2021.12.05. 14:00-1530

オンラインフォーラム
向井利夫先生・宮仕勉先生と光化学

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向井先生と宮仕先生の思い出

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向井先生の思い出

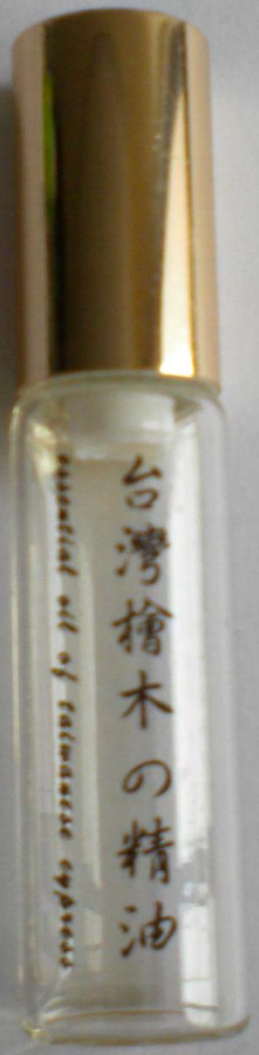
伝統の野副トロポロン化学から離れて光化学研究を開始

日本に有機光化学研究の流れを作る
故松浦輝男（京大）、徳丸克己（筑波大）先生

光化学への情熱と責任感
小泉先生のお宅に一升瓶を抱えて訪問、光化学研究施設を作ろうと提案

1983 Gordon Research Conferenceにご一緒に参加

I am showing one example of very successful Taiwan-Japan Collaborations which Masuhara knows as an alumnus of Department of Chemistry of Tohoku University.



finally to −20° (sixth extract). The resulting large dextro- and levorotation were obviously based on lanosterol ($[\alpha]_D$ +61°) and cholesterol ($[\alpha_D$ −30°), respectively. Agnolic acids (18) and hydroxy acids are dextro- and levorotatory, respectively, but the $[\alpha]_D$s of both acids were small, so I assumed that the large dextro- and levorotation of the aforementioned wax fractions were caused by lanosterol (or agnosterol) and cholesterol, respectively. On the basis of these findings, grease from the sebaceous glands of sheep should have consisted mainly of lanosterol wax, and the final extract should have contained cholesterol wax, which existed in the cells of surface skin. This point and the physiological or physical meanings of the aforementioned components of wool wax had not yet been elucidated. At that time, it had not yet been clarified that lanosterol was an important precursor of cholesterol during biosynthesis. Unfortunately, beginning in 1942, we had to completely terminate our research because of the war effort. The precious experimental materials, mammalian lipids, were lost during our evacuation.

Hinokitin and Hinokitiol. During this time, I was also involved in a small research project at Taihoku Imperial University. While I was reviewing my previous study of the essential oils of the *taiwanhinoki*, I became interested in the components of the essential oils of three important conifers: *taiwanhinoki*, *benihi*, and Japanese *hinoki* (*Chamaecyparis obtusa* Sieb. et Zucc.), all of which looked very similar to us. However, these conifers are extremely different in their constituents, which vary depending on the species and the part (leaf or heartwood) of the plant. I was particularly attracted to the acidic substances that were present in minute quantities in these essential oils.

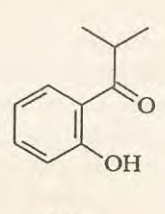
It had already been reported[31] that the acidic portion of the heartwood of the *taiwanhinoki* contained a small quantity of a supposedly phenolic substance ($C_{10}H_{12}O_2$), whereas a dark-red wood pigment "hinokitin," erroneously assigned the formula $C_{30}H_{34}O_{10}$, was isolated by Hirao[32] from the same oil. Hirao speculated that the pigment was derived from an unidentified acid ($C_{10}H_{16}O_2$) by oxidation. Another supposedly phenolic substance ($C_{10}H_{12}O_2$), which had been reported by Kawamura,[33] was isolated from the acidic portion of the wood oil of *hiba* (*Thujopsis dolabrata* Sieb. et Zucc.), which also belongs to the same class, *Cuppressaceae*, that grows in northern Japan. This substance was strongly resistant to wood-decaying fungi. A common characteristic of all these acidic substances was the red coloration with ferric chloride. Therefore, I speculated that a certain common substance may be present in the acidic portions of those wood oils.

