92)	304 (1.38)
315.5 (0.95)	315 (1.05)	317 (1.48)
362 (0.87)	364 (0.77)	364 (1.19)

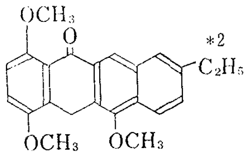
	Maximum		
	XVIII[a]	XIX[a]	VIII
α	1661	1652	1656
β	1623	1626	1613
γ	1592	1589	1592
δ	1567	1564	1560

Fig. 1. Ultraviolet (in 95% EtOH) and Infrared (in Nujol) Spectra of Methyl 2-Ethyl-11-oxo-5, 7, 10-trimethoxy-6, 11-dihydro-1-naphthacenecarboxylate (VIII) and Related 5(12*H*)-Naphthacenones

a)



XVIII



XIX

As to a demethylation of IX to I, we found that the procedure of McOmie and Watts[6] employing boron tribromide gave a satisfactory result. Prior to this experiment, 1,4,6-trimethoxynaphthacenequinone (X)[4] was selected as a model compound and its demethylation was examined. Treatment of X with 23 molar equivalents of boron tribromide in dry methylene chloride at room temperature for one hour gave 1,4,6-trihydroxynaphthacenequinone (XI)[7] in a quantitative yield, while employment of 5 molar equivalents of the demethylating reagent yielded 4-methoxy-1,6-dihydroxynaphthacenequinone (XII)[4] in 31% yield. Similar reaction of IX with 35 molar equivalents of boron tribromide gave two products, I and the corresponding free acid (XIII).

The infrared spectra of I, XIII, and IX were well in agreement with those of η-pyrromycinone, η-pyrromycinonic acid, and η-pyrromycinone trimethyl ether, respectively.

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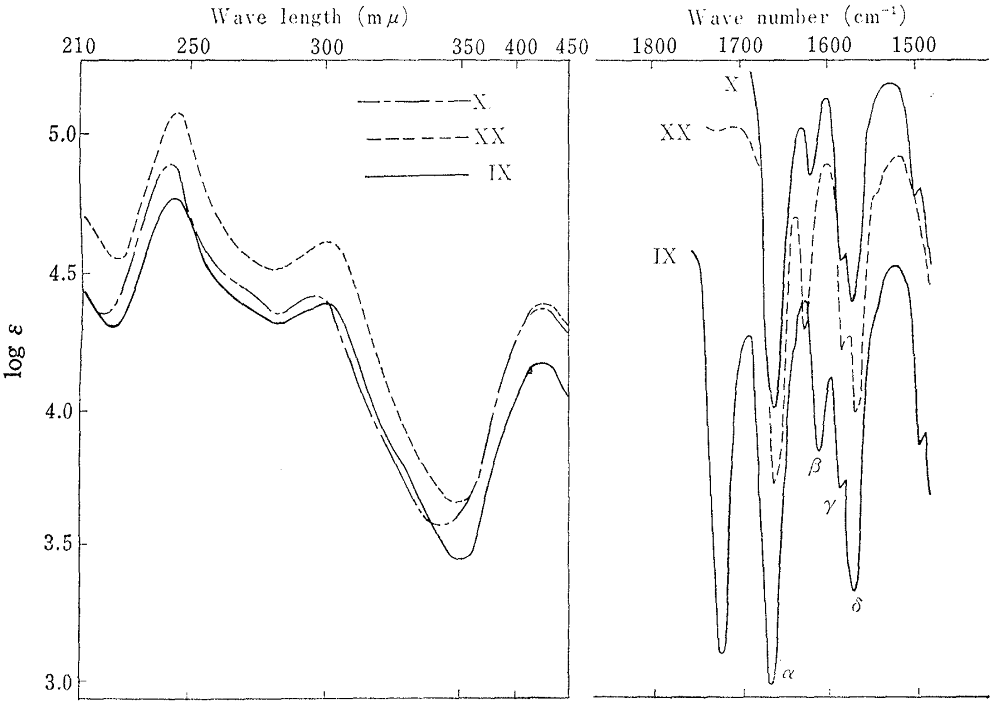
6) J. F. W. McOmie, M. L. Watts: Chem. Ind. (London), **1963**, 1658.
7) H. Brockmann, W. Müller: Chem. Ber., **92**, 1164 (1959).

