washed with $H_2O$ and the filtrate combined with washings was acidified with HCl. Extraction with 5 portions of 200 ml. each of $Et_2O$, gave a crude reduction product (460 mg.) that was washed with $CHCl_3$, crystallized from $CHCl_3$–$Me_2CO$ to give colorless leaflets (under microscope), m.p. 145°. This substance is insoluble in petr. benzin or $CHCl_3$ and gives a red coloration with $FeCl_3$ in EtOH. When it was heated rapidly up to 120°, it decomposed with effervescence, but when the temperature was raised slowly, it did not melt below 145°. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 941, 1200, 1420, 1695, 1715 (COOH), 1380 ($CH_3$), 1516, 1594, 1626 (phenyl). Neutral. equivalent; 143.

**Acetylation of $C_{14}H_{18}O_5$ Acid**——The above-obtained $C_{14}H_{18}O_5$ acid (500 mg.) was boiled with $Ac_2O$ (4 ml.) for 1 hr. Then the solution was evaporated *in vacuo* to remove $Ac_2O$, and the resinous substance remained washed with ligroin, dissolved in $Et_2O$, decolorized with active charcoal, and then crystallized by adding petr. benzin. A sample for analysis was prepared by further recrystallization from $H_2O$. Colorless needles, m.p. 148°. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1225, 1760 (phenolic or enolic $COCH_3$), 1373 ($CH_3$), 1506, 1584, 1623 (phenyl), 1695, 1711 (COOH). *Anal.* Calcd. for $C_{16}H_{20}O_6$: C, 62.32; H, 6.54; Acetyl (monoacetate), 13.96. Found: C, 62.34; H, 6.56; Acetyl, 14.29; neutral. equivalent (phenolphthalein), 162.

The authors express their gratitude to the members of the Mitsubishi Kasei Co., Ltd., who performed the measurement of the NMR spectra. The IR and UV spectral measurements and microanalyses were carried out by the members of microanalytical laboratories of the Faculty of the Pharmaceutical Sciences and the Institute for Applied Microbiology of the University of Tokyo, and of the Hoshi College of Pharmacy, to whom the authors' thanks are due.

## Summary

The ozonolysis of anhydroitaconitin which was prepared from itaconitin by the action of acetic or propionic anhydride followed by hydrolysis, yielded 2,4-cresotaldehyde liberating acetaldehyde and carbon dioxide. Treatment of the same substance with nitric acid afforded 2,4,6-trinitro-*m*-cresol. These and other experimental results showed that the anhydroitaconitin was an aromatic compound having a *m*-cresyl grouping with an adjacent ethylenic linkage. The catalytic hydrogenation of anhydroitaconitin in acetone gave dihydroanhydroitaconitin, whereas in alkali gave a carboxylic acid, $C_{14}H_{18}O_5$.

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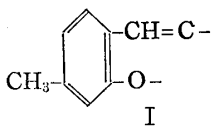
[Chem. Pharm. Bull. 13(1) 64 ~ 69 (1965)]

*UDC 581.19 : 582.282.12*

# 11. Shoichi Nakajima: Studies on the Structure of Itaconitin. V.*1 On the Alkaline Hydrogenation Product of Anhydroitaconitin.*2

(*Hoshi College of Pharmacy**3)

On the basis of the experimental results reported in the preceding paper*1 anhydroitaconitin,[1] a dehydration product of itaconitin, was formulated partially as I.




I

By the present study, it was found that ozonolysis of acetylanhydroitaconitin*1,1) yielded 2,4-cresotaldehyde. This appears to suggest that the O-functional group directly attached to the benzene nucleus in

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*1 Part Ⅳ. S. Nakajima, K. Kinoshita, S. Shibata: This Bulletin, **13**, 58 (1965).

*2 Presented at Ⅷth Japanese Symposium on the Chemistry of Natural Products (Oct. 1963). Proceedings, p. 144 (in Japanese).

*3 2-Chome, Ebara, Shinagawa-ku, Tokyo (仲嶋正一).

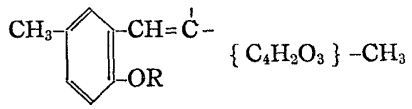
1) Part I. K. Kinoshita, S. Nakajima: *Ibid.*, **6**, 31 (1958).

anhydroitaconitin is hindered for acetylation. However, there would be another possibility of forming 2,4-cresotaldehyde by the deacetylation of original O-acetate during the treatment after ozonization.

