

Research Records

(Nov. 1961~Oct. 1962)

I. Articles Published In Scientific Journals

(a) In "Yakugaku Zasshi" (Journal of the Pharmaceutical Society of Japan)

Koichi Nakazawa and Tsuyako Miyata: A Novel Benzylolation of Phenolic Hydroxyl Group. Complete benzyl ether of phenol can be obtained easily and in good yield by boiling for 0.5~1.0 hour a mixture of PhCH_2Cl , K_2CO_3 and HCONMe_2 with phenol compounds (including polyhydric phenols and phenol compounds with a hydroxyl adjacent to electron-attracting group) [82 (6), 927 (1962)].

Shin Matsuura and Kazuhiko Ohta: Studies of Polyhydroxyanthraquinones. I. Synthesis of 2-Substituted 1,3,6,8-tetrahydroxyanthraquinones. The Friedel-Crafts reaction of γ -methylresorcinol and 3,5-dimethoxyphthalic anhydride gave 2-(3-methyl-2,4-dihydroxybenzoyl)-3,5-dimethoxybenzoic acid and dehydrative cyclization of its methyl derivative afforded 1-hydroxy-2-methyl-3,6,8-trimethoxyanthraquinone in a good yield. This anthraquinone compound was derived to 1,3,6,8-tetramethoxy-2-anthraquinonecarboxylic acid in five steps. The position of the hydroxyl groups in this acid was confirmed with tetrahydroxyanthraquinone formed by its demethylation [82, (1962)].

Shin Matsuura and Kazuhiko Ohta: Studies of Polyhydroxyanthraquinones. II. Studies of Rhodocladonic Acid. (I)

Starting with 2-methyl-1,3,6,8-tetrahydroxyanthraquinone (I), formed by demethylation of 1-hydroxy-2-methyl-3,6,8-trimethoxyanthraquinone, attempt was made to synthesize rhodocladonic acid by 1) introduction of CH_2OH group into the 7-position of (I); 2) oxidation of CH_2OH group in 2-hydroxymethyl-1,3,6,8-tetrahydroxyanthraquinone (II), derived from (I); and 3) introduction of CH_3 or CHO group into 7-position of (II). However, none of these reactions progressed [82, (1962)].

Shojiro Ueo, Kanichi Ueda, Yoshikimi Yamamoto, Naohiko Hazama and Yoshibumi Maki:
Taxin (VIII) Taxinine and Taxinol

The molecular formula $\text{C}_{35}\text{H}_{42}\text{O}_9$ was presented as the most adequate one for taxinine on the basis of elemental analytical value, NMR (in CHCl_3) $\tau=7.90$ ($3\text{CH}_3\text{CO}$) and molecular weight determination value by X-ray diffraction method. Both taxinine and taxin gave taxinol, mp $252\sim 254[\alpha]_{\text{D}}-3.99$ (T.H.F.C=0.501), by LiAlH_4 reduction.

The molecular formula of taxinol was previously reported to be $\text{C}_{16}\text{H}_{26}\text{O}_4$. However, it should be corrected to $\text{C}_{20}\text{H}_{32}\text{O}_5$ according to the fact that acetyltaxinol and dihydro acetyltaxinol were proved to have four acetyl groups by mean of N.M.R. measurement.

It was supported that taxinol had four secondary hydroxygroups, because N.M.R. of acetyltaxinol showed that four carbon atom bonding acetoxy have one hydrogen respectively. Taxinol has one ketone group ($\nu_{\text{max}}^{\text{nujol}} 1686\text{cm}^{-1}$) and show positive Zimmermann reaction, so the presence of active methylene group is presumed. Taxinol also has four methyl group, which consist of three tertiary and one secondary, because of presenting four methyl signal in N.M.R of tetracetyl-taxinol.

Taxinol and dihydrotaxinol may have α -glycol group as they react with sodium periodate. Furthermore, the presence of α -glycol group may be supported by the following fact: both condensed with acetone to give isopropylidenetaxinol, mp. 225~226° and isopropylidene dihydrotaxinol, mp 236~238°, which were insensitive to reaction with sodium periodate.