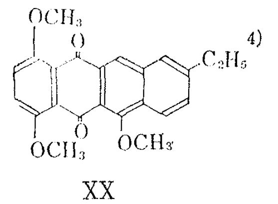


Maximum, mμ ($\varepsilon \times 10^{-4}$)		
X	XX$^{a)}$	IX
242.2 (8.02)	245.3 (12.35)	246.5 (6.07)
295 (2.63)	301 (4.27)	300 (2.50)
425 (2.42)	427 (2.52)	428 (1.48)

	Maximum		
	X	XX$^{a)}$	IX
α	1663	1663	1663
β	1620	1626	1608
γ	1584	1582	1586
δ	1570	1567	1569

Fig. 2. Ultraviolet (in 95% EtOH) and Infrared (in Nujol) Spectra of Methyl 2-Ethyl-6,11-dioxo-5,7,10-trimethoxy-6,11-dihydro-1-naphthacenecarboxylate (IX) and Related Methoxynaphthacenequinones

a)



XX

Here, those of both synthetic and natural η-pyrromycinone are shown in Fig. 3.

The total synthesis thus accomplished confirmed unequivocally the structure of η-pyrromycinone. This would give also a support to the structures of ε- and ζ-pyrromycinone (XIV and XV) as well as of ε- and ζ-isorhodomycinone (XVI and XVII) since these anthracyclinones have been related to I.

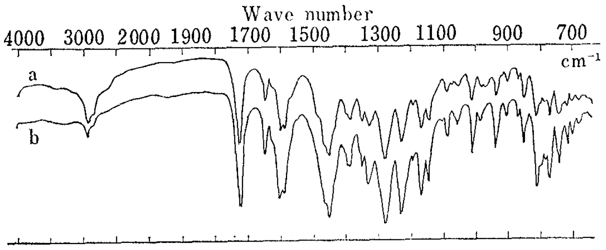


Fig. 3. Infrared Spectra of η-Pyrromycinone (in KBr disk)

a: synthetic; b: natural

Experimental*4

Methyl 2-Ethyl-5-methoxy-6-(6-methoxycarbonyl-2,5-dimethoxybenzoyl)-1-naphthoate (Ⅲ)——A mixture of 2.8 g. of methyl 2-ethyl-5-hydroxy-6-(2-carboxy-3,6-dimethoxybenzoyl)-1-naphthoate (Ⅱ),4) 30 g. of anhyd. K_2CO_3, 25 g. of Me_2SO_4 and 50 ml. of acetone was refluxed for 10 hr. After removing acetone, 200 ml. of H_2O containing 5 ml. of 28% aq. NH_3 was added to the reaction mixture to destroy the excess of Me_2SO_4. The mixture was extracted with benzene, and the extract was washed with H_2O, dried over anhyd. Na_2SO_4 and evaporated to give 3 g. of a pale brown paste which gave crystals on trituration with MeOH. Recrystallization from MeOH gave 2.7 g. (91%) of Ⅲ as colorless leaflets, m.p. 159~161°, which were identified with the authentic sample obtained in the preceding paper4) by mixed melting point determination and IR spectral comparison.