In the purpose to solve this problem, anhydroitaconitin was methylated with diazomethane or dimethyl sulfate and alkali to afford a colorless compound, $C_{17}O_{20}O_5$, m.p. 117°, which was suggested to be a conjugated diester in regard to its infrared absorption bands at 1280, 1714, and 1730 $cm^{-1}$ (in KBr). As the infrared spectrum of anhydroitaconitin shows no indication of carboxyl function (Fig. 3 in Part Ⅳ*[1]), the above conjugated diester grouping must be newly formed during the methylation.

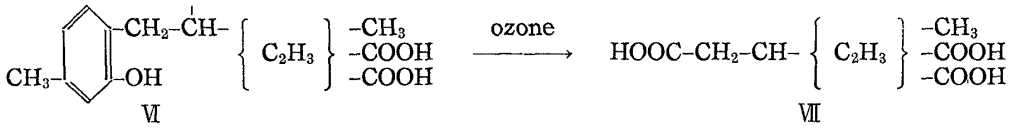
By heating with sodium hydroxide solution, the above ester afforded a sodium salt, which was further converted by warming with conc. HCl into a product, $C_{15}H_{14}O_4$, yellow needles of melting at 156°. This product would be methylanhydroitaconitin having the same location of carbonyl groupings as anhydroitaconitin, as it shows similar infrared absorption bands at 1753, 1810, and 1845 $cm^{-1}$.

Ozonolysis of the methylanhydroitaconitin, followed by treatment with hot water and then by oxidation with ammoniac silver nitrate solution, yielded a carboxylic acid, $C_9H_{10}O_3$, which was identical with the synthetic 2-methoxy-4-methylbenzoic acid. Consequently, it has been concluded that anhydroitaconitin possesses a free hydroxyl group to be formulated as Ⅱ, while methylanhydroitaconitin, acetylanhydroitaconitin, and propionylanhydroitaconitin are formulated as Ⅲ, Ⅳ, and Ⅴ, respectively.




Ⅱ : R=H Ⅳ : R=$COCH_3$
Ⅲ : R=$CH_3$ Ⅴ : R=$COC_2H_5$

The reduction product,*[1] $C_{14}H_{18}O_6$, derived from anhydroitaconitin by the alkaline catalytic hydrogenation, seems to be a dibasic acid on the basis of the two carbonyl bands at 1695 and 1715 $cm^{-1}$ in its infrared spectrum (Fig. 4 in Part Ⅳ*[1]). This was verified by the titration with alkali and also by the formation of bis(4-phenylphenacyl)ester, $C_{42}H_{38}O_7$, m.p. 173°, and thus the representation (Ⅵ) has become possible for the above dibasic acid.




Ⅵ Ⅶ

When the $C_{14}H_{18}O_5$ acid was treated with ozone for eight hours, a colorless water-soluble acidic substance, $C_8H_{12}O_6$, m.p. 179°, was produced. This product was shown to be a nonaromatic fatty acid by the ultraviolet and infrared spectra. If one assumes that the cleavage of the benzene nucleus occurred by ozonization of Ⅵ, the product can be formulated as Ⅶ.

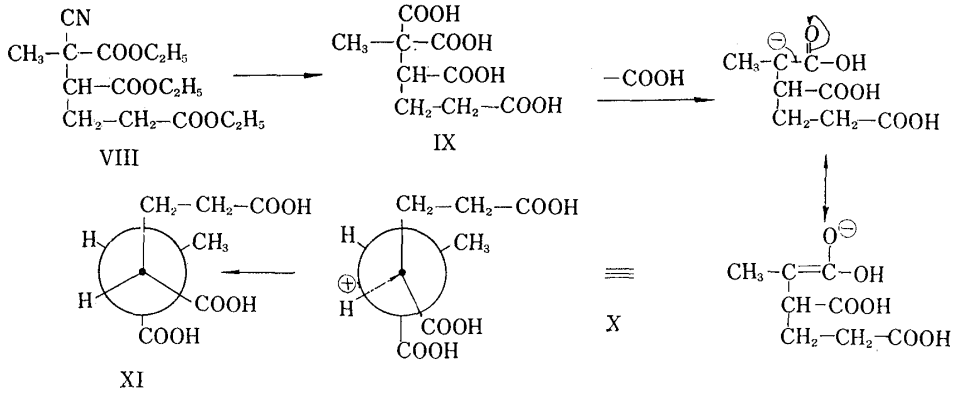
This compound formed a trimethyl ester, $C_{11}H_{18}O_6$, and a ditoluide, $C_{22}H_{24}O_3N_2$, m.p. 176°. The infrared spectrum of the ditoluide revealed that it contained a five-membered ring imide ($\nu_{max}^{KBr}$ $cm^{-1}$ : 1708, 1769) as well as an amide function ($\nu_{max}^{KBr}$ $cm^{-1}$ : 1520, 1668).