The catalytic reduction of tetraacetyltaxinol yielded dihydrotetraacetyltaxinol accompanied with dihydrodeoxytriacetyl taxinol, mp. 199~200°, N.M.R. (in CHCl_3) τ =8.01, 8.00, 7.98 (9H), eliminating one acetyl group.

Isopropylidenetaxinol was converted to dehydroisopropylidene taxinol, mp. 197~198°, by the oxidation with CrO_3 -pyridine complex, under oxidation of one of two hydroxy group in the former, followed by catalytic reduction to dihydrodeoxydehydroisopropylidenetaxinol, mp. 129~136°, missing hydroxyl group in I.R.

From these facts, the presence of partial Structure, $>\text{C}=\overset{|}{\text{C}}-\text{CH}(\text{OH})-$, (allylic hydroxyl group) was expressively supported [82, 1081 (1962)].

(b) In "The Journal of Japanese Biochemical Society"

Isao Ishiguro and (Miss) Zyunko Naito: Studies on the Kynurenine in the Hair of Rats (IV)

The authors have confirmed the distribution of tryptophan pyrrolase activity in various organs of rats by Knox's method. The activity of enzyme was most remarkable in the liver and was very weak in other tissues. On the other hand, the activities of tryptophan pyrrolase, kynureninetransaminase and kynureninase in the liver and kidney of various animals were observed. Regarding the above mentioned 3 kinds of enzymatic activity, we found no speciality in rats, and the kynurenine degrading enzyme seems to be more active in them than in other animals [33, 1 (1961)].

Isao Ishiguro and (Miss) Zyuko Naito: Studies on the Kynurenine in the Hair of Rats (IV)

The fluctuation of kynurenine content in hair and tryptophan pyrrolase activity in liver of rats were studied in an abnormal environment.

Tryptophan pyrrolase activity increased to 3-fold in quantity in the circumstances of dark room, low temperature and irradiation of ultra violet rays, but the increase of kynurenine content in hair was remarkable both in the higher and lower temperature.

The effects of temperature on the kynurenine content in hair, which seems necessary for preserving the temperature of rats, were found most remarkable [33, 4 (1961)].

(c) In Tetrahedron Letters

Koichi Nakazawa and Manzo Ito: Synthesis of Ginkgetin

The condensation of 5-benzoyloxy-3'-iodo-7,4'-dimethoxyflavone and 7,4'-dibenzoyloxy-5-benzoyloxy-8-iodoflavone was carried out at 230° for 40min. in the presence of activated copper powder. CHCl_3 -Extract of the reaction mixture was hydrolyzed with 10% H_2SO_4 in acetic acid, dissolved in a mixture of dioxane and ether and shaken with 10% K_2CO_3 to deposit yellow, sandy crystals of K compound of ginkgetin, which were decomposed with dilute H_2SO_4 and the free ginkgetin thus obtained was recrystallized from methyl ethyl ketone (21%) Yellow, small plates, mp 336°. Acetate. mp 259°. Identification with natural ginkgetin and its acetate was effected by analysis, mixed mp and infrared spectra [No, 8 may pp. 317~319 (1962)].

(d) In "Yakkyoku no Ryoiki"

Kichitaro Takatori: Study on the New Fungicidal Agent [10, 49 (1961)].

(e) "The Journal of Hygienic Chemistry"

Yōki Ose, Taira Ikeda and Shinichi Ōoto: Fundamental Studies on the Environs of Schools III-2 Air Contamination in class room when Snow Fall.

Many Schools use the braziers and shut the window in winter. Under these conditions air contamination in class rooms was studied.

CO₂ concentration rose to 0.7%. The room temperature of these class rooms equipped with ventilators dropped only ca 2°C [8 (2) 43 (1961)].

(f) In "Research Journal of Physical Education"

Yōki Ose, Ryoichi Hayashi, Sumi Nishiwaki and Shōzō Morishita: Studies on Swimming Pool Sanitation (3) Filtration of Bleaching Powder Solution.

To filtrate the bleaching powder solution, many coagulating agents were studied. The mixture of a port hydrolyte products of polyacrylamine Silicon compounds and nonionic surface active agents coagulated the calcium component in bleaching powder. This mixture eluted dissolved chlorine sufficiently.

II. Articles to be Published in Scientific Journals

(a) Chem. Pharm. Bull.