2-Ethyl-5-hydroxy-6-(2-carboxy-3,6-dimethoxybenzyl)-1-naphthoic Acid (Ⅴ)——A mixture of 0.3 g. of Ⅱ, 3 g. of NaOH, 2 g. of Zn powder (activated with ammoniacal $CuSO_4$) and 60 ml. of H_2O was refluxed for 37 hr., during whose time 1 g. of NaOH and 2 g. of Zn powder were added on every 8 hr. The hot alkaline solution was decanted, and the residual Zn powder was washed with boiling 5% aq. NaOH (50 ml. × 2). The alkaline solution and washings were combined, acidified with 20% H_2SO_4 and extracted with AcOEt. The extract was washed with H_2O, dried over anhyd. Na_2SO_4 and evaporated. Trituration of the residue with $CHCl_3$ gave 0.28 g. of colorless crystals, m.p. 222~224° (decomp.). An analytical sample (colorless microplates) was prepared by three recrystallizations from EtOH-H_2O, which melted at 204~207°. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1661 (C=O). *Anal.* Calcd. for $C_{23}H_{22}O_7 \cdot C_2H_6O$: C, 65.78; H, 6.18. Found: C, 65.30; H, 6.05.

2-Ethyl-5-methoxy-6-(6-methoxycarbonyl-2,5-dimethoxybenzyl)-1-naphthoic Acid (Ⅳ)——A) From Ⅲ: A suspension of 2.2 g. of Ⅲ, 20 g. of NaOH, 20 g. of Zn powder (activated with ammoniacal $CuSO_4$) and 100 ml. of H_2O was refluxed for 8 hr. Another 10 g. of Zn, 10 g. of NaOH and 50 ml. of H_2O were added, and refluxing was continued for 9 hr. Then, further 5 g. of Zn was added, and followed by 10 hrs' refluxing. After cooling, the alkaline solution was decanted, and the residual Zn mass was washed with hot H_2O (50 ml. × 2). The alkaline solution and the washings were combined and acidified with 20% H_2SO_4. Recrystallization of the precipitates from MeOH-ether (1:2) gave 1.9 g. (95%) of Ⅳ, m.p. 125~130° (decomp.). Further recrystallization from MeOH-ether (1:2) gave an analytical sample as colorless microprisms, m.p. 130~132° (decomp.). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1724, 1678 (C=O). *Anal.* Calcd. for $C_{25}H_{26}O_7 \cdot C_4H_{10}O$: C, 67.95; H, 7.08. Found: C, 67.64; H, 7.13.

B) From Ⅴ: To a stirred mixture of 280 mg. of Ⅴ, 12 g. of KOH and 50 ml. of H_2O was added 13 g. of Me_2SO_4 over a period of 5 min. and the mixture was stirred for 20 min. To this was added with stirring additional 12 g. of KOH and 13 g. of Me_2SO_4, and the mixture was stirred for further 30 min. at 100°. Ether extraction of the cooled mixture and evaporation of the resulted ether layer gave 30 mg. of colorless crystals, m.p. 126~127°, which were identified with the sample of methyl 2-ethyl-5-methoxy-6-(6-methoxycarbonyl-2,5-dimethoxybenzyl)-1-naphthoate (Ⅵ) prepared in the later experiment by mixed fusion and infrared spectral comparison. Acidification of the alkaline layer with 20% H_2SO_4, extraction with ether and evaporation of the extract gave 200 mg. of colorless crystals, m.p. 130~132°, which were identified with the authentic sample of Ⅳ obtained in A) by infrared spectral comparison in Nujol.

Methyl 2-Ethyl-5-methoxy-6-(6-methoxycarbonyl-2,5-dimethoxybenzyl)-1-naphthoate (Ⅵ)——A) Methylation of Ⅳ with Me_2SO_4 and K_2CO_3: A mixture of 550 mg. of Ⅳ, 10 g. of anhyd. K_2CO_3, 10 g. of Me_2SO_4 and 20 ml. of acetone was refluxed for 10 hr. After removing acetone, 100 ml. of H_2O containing 3 ml. of 28% aq. NH_3 was added to the residual mass to destroy the excess of Me_2SO_4, and the mixture was extracted with ether. The extract was washed with 5% HCl and then H_2O, dried over anhyd. Na_2SO_4 and evaporated to give 550 mg. of a paste, which crystallized on trituration with a small amount of MeOH. Recrystallization from MeOH gave 500 mg. (88%) of Ⅵ as colorless prisms, m.p. 126~127°. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1723 (C=O). *Anal.* Calcd. for $C_{26}H_{28}O_7$: C, 69.01; H, 6.24. Found: C, 68.82; H, 6.18.