The presence of the former system proved that two carboxyl groups are located in the adjacent positions. Distillation of Ⅶ afforded an isomer of melting at 142°, and an anhydride, $C_8H_{10}O_6$, melting at 99° at the same time. The latter product showed infrared absorption bands at 1778, and 1854 $cm^{-1}$ (satd. five-membered anhydride) as well as the bands at 971, 1255, 1430, 1710, 1726 $cm^{-1}$ (COOH).

It was revealed by nuclear magnetic resonance spectrum*[4] that the methyl group present in Ⅶ was attached to the carbon bearing one hydrogen, since its signal showed a doublet (J=7.5 c.p.s.) centered on 3.73 p.p.m. from the proton signal of the internal water reference. Consequently, it has been concluded that the tricarboxylic acid (Ⅶ)

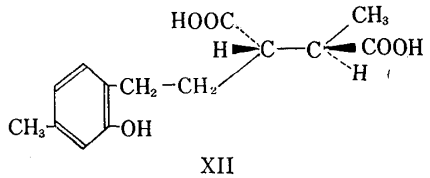
*[4] The NMR spectrum was measured in $D_2O$ at 60 Mc.p.s. using a J. E. O. L. 3H-60 apparatus.

and its isomer must be *cisoid*-dihydrohaematinic acid, m.p. 176° (XI) and *transoid*-dihydrohaematinic acid, m.p. 144°,[2] respectively. It has been known that the former is converted into the latter by heating at 200° for five hours followed by distillation.[2] The synthesis of the *cisoid*-dihydrohaematinic acid was achieved by Haworth-Perkin's procedure[3] starting from triethyl 4-cyano-1,3,4-pentane tricarboxylate (VIII), and the identity with VII was established by a mixed fusion and a comparison of infrared spectra.



It should be noted that by this reaction the thermo-unstable *cisoid*-dihydrohaematinic acid was afforded instead of thermo-stable *transoid*-dihydrohaematinic acid. In analogy of the decarboxylation reaction of malonic acid,[4] the intermediate 1,3,4,4-pentanetetracarboxylic acid (IX) would be decarboxylated following a first-order reaction mechanism. The elimination of the carboxyl group may take place affording the intermediate (X) in which an electron pair of carbanion is conjugated with the adjacent carbonyl resulting a planarity of the configuration, that makes a proton to attack from the sterically less hindered direction forming the thermo-unstable *cisoid*-dihydrohaematinic acid (XI).

The above described findings support the formulation of the dibasic acid, $C_{14}H_{18}O_5$, as XII. The configuration at two asymmetric carbons was resulted by the *cis*-addition of hydrogen on catalytic hydrogenation.



XII

The formula (XII) was also supported by the following spectroscopic evidences. The ultraviolet spectrum of this compound showed absorption maxima at 219 mμ (log ε 3.78), 276 mμ (log ε 3.23), and 283 mμ (log ε 3.20) as quite similar as given by *p*-xylenol, whose main absorption bands appear at 216 mμ (log ε 3.83), 275 mμ (log ε 3.29) and 283 mμ (log ε 3.26) in EtOH[5] (Fig. 1).