Koichi Nakazawa and Manzo Ito: Syntheses of Nuclear-substituted Flavonoids and Allied Compounds. X. Synthesis of Ginkgetin.

III. Oral Reports in Scientific Society

(a) In the Ordinary Meeting of the Tokai Branch of the Pharmaceutical Society of Japan. (Dec. 1961)

Kichitaro Takatori, Isao Ishiguro, (Miss) Junko Naito, (Miss) Mitoko Shamoto Copper Metabolism of Experimental Hepatic Carcinoma by DAB.

Kichitaro Takatori, Isao Ishiguro, (Miss) Zyunko Naito and (Miss) Mitoko Shamoto: Copper Metabolism of Experimental Hepatic Carcinoma by DAB

Yoshifumi Maki, Kazunaga Ōgata: Studies of Rearrangement Reactions (1)

Ring contraction from Pyridazone Derivatines to Pyrazolone Derivatines(1)

Isao Ishiguro, (Miss) Zyunko Naito, Masayoshi Harata and (Miss) Miyoko Ōtuka: The Enzymatic Degradation of the FAD in the Milk.

(b) In the 15th Annual Meeting of "The Pharmaceutical Society of Japan" (April 1962)

Hideo Takenaka, Hajime Ito and Masanori Kayano: Studies on the Pharmaceutical Applications of Fatty Acids Esters of Sucrose III. The Effect of Sucrose Fatty Acids Esters on the Blood Concentration (Rabbit) of Sulfa Drugs

Yōki Ose, Tamesaburo Matsui, Shōzō Morishita, and Sumi Nishiwaki: Studies on Swimming Pool Sanitation (IV-2) Manganese in Swimming Pool water.

Yōki Ose, Taira Ikeda, Shōzō Morishita and Saburo Yoshida: Air Contamination in Car.

(c) In the Ordinary Meeting of the Tokai Branch of the Pharm. Soc. of Japan (Feb. 1962)

Koichi Nakazawa and Manzo Ito: Synthesis of Nuclear-substituted Flavonoids and Allied Compounds. X. Synthesis of Ginkgetin.

Hideo Takenaka, Hajime Ito, Kaoru Ōhashi and (miss) Takako Tanino: Studies on the Pharmaceutical Applications of Fatty Acid Esters of Sucrose I. The Effect of Sucrose Fatty

Acid Esters on the Stability of Vitamin A.

Hideo Takenaka, Hajime Ito, Kaoru Ohashi and Masanori Kayano: Studies on the Pharmaceutical Applications of Fatty Acid Esters of Sucrose II. The Effect of Sucrose Fatty Acid Esters on the Blood Concentration (Rabbit) of Vitamin A.

(d) **In the Ordinary Meeting of the Tokai Branch of the Pharmaceutical Society of Japan.** (May. 1962)

Kichitazo Takatori, Shingo Asano, Hideko Washizu, Tetsuko Terada: Acylation by Phenyl ester (V). Acylation by phenyl ester of heterocyclic acid.

Yoshifumi Maki, Atsushi Numata: Synthesis of 5-Methyl-4,5,6,7-tetrathiazolo[4,5-c]pyridine-2[1H]-one

(e) **In Annual Meeting of "The Japanese Biochemical Society".** (Oct. 1961)

Isao Ishiguro, and (Miss) Zyunko Naito: Studies on the Kynurenine in the Hair of Rats (VI).

(f) **Symposium on Chemical Physiology and Pathology** (Dec. 1961)

Isao Ishiguro and (Miss) Zyunko Naito: Studies on the Kynurenine in the Hair of Rats.

(g) **In Annual Meeting of "The Japanese Vitamin Society"** (Apr. 1962)

Isao Ishiguro, (Miss) Zyunko Naito and Rikio Shinohara: The Enzymatic Degradation of FAD and FMN by Phosphatase in the Milk

(h) **In the Annual Meeting of the Tokai Branch of the Pharmaceutical Society of Japan** (Sept. 1962)

Kichitaro Takatori, Koji Minagami, Shingo Asano: Syntheses of Fluorine-Containing Antihistamine Drugs. III.