B) Methylation of Ⅳ with MeI and K_2CO_3: A mixture of 0.5 g. of Ⅳ, 5 g. of anhyd. K_2CO_3, 20 g. of MeI and 20 ml. of acetone was refluxed for 15 hr. After removing acetone, the residual mass was extracted with hot $CHCl_3$. Evaporation of the $CHCl_3$ extract gave 0.4 g. (78%) of Ⅵ as colorless crystals, m.p. 125~127°, which were identified with the sample obtained in A) by infrared spectral comparison.

Polyphosphoric Acid Cyclization of Ⅵ[2-Ethyl-11-oxo-5,7,10-trimethoxy-6,11-dihydro-1-naphthacenecarboxylic Acid (Ⅶ) and its Methyl Ester (Ⅷ)]——A mixture of 550 mg. of Ⅵ and 125 g. of polyphosphoric acid was stirred at 100° for 10 min. and poured onto 300 g. of cracked ice. The reddish brown precipitates were collected, washed with H_2O, shaken with 20 ml. of satd. aq. $NaHCO_3$ and filtered. The filtrate was acidified with 10% HCl. Recrystallization of the precipitates (200 mg.) from acetone gave 150 mg. (30%) of Ⅶ as pale yellow needles, m.p. 258~260° (decomp.). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3115 (hindered COOH), 1706, 1645 (C=O). *Anal.* Calcd. for $C_{24}H_{22}O_6$: C, 70.92; H, 5.46. Found: C, 70.89; H, 5.45.

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*4 All melting points are uncorrected.

The insoluble material in aq. $NaHCO_3$ was collected, washed with H_2O and dried at 50° *in vacuo* to give 300 mg. of reddish powder which was presumed to be VIII contaminated with a small amount of VI from its IR spectrum, but could not be purified by recrystallization or by chromatography over silica gel employing $CHCl_3$ as eluent, due to great solubilities in most solvents except for hexane or cyclohexane and also due to less stabilities*[2] in polar solvents. A pure sample was obtained from pure VII by esterification with CH_2N_2 in the experiment behind.

Esterification of VII with Diazomethane——To a suspension of 20 mg. of VII in 50 ml. of ether was added dropwise a solution of CH_2N_2 in ether under ice-cooling until the crystals disappeared and a yellow color persisted for 1 hr. The solvent was removed under a reduced pressure and washing the residue with a small amount of ether gave 10 mg. of crystals. Two recrystallizations from cyclohexane gave slightly yellow colored needles, m.p. 174~176°. IR ν_{max}^{Nujol} cm^{-1}: 1714, 1656 (C=O).

Methyl 2-Ethyl-6,11-dioxo-5,7,10-trimethoxy-6,11-dihydro-1-naphthacenecarboxylate (IX)——To an ice-cooled solution of 250 mg. of VIII in 10 ml. of AcOH freshly distilled over $KMnO_4$ was added a solution of 200 mg. (2.5 mole equiv.) of CrO_3 in 4 ml. of AcOH freshly distilled over $KMnO_4$, and the mixture was allowed to stand at room temperature for 1 hr. The dark brown mixture was diluted with 50 ml. of $CHCl_3$, washed three times with H_2O, twice with satd. aq. $NaHCO_3$ and then with H_2O and dried over anhyd. Na_2SO_4. Evaporation of the solvent gave a yellowish brown solid, which was subjected to column chromatography on alumina employing $CHCl_3$ as eluent. The first fraction gave 34.5 mg. (13%) of IX as bright yellow needles, m.p. 235~237° after recrystallization from MeOH. IR ν_{max}^{KBr} cm^{-1}: 1721, 1663 (C=O), 1608, 1586, 1569 (arom.). *Anal.* Calcd. for $C_{25}H_{22}O_7$: C, 69.11; H, 5.10. Found: C, 68.72; H, 5.06.