The nuclear magnetic resonance spectrum*[5] of XII is shown on Fig. 2. A doublet centered on 1.58 p.p.m. with a magnitude of three protons, can be assigned to an aliphatic methyl adjacent to a carbon bearing one hydrogen, a singlet at 2.17 p.p.m. to a toluene methyl, the complex signal of four protons near 2.5 p.p.m. to the two adjacent methylenes in the side-chain, and the signal near 3.26 p.p.m. to the two adjacent methines to which the carboxyl groupings attach.

*[5] The NMR spectrum was measured in pyridine at 60 Mc.p.s. using a Varian Associates DP-60 apparatus and tetramethylsilane as an internal standard.

2) G. E. Ficken, R. B. Johns, R. P. Linstead : J. Chem. Soc., **1956**, 2280.
3) W. N. Haworth, W. H. Perkin, jun. : J. Chem. Soc., **1908**, 581.
4) G. A. Hall : J. Am. Chem. Soc., **71**, 2691 (1949).
5) R. A. Friedel, M. Orchin : "Ultraviolet Spectra of Aromatic Compounds." No. 40 (1951), John Wiley & Sons Inc., New York, N. Y.

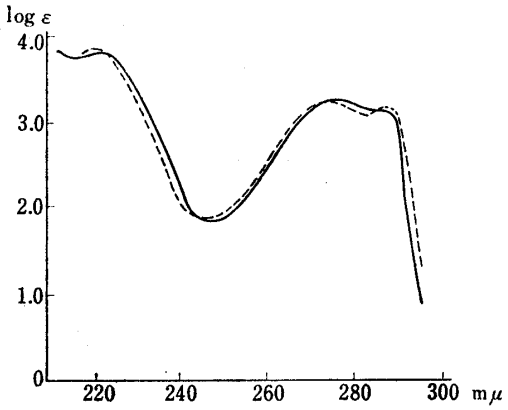



Fig. 1. Ultraviolet Absorption Spectra (in EtOH)

——— $C_{14}H_{18}O_5$ Acid
– – – – – *p*-Xylenol

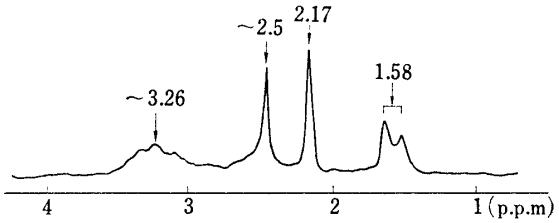



Fig. 2. Nuclear Magnetic Resonance Spectrum of $C_{14}H_{18}O_5$ Acid, measured in Pyridine at 60 Mc.p.s.

## Experimental*6

**Ozonolysis of Acetylanhydroitaconitin (2,4-Cresotaldehyde)**——To a cooled solution of acetylanhydroitaconitin (1 g.) in AcOEt (30 ml.) at 0°, a stream of ozone was introduced for 2 hr. The brown resinous substance remained after evaporation of the solvent *in vacuo* was subjected to a steam-distillation. The long colorless prisms (90 mg.), m.p. 60°, separated from the distillate were confirmed to be identical with the 2,4-cresotaldehyde, which was formerly obtained on ozonolysis of anhydroitaconitin, by mixed melting point determination.

**Treatment of Anhydroitaconitin with Diazomethane (Monomethyl Ether Dimethyl Ester)**——Anhydroitaconitin (1.8 g.) was treated with an ethereal solution of diazomethane, and the mixture was allowed to stand in an ice-box for 15 hr. The yellow residue obtained by usual way was dissolved in $Me_2CO$ and filtered. The residue of the filtrate was washed with hexane, dissolved again in benzene–$CHCl_3$ (1:1) and passed through the column of $CaHPO_4$. The crystals thus obtained (1.3 g.) were recrystallized from EtOH yielding colorless needles, m.p. 117°. This substance is readily soluble in $Me_2CO$, $CHCl_3$, and benzene, soluble in MeOH and EtOH, insoluble in hexane. IR $\nu_{max}^{KBr}$ $cm^{-1}$ : 973 (*trans* CH=CH), 1280, 1714, 1730 (conj. ester), 1392 ($CH_3$), 1509, 1569, 1591 (phenyl). *Anal.* Calcd. for $C_{17}H_{20}O_5$ : C, 67.09; H, 6.62. Found : C, 66.98; H, 6.89.