On shaking an ethereal solution of hinokitin with an aqueous alkaline solution, I obtained a gelatinous precipitate of ferric hydroxide

and an enolic compound having a molecular formula of $C_{10}H_{12}O_2$ as the alkaline salt. I named the compound "hinokitiol".[34] I also confirmed that hinokitiol was present in *hiba* oil but not in the Japanese *hinoki* or *benihi* oil. My experiment proved that hinokitin, which had been considered a natural pigment, is an iron complex ($C_{30}H_{33}O_6Fe$) of hinokitiol instead. The percentages of C and H in Hirao's formula, which were obtained by elemental analysis, were also correct for the iron complex. It is understandable then not to have noticed the presence of Fe in such a natural compound that was sublimable in vacuo and soluble in organic solvents (diethyl ether or chloroform).

On the basis of experimental facts that hinokitiol was a monobasic acid that gave acetone by oxidation with various reagents and readily formed neutral metallic complexes with almost any metallic salt, I first proposed formula 23 for hinokitiol. However, I soon realized that the composition and physical properties of the metal complexes of hinokitiol were entirely different from those of *o*-hydroxyacetophenone derivatives. I then considered the five-membered *β*-diketone (24) and the six-membered *α*-diketone (25), as well as a formula containing an isopropenyl group (26). However, none of these structures seemed to be consistent with the properties of hinokitiol. Although the enol form (27) of the seven-membered *α*-diketone was the last remaining possibility, the common knowledge at that time that no such compound could exist in nature in a stable form led me to abandon the formula for a while.

In 1936, a special issue of the *Bulletin of the Chemical Society of Japan* had been planned in celebration of Professor Riko Majima's 60th



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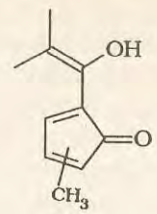

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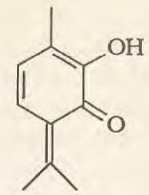

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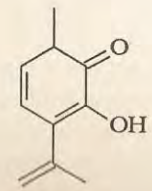

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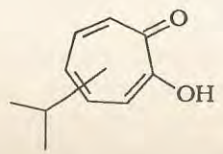