Yoshio Kato, (miss) Noriko Kanematsu, (miss) Naoko Takagi and (miss) Yumiko Chimura: Pharmaceutical Studies on the Digestive Ferments. (4). Influence of Metal Ions on Peptic Activity of Pepsin.

Isao Ishiguro, (Miss) Zyunko Naito, Rikio Shinohara and Masayoshi Watanabe: Biochemical Studies of the Royal Jelly (IV)

Yoshifumi Maki, Kazunaga Obata: Studies of Rearrangement Reactions (III)
Smiles Rearrangement in Heterocyclic Compounds (1)

(i) **In the 8th Annual Meeting of "The School Health Society of Japan"** (Nov. 1961)

Yōki Ose, Tamesaburo Matsui, Shōzō Morishita, Noboru Kondō, Bunzi Tazima: Studies on Swimming Pool Sanitation (IV-1) Brownd by Chlorination in Swimming Pool Water.

(j) **In the 8th Annual Meeting of "The Tokai Public Health Association"** (May. 1962)

Yōki Ose and Taira Ikeda: The Relation between the Water Components and the Structure of Domestic Scale Sewage Treatment Plants.

(k) **In the 5th Annual Meeting of "The Tokai School Health Association"**

Yōki Ose, Taira Ikeda and Shōzō Morishita: The Fundamental Studies of School Environs (XIX), Water Contaminations of Canteen.

(l) **In the Annual Meeting of "Pharmacological Society of Japan"** (April 1962)

Kiichiro Fujii and Hajime Ito: Separating studies of Some Biogenic Amines.

(m) **In the 12th Annual Meeting of "The Physical Education Society of Japan"** (Nov. 1961)

Ryoichi Hayashi, Syoichi Nagata and Masaru Nakagami: Hygienic studies on the Actual Conditions of and the physical Educations for so called Delicate Children (1)

(n) **In the 8th The School Health Society of Japon** (Nov. 1961)

Masaru Nakagami: Lygenic studies on the Actual Conditions of and the physical Educations

for so called Delicate children (2)

Ryoichi Hayashi, Masaru Nakagami and Yōki Ose: Hygienic studies and physical Educations on the relation try to improve one's physical Condition of the students.

(o) In the 32nd Annual Meeting of "The Hygienic Society of Japan" (April, 1962)

Syoichi Nagata, Eisaburo Iwata, Masaru Nakagami, Makoto Nakamura, Isamu Okada, Sengi Kishimoto and Yoshio Hayashi: Biological and Hygienic studies on Iron Bacteria Collected in Gifu Prefecture (3)

Syoichi Nagata, Sengi Kishimoto, Makoto Nakamura, Isamu Okada, Masaru Nakagami, Yoshio Hayashi and Eisaburo Iwata: Biological and Hygienic studies on Plankton in Fresh Water.

(p) In the 5th Meeting of the Tokai School Health Society (June, 1962)

Masaru Nakagami: Hygienic studies on the Actual Conditions of the Physical Education for so called "Delicate children" (3)

(q) In the 10th Annual Meeting of The Tokai Branch of the Physical Education Society of Japan (June, 1962)

Masaru Nakagami: Hygienic studies on the Actual Conditions of the Physical Education for so called Delicate children (4)

Ryoichi Hayashi, Masaru Nakagami and Yōki Ose: Hygienic studies and physical Educations on the relation try to improve one's physical condition of the students (2)

(r) In the 18th Annual Meeting of the Public Hygienic Society of Japan (Oct. 1962)

Syoichi Nagata, Makoto Nakamura, Isamu Okada, Masaru Nakagami, Yoshio Hayashi and Kunio Takahashi: A study of the social Extermination of Trachoma.

(s) In the Societas Herbraia Orientali-Asiatica (March, 1962)

Mizuo Mizuno: On the Distribution of the Sect. Chrysocoptis in Japan.

IV 著 書

加藤好夫, 竹中英雄 (分担執筆): 最新薬剂学 (改訂版) (広川書店) (昭和37年4月)

吉田甚吉: 薬業経営論 (評論社) (昭和37年9月)

奥田高千代 (分担執筆): 最新物理化学 (広川書店) (昭和37年4月)

小瀬洋喜, 元山 正: 基礎調理学IV, 食品簡易鑑別法 (朝倉書店) (昭和37年6月)