This specimen was proved to be identical with the trimethyl ether of natural η-pyrromycinone by mixed fusion and comparison of their IR spectra (KBr).

1,4,6-Trihydroxynaphthacenequinone (XI)——To a cold solution of 100 mg. of 1,4,6-trimethoxynaphthacenequinone (X)[4] in 10 ml. of dry CH_2Cl_2 was added a cold solution of 5 g. (23 equiv.) of BBr_3 in 5 ml. of dry CH_2Cl_2 at −60°. The mixture was allowed to warm up to room temperature, during whose time a vigorous evolution of gas was observed. After standing at room temperature for further 1 hr., the deep blue mixture resulted was poured onto cracked ice and extracted with AcOEt. The extract was washed with satd. aq. $NaHCO_3$ and H_2O, dried over anhyd. Na_2SO_4 and evaporated. Washing the dark red residue (90 mg.) with a small amount of AcOEt gave 85 mg. of XI, m.p. 290~294°. Two recrystallizations from benzene gave deep red needles, m.p. 291~294° (lit.,[7] m.p. 294°). *Anal.* Calcd. for $C_{18}H_{10}O_5$: C, 70.59; H, 3.29. Found: C, 70.51; H, 3.21.

Another experiment employing 1 g. (4.6 equiv.) of BBr_3 gave 28 mg. (31%) of red needles, m.p. 248~250° (from benzene). This specimen was proved to be identical with the authentic sample of 4-methoxy-1,6-dihydroxynaphthacenequinone (XII)[4] by infrared spectral comparison and mixed fusion. *Anal.* Calcd. for $C_{19}H_{12}O_5$: C, 71.25; H, 3.78. Found: C, 71.24; H, 3.75.

Demethylation of IX with Boron Tribromide [Methyl 2-Ethyl-6,11-dioxo-5,7,10-trihydroxy-6,11-dihydro-1-naphthacenecarboxylate (η-Pyrromycinone) (I) and 2-Ethyl-6,11-dioxo-5,7,10-trihydroxy-6,11-dihydro-1-naphthacenecarboxylic Acid (η-Pyrromycinonic Acid) (XIII)]——To a cold solution of 50 mg. of IX in 20 ml. of dry CH_2Cl_2 was added a mixture of 5 g. (34.6 equiv.) of BBr_3 and 10 ml. of dry CH_2Cl_2 in one portion at −60°, and the mixture was allowed to warm up to room temperature and stand for 1 hr. The resulted deep blue mixture was poured onto cracked ice and extracted with AcOEt. The extract was washed with satd. aq. $NaHCO_3$ (30 ml. × 3) and H_2O, dried over anhyd. Na_2SO_4 and evaporated. The residual bright red solid was chromatographed over silica gel employing $CHCl_3$ as eluent to give 1 mg. of I as bright red needles, m.p. 238~239° as the first fraction. IR ν_{max}^{KBr} cm^{-1}: 1724, 1644 (C=O). This specimen was proved to be identical with natural η-pyrromycinone (lit.,[8] m.p. 236~237°, IR ν_{max}^{KBr} cm^{-1}: 1730, 1653; lit.,[9] m.p. 239~242°, IR ν_{max}^{KBr} cm^{-1}: 1721, 1675; lit.,[10] m.p. 239°, IR ν_{max} cm^{-1} 1724) by comparison of their infrared spectra (KBr). The second fraction gave a small amount of deep red needles, m.p. 257~261° (decomp.), which was proved, by infrared spectral comparison (KBr), to be identical with XIII obtained from an acidic fraction as shown in subsequent description below.