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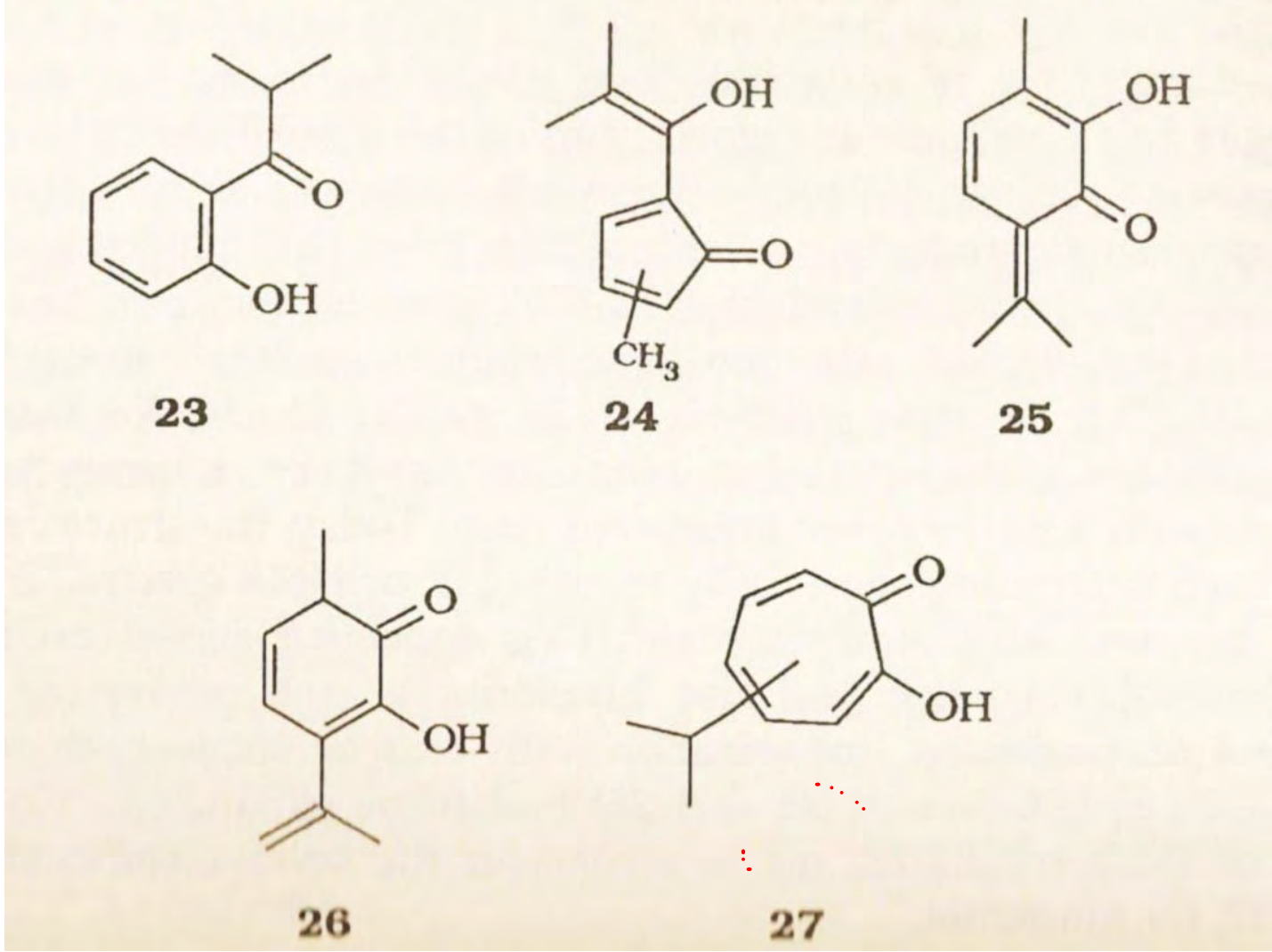

Prof. Nozoe convinced himself by reading "Nature of Chemical Bond" by Linus Pauling that the 7-membered ring is stabilized by resonance.

→ Non-benzenoid chemistry is opened by him.

Seventy Years in Organic Chemistry

Tetsuo Nozoe

PROFILES, PATHWAYS, AND DREAMS
Autobiographies of Eminent Chemists

Jeffrey I. Seeman, Series Editor

American Chemical Society, Washington, DC 1991

Seventy Years in Organic Chemistry

Tetsuo Nozoe

野副鉄男

PROFILES, PATHWAYS, AND DREAMS
Jeffrey I. Seeman, Series Editor

向井利夫先生　増原宏

1922-48年野副鉄男教授　台北帝国大学・台湾大学
1957年東北大学助教授(理学部)
1962年東北大学理学部入学
1964-87年東北大学教授(理学部)
1965年東北大学理学部4年生配属（小泉研究室）
1966年野副鉄男先生御退官
1966年東北大学理学部化学第二学科卒業（小泉研究室）
1968年東北大学大学院理学研究科化学専攻修士課程修了（小泉研究室）
1968年大阪大学大学院基礎工学研究科化学系化学専攻博士課程入学（又賀研究室）
1971年大阪大学大学院基礎工学研究科化学系化学専攻博士課程修了（又賀研究室）
1976年光化学協会(JPA)設立
1977-79年光化学協会副会長
1979年日本化学会賞受賞
1980-87年東北大学理学部附属光エネルギー化学実験施設長併任
1983-85年光化学協会会長
1984年京都工芸繊維大学繊維学部教授
1987年東北大学理学部御退職
2007年　大阪大学大学院工学研究科退職（応用物理教室）
2008年－現在　台湾国立陽明交通大学理学院講座教授