**Methylanhydroitaconitin (III)**——a) The monomethyl ether dimethyl ester (110 mg.) prepared as above was refluxed with 20% aq. NaOH solution (30 ml.) for 10 hr., and the hot solution was acidified with conc. HCl, and heated for further 20 min. in a boiling water bath. The crude product precipitated after cooling was filtered up, washed with $H_2O$, dried and crystallized from MeOH to obtain yellow needles, m.p. 156°. Yield, 88 mg. IR $\nu_{max}^{KBr}$ $cm^{-1}$ : 980 (*trans* CH=CH), 1390 ($CH_3$), 1504, 1580, 1629 (phenyl), 1604 (conj. double bond), 1753, 1810, 1845 (C=O). *Anal.* Calcd. for $C_{15}H_{14}O_4$ : C, 69.75; H, 5.46. Found : C, 69.58; H, 5.33.

b) To a solution of anhydroitaconitin (3.0 g.) in 30% NaOH (110 ml.) was added $Me_2SO_4$ (60 ml.) dropwise with stirring on a steam-bath during a period of 40 min. On cooling, a large amount of the colorless crystals were separated and identified with the monomethyl ether dimethyl ester, $C_{17}H_{20}O_5$, by a mixed fusion. To this reaction mixture was added NaOH (20 g.) and $H_2O$ (130 ml.), and the total mixture was refluxed for 7 hr. getting a complete solution. The hot light yellow solution thus obtained was dropped while hot into a hot 18% HCl solution, and the mixture was treated as described in a) to obtain yellow needles, m.p. 156°. Yield, 2.9 g.

**Ozonolysis of III**——To a cooled solution of III (2 g.) in AcOEt (160 ml.) at 0°, a stream of ozone was introduced for 90 min. After removing the solvent under a diminished pressure, $H_2O$ (10 ml.) was added, and the mixture was heated in a boiling water bath for 10 min. The mixture was then extracted with $Et_2O$, and the extract was washed with 10% aq. $NaHCO_3$ solution and $H_2O$ successively, dried over anhyd. $Na_2SO_4$ and evaporated to dryness. The resinous residue was mixed with 6% $H_2O_2$ (30 ml.) and 5*N* NaOH (10 ml.), and was boiled for 1 hr. giving complete solution. The crude product deposited on acidification of the solution was dissolved in aq. $NaHCO_3$ solution, filtered to remove yellowish insolubilities, and

*6 All melting points were uncorrected. Ultraviolet spectra were measured with Shimadzu Model RS-27 recording spectrophotometer, and infrared spectra with Koken Model DS-301 spectrophotometer.

again acidified. The precipitate was dissolved in boiling $H_2O$, filtered from resinous impurities and cooled to obtain colorless plates, m.p. 106°. Repeated recrystallization from water gave an analytical sample. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 933, 1663 (aromatic COOH), 1375 ($CH_3$), 1506, 1572, 1611 (phenyl).

It was identified with 2-methoxy-4-methylbenzoic acid*[7] by a mixed fusion and a comparison of IR spectra with the authentic sample.

**4-Phenylphenacyl Ester of XII**——The acid, $C_{14}H_{18}O_5$ (XII) (143 mg.), prepared by alkaline hydrogenation of anhydroitaconitin*[1] was dissolved in $H_2O$ (1.5 ml.) with warming. This solution was neutralized with dil. NaOH and mixed with an equimolecular amount (275 mg.) of 2-bromo-4'-phenylacetophenone. After boiling for 2 hr., EtOH was distilled off, and the crude crystalline precipitates were collected on filter, washed with dil. HCl, and recrystallized from small quantity of $Me_2CO$-EtOH then from benzene to yield colorless prisms (228 mg.) of melting at 173°. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1370 ($CH_3$), 1502, 1580, 1604 (phenyl), 1696 (phenyl ketone), 1740 (alcoholic $COCH_3$), 3544 (OH). *Anal.* Calcd. for $C_{42}H_{38}O_7$ (diester): C, 77.04; H, 5.85. Found: C, 76.89; H, 5.81.