The $NaHCO_3$ washings were combined, acidified with conc. HCl and extracted with AcOEt. Evaporation of the AcOEt extract gave a dark red residue (20 mg.). The residue was extracted with boiling acetone, and the extract was evaporated to give a deep red residue, which was subjected to thin-layer chromatography over silica gel employing $AcOH-CHCl_3$ (1:20) as eluent. A pink red spot of the least Rf value was scraped. The scraped spots were combined and extracted with $AcOH-CHCl_3$ (1:5) to give 1.5 mg. of dark red needles, m.p. 255~260° (decomp.). Recrystallization from AcOH gave 0.8 mg. of XIII as deep red needles, m.p. 260~262° (decomp.) IR ν_{max}^{KBr} cm^{-1}: 1704 (C=O), 1648, 1600, 1587 (arom.). This specimen was proved to be identical with η-pyrromycinonic acid [(lit.,[8] m.p. 263° (decomp.), IR ν_{max}^{KBr} cm^{-1}: 1704] by comparison of their infrared spectra (KBr).

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10) W. D. Ollis, I. O. Sutherland, J. J. Gordon: Tetrahedron Letters, No. 16, 17 (1959).

Trimethyl Ether of Natural η-Pyrromycinone——A mixture of 20 mg. of natural η-pyrromycinone, 5 g. of anhyd. K_2CO_3, 20 g. of MeI and 20 ml. of acetone was refluxed for 11.5 hr. After removing the solvent, the residual mass was extracted with $CHCl_3$ (30 ml. × 3). The $CHCl_3$ extract was filtered and evaporated. Washing the residue with a small amount of ether, followed by recrystallization from MeOH, gave 22 mg. of bright yellow needles, m.p. 235~237°. *Anal.* Calcd. for $C_{25}H_{22}O_7$: C, 69.11; H, 5.10. Found : C, 68.62; H, 5.12.

The authors are grateful to Professors H. Brockmann, V. Prelog, W. D. Ollis, and Dr. W. Keller-Schierlein for providing η-pyrromycinone, η-pyrromycinonic acid and their infrared spectra.

Summary

η-Pyrromycinone (I), η-pyrromycinonic acid (XIII) and η-pyrromycinone trimethyl ether (IX) were synthesized by a series of reactions shown in Chart 1. The syntheses provide unequivocal confirmations for their structures.

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105. **Takuzo Nishimura and Bunji Shimizu** : Studies on Synthetic Nucleosides. V.[*1] Anomeric Pyrimidine Nucleosides of D-Arabinose and D-Lyxose.

(*Research Laboratories, Sankyo Co., Ltd.*[*2])

Previous papers of this series[1] have described the facile synthesis of glucose and ribose nucleosides by the fusion of acyl halogeno sugars with trimethylsilylated pyrimidines or purines followed by removal of the protecting groups. In addition, it has been shown that the method introduced gave not only β- but α-nucleosides having 1′,2′-*cis* configuration. Such type of compounds have scarcely been prepared[2] and are of interest in biological studies.

The "silyl method" has now been applied to the synthesis of anomeric pyrimidine nucleosides of arabinose and lyxose which have opposite hydroxyl configuration to ribose or glucose at 2′-carbon atom. The spectral and chromatographic properties and the determinations of the structures of the nucleosides prepared are reported. Methyl 2,3,5-tri-O-benzoyl-α-D-arabinofuranoside, which was prepared according to the procedure of Wright and Khorana,[3] was converted to 2,3,5-tri-O-benzoyl-α-D-arabinofuranosyl bromide (III) in good yield. Bis(trimethylsilyl)uracil (I)[1] and III were condensed by heating together at 190° for 40 minutes. After treatment of the reaction mixture with aqueous ethanol, the product was chromatographed on silica gel and the required tribenzoylarabinofuranosyluracil was obtained in 50% yield. Trituration of the tribenzoate with ethanol yielded fine needles (IVb). Tribenzoate was debezoylated

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[*1] Part IV : This Bulletin, 12, 1471 (1964).

[*2] 2-58, 1-Chome, Hiromachi, Shinagawa-ku, Tokyo (西村卓三, 清水文治).

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3) R. S. Wright, H. G. Khorana : *Ibid.*, **80**, 1994 (1958).