3.1 Regional Photochemistry Associations

In resonance with the movement of forming the photochemistry association in Europe and America, scientists in the field of photochemistry in Japan were strongly prompted to have also a photochemical society in Asia/Japan as the counterpart of those in Europe and America. In 1976 Dr. Toshio Mukai, a professor at Tohoku University, proposed his idea with much enthusiasm in the general assembly of the Japanese Symposium on Photochemistry, which has been held annually, to found the Japanese Photochemistry Association at first prior to a starting an Association in Asia and Oceania area. His proposal was well accepted and fully agreed among the Japanese scientists in the field of photochemistry. The Japanese Photochemistry Association (JPA) as the first photochemistry association in Asia, thus, formally started in the next year 1977. Dr. Ikuzo Tanaka, a professor at Tokyo institute of Technology, was elected as the Founding President and the Vice President was Dr. T. Mukai. From the beginning of the JPA, many of the core members, especially the successive Presidents of the JPA such as Drs. Tanaka, Sakurai, Honda, Mukai, Matsuura, Baba, [illegible] expecting to Association to ng cooperation the field of S. C. Shim and , Dr. J.P. Mittal ong-Kong, and noted here that Hideo Tomioka, d visited Asian starting the informal JPA other regional ished in India d Australia and

Dr. Ikuzo Tanaka
The Founding President
of the JPA (1977-79)

Dr. Toshio Mukai
The 3rd President of
the JPA (1983-85)

The Asian and Oceanian Photochemistry Association (APA)

Number of members: 1126 as of March, 2012.

Society members:
Australia and New Zealand (12), China (80), Hong Kong (16), India (57), Japan (700), Korea (200), Singapore (10), Taiwan (51) as of March 2012.

Executive members of the APA (2011-2012)

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1983 Gordon Research Conferenceにご一緒に参加


GORDON RESEARCH CONFERENCE
Proctor Academy
ORGANIC PHOTOCHEMISTRY
Samir Farid, chairperson
Peter J. Wagner, vice chairperson
July 18-22, 1983
Achber Studio, Laconia, N.H.

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2. T. W. Ebbesen (Univ. of Not
"Photochemistry of Me

3. R. A. Caldwell and S. N. Db
"pK_a of a Norrish II

4. C. V. Kumar, S. K. Chattop
"Probing Biradicals

5. K. Mizuno (Univ. of Osaka)
"Inter- and Intramol

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宮仕勉先生　増原宏

1962年東北大学理学部卒業（野副鐵男教授）

1962年東北大学理学部入学

1965年東北大学大学院理学研究科修士課程修了

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1968年東北大学大学院理学研究科博士課程修了理学博士

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1968年大阪大学大学院基礎工学研究科化学系化学専攻博士課程入学（又賀研究室）

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1971年大阪大学大学院基礎工学研究科化学系化学専攻博士課程修了（又賀研究室）

1980年東北大学理学部附属光エネルギー化学実験施設助教授

1984年京都工芸繊維大学繊維学部教授

1987年東北大学理学部化学科教授

1990年光化学協会賞受賞

1989-91年、2000-01年光化学協会理事

1992-95年光化学協会常任理事

1995-2003年東北大学大学院理学研究科化学専攻教授

2000年光化学協会長

2007年大阪大学大学院工学研究科退職（応用物理教室）

2008年－現在台湾国立陽明交通大学理学院講座教授

宮仕先生の思い出

一貫して良き先輩

怖い指導者、3年生に将来について示唆
（学生実験、やらせておいて煙草スパスパ）

日本の有機光化学研究の流れを支えた

“男気”のあるご意見、ご決断

向井利夫先生、宮仕勉先生のご冥福をお祈りいたします

Funding and Support in Taiwan
MOE (Ministry of Education) SPROUT Project (National Yang Ming Chiao Tung University), Taiwan
MOST (Ministry of Science and Technology), Taiwan
Prof. Yuan-Pern LEE (National Yang Ming Chiao Tung University)

ご清聴ありがとうございます
状況が良くなれば台湾へおいでください