**Ozonolysis of XII (*cisoid*-Dihydrohaematinic Acid (XI))**——The compound (XII) (600 mg.) was dissolved in $Me_2CO$ (200 ml.), and was subjected to ozonization for 8 hr. under cooling at −10° with a freezing mixture. After removal of the solvent, $H_2O$ (1 ml.) was added and evaporated again to dryness. The residue was washed with $CHCl_3$ and hexane to yield a crude product, m.p. 172° (decomp.). For further purification this substance was treated with a saturated aq. $NaHSO_3$ solution, and the precipitates were removed by filtration. Then the filtrate was extracted with $Et_2O$, and the extract was evaporated to dryness. Recrystallization of the residue thrice from $Me_2CO$-benzene then once from $Me_2CO$ gave colorless needles, m.p. 179°. Yield, 330 mg. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 948, 1416, 1700, 1720 (COOH), 1380 ($CH_3$). *Anal.* Calcd. for $C_8H_{12}O_6$: C, 47.06; H, 5.92; mol. wt., 204. Found: C, 47.05; H, 6.09; mol. wt., 216 (Rast); neutral. equivalent (phenolphthalein), 70.0.

This product was shown to be identical with the *cisoid*-dihydrohaematinic acid by a mixed fusion and a comparison of IR spectra.

**Treatment of XI with Diazomethane (*cisoid*-Dihydrohaematinic Acid Trimethyl Ester)**——The compound (XI) (1 g.) from XII was reacted with $CH_2N_2$, being allowed to stand in a refrigerator for 3 hr. After filtration, the usual treatment gave an oily residue which was decolorized with active charcoal in $Me_2CO$ solution. Removal of the solvent under a diminished pressure yielded a colorless sticky liquid (775 mg.). IR $\nu_{max}^{cap.}$ $cm^{-1}$: 1737 (alcoholic ester), 2848, 2946 ($CH_2$). *Anal.* Calcd. for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.66; H, 7.17.

**Treatment of XI with *p*-Toluidine (*transoid*-Dihydrohaematinic Acid Di-*p*-toluide)**——The compound (XI) from XII was boiled with 5 times of its weight of *p*-toluidine under $N_2$ atmosphere. The reaction mixture was washed with dil. HCl, and $H_2O$ and dried. Recrystallization twice from EtOH gave colorless leaflets, m.p. 176°. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1378 ($CH_3$), 1520, 1668 (CONHR), 1602 (phenyl), 1708, 1769 (satd. 5-membered imide). *Anal.* Calcd. for $C_{22}H_{24}O_3N_2$: C, 72.50; H, 6.64; N, 7.69. Found: C, 72.68; H, 6.21; N, 7.69.

**Isomerization and Dehydration of XI (*transoid*-Dihydrohaematinic Acid and Its Anhydride)**——On heating in an oil bath at 220° under $N_2$ stream, XI (2 g.) was decomposed liberating $H_2O$ and $CO_2$. The effervescence almost ceased within 10 min., affording 180 mg. of $H_2O$ and 115 mg. of $CO_2$. Then the residue was distilled at 1 mm. Hg. to yield a brownish liquid that solidified on cooling. The solid was treated with $CHCl_3$ and divided into a soluble and an insoluble portions. From the former portion was obtained colorless leaflets, m.p. 99°, on recrystallization from $CHCl_3$-hexane. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 971, 1255, 1430, 1710, 1726 (COOH), 1390 ($CH_3$), 1778, 1854 (satd. 5-membered anhydride). *Anal.* Calcd. for $C_8H_{10}O_5$ (*transoid*-dihydrohaematinic acid anhydride): C, 51.61; H, 5.41; mol. wt., 186. Found: C, 51.65; H, 5.40; mol. wt., 214 (Rast).

The $CHCl_3$-insoluble portion (630 mg.) was crystallized from $CHCl_3$-$Me_2CO$ to give colorless cubes, m.p. 142°. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1263, 1707, 1717 (COOH). *Anal.* Calcd. for $C_8H_{12}O_6$ (*transoid*-dihydrohaematinic acid): C, 47.06; H, 5.92. Found: C, 46.56; H, 5.91.

