

The 7th Taiwan-Japan Bilateral Symposium on Architecture of Functional Organic Molecules

A small reminder of old and recent collaborations
between Taiwan-Japan in Chemistry
as an Opening Remark

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台灣と日本の古い関係

Introduction of old collaboration of Taiwan–Japan in chemistry

Hinokitiol & Prof. T. Nozoe in Taipei imperial, national Taiwan, and Tohoku universities

台灣と日本の新しい関係

Introduction of recent collaboration of Taiwan–Japan in chemistry

Some Japanese laboratories in National Ciao Tung University in Hsinchu

*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

(64~86年前の話題)

Late Prof. Tetsuo NOZOE (野副鉄男教授)

1902 Born in Sendai (仙台)

1926 Graduated from Tohoku Imperial University (東北帝国大学)

1926-1929

Camphore Research Laboratories of the Monopoly Bureau

Department of Chemical Industry of the Central Research Institute of the Formosa Government

1929 -1945

Department of Chemistry, Faculty of Science and Agriculture, Taihoku Imperial University (台北帝国大学)

1946 - 1948

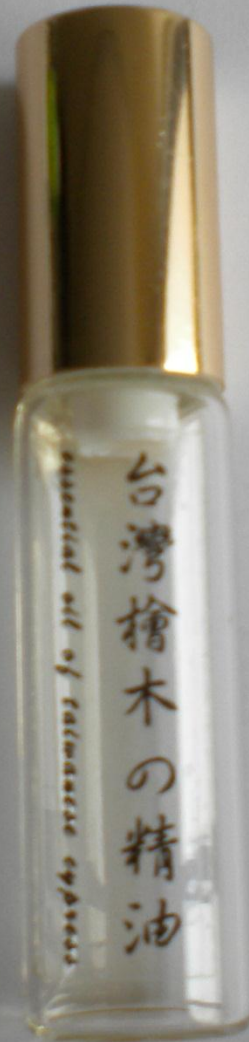
Department of Chemistry, National Taiwan University (国立台湾大学)

1948 - 1966

Department of Chemistry, Tohoku University (東北大学)

Masuhara graduated from Tohoku University in 1966

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 ($[\alpha]_D +61^\circ$) and cholesterol ($[\alpha]_D -30^\circ$), 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.

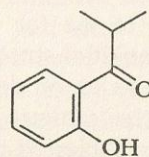
It had already been reported³¹ that the acidic portion of the heartwood of the *taiwanhinoki* contained a small quantity of a supposedly phenolic substance ($C_{10}H_{12}O_2$), whereas a dark-red wood pigment "hinokitin," erroneously assigned the formula $C_{30}H_{34}O_{10}$, was isolated by Hirao³² 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, *Cupressaceae*, 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

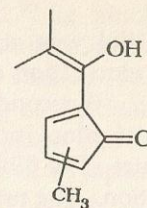
and an enolic compound having a molecular formula of $C_{10}H_{12}O_2$ as the alkaline salt. I named the compound "hinokitiol".³⁴ I also confirmed that hinokitiol was present in *hiba* oil but not in the Japanese *hinoki* or *benihi* oil. My experiment proved that hinokitin, which had been considered 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.

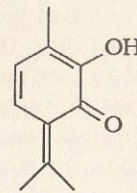
In 1936, a special issue of the *Bulletin of the Chemical Society of Japan* had been planned in celebration of Professor Riko Majima's 60th



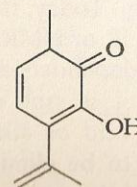
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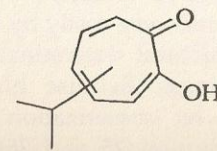
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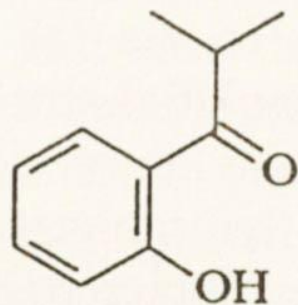
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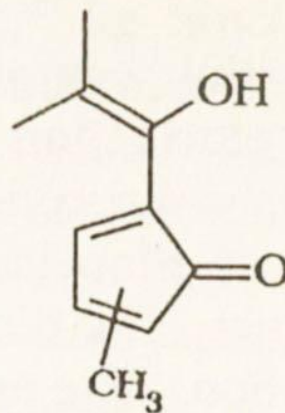
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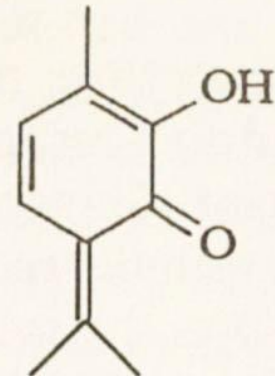
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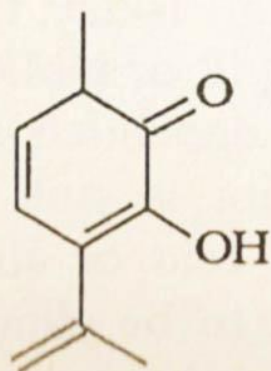
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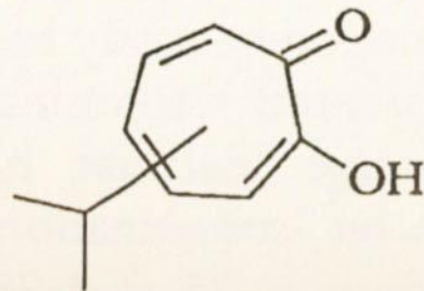
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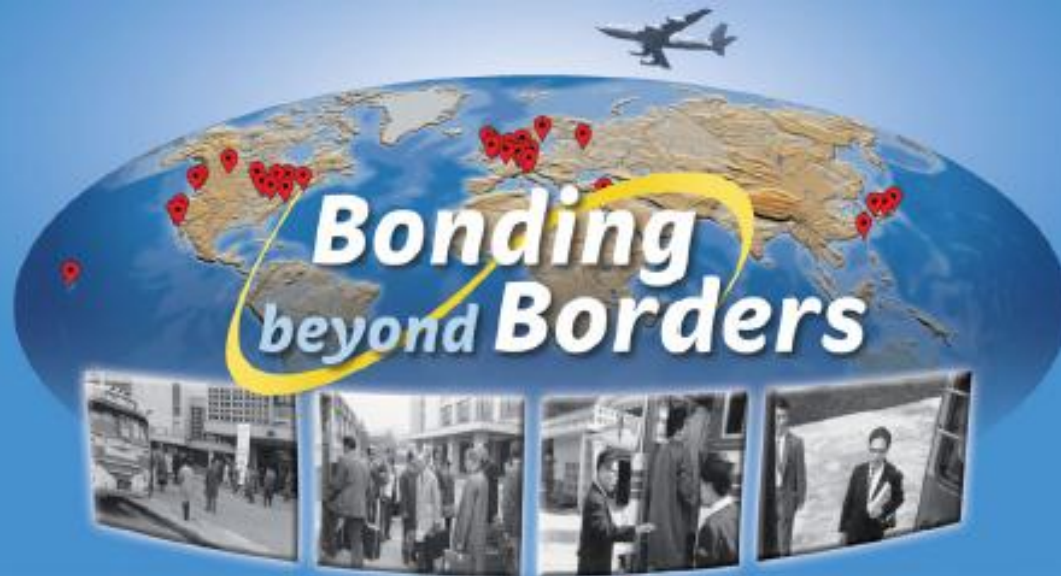
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Prof. Nozoe convinced himself by reading “Nature of Chemical Bond” by Linus Pauling that the 7-membered ring is stabilized by resonance.