**Triethyl 4-Cyano-1,3,4-pentanetricarboxylate***[8]——To a EtONa-EtOH solution (3.1 g. of Na and 52 ml. of EtOH) was added diethyl 1-cyano-2-methylsuccinate[3] (b.$p_3$ 110~115°). The clear yellow solution was then treated with ethyl β-bromopropionate (27.4 g.) quickly. After boiling for 1 hr., the reaction mixture was separated from NaBr and evaporated. The oilly residue was washed 4 times with $H_2O$, dried over $CaCl_2$ and distilled under a diminished pressure to give a colorless liquid (30 g.), b.$p_{13}$ 204~210°, which agreed with the description in the literature.[3]

*[7] Synthesized from *m*-cresol by Kolbe-Schmidt reaction, followed by methylation with $Me_2SO_4$ and hydrolysis with NaOH successively.

*[8] This method is more convenient than the method by Haworth, *et al.*,[3] who used ethyl β-iodopropionate in place of ethyl β-bromopropionate.

**Summary**

Methylanhydroitaconitin (Ⅲ) which was prepared from anhydroitaconitin by treatment with the methylating agent followed by hydrolysis gave 2-methoxy-4-methylbenzaldehyde on ozonolysis. While the ozonolysis of the compound, $C_{14}H_{18}O_5$, which was obtained by alkaline hydrogenation of anhydroitaconitin yielded *cisoid*-dihydrohaematinic acid (Ⅺ). From these and other experimental results the structure of the compound, $C_{14}H_{18}O_5$ was established as Ⅻ.

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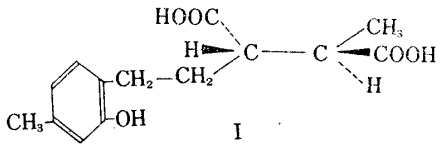
*UDC 581.19 : 582.282.12*

## 12. Shoichi Nakajima : Studies on the Structure of Itaconitin. VI.*1 The Structures of Anhydroitaconitin and Its Derivatives.*2

(*Hoshi College of Pharmacy**3)

In previous paper*1 of this series, it was reported that the chemical structure of the alkaline hydrogenation product, $C_{14}H_{18}O_5$, of anhydroitaconitin was established as I. The present paper concerns with the determination of the structures of anhydroitaconitin and all its derivatives so far prepared.

Considering from the chemical structure (I) of $C_{14}H_{18}O_5$ acid, dihydroanhydroitaconitin which was yielded by catalytic hydrogenation of anhydroitaconitin under neutral condition[1] could be represented as the structure (Ⅱ). In neutral solvent, the hydrogenation of anhydroitaconitin took place at the double bond in the side-chain remaining the unsaturated acid anhydride ring unaffected, whereas in alkaline condition, the ring opening of the anhydride moiety caused the hydrogenation at the double bond located between two carboxyl groups and thus two moles of hydrogen was uptaken giving the compound (I).



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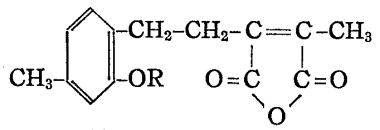

Ⅱ : R=H
Ⅲ : R=$COCH_3$

Favoring the proposed formula (Ⅱ) of dihydroanhydroitaconitin, its ultraviolet spectral curve (Fig. 1) was almost superimposable with the added spectral curve of *p*-xylenol (UV $\lambda_{max}^{EtOH}$ mμ (log ε) : 216 (3.83), 275 (3.29), 283 (3.26))[2] and 3,4,5,6-tetrahydrophthalic anhydride (UV $\lambda_{max}^{cyclohexane}$ mμ (log ε) : 250 (3.55))[3].

*1 Part Ⅴ. S. Nakajima : This Bulletin, **13**, 64 (1965).
*2 Presented at Ⅷth Japanese Symposium on the Chemistry of Natural Products (Oct. 1963). Proceedings, p. 144 (in Japanese).
*3 2-Chome, Ebara, Shinagawa-ku, Tokyo (仲嶋正一).
1) Part Ⅳ. S. Nakajima, K. Kinoshita, S. Shibata : This Bulletin, **13**, 58 (1965).
2) R. A. Friedel, M. Orchin : "Ultraviolet Spectra of Aromatic Compounds," No. 40 (1951), John Wiley & Sons Inc., New York, N. Y.
3) J. E. Baldwin, D. H. R. Barton, J. L. Bloomer, L. M. Jackman, L. Rodriguez-Hahn, J. K. Sutherland : Experientia, **18**, 345 (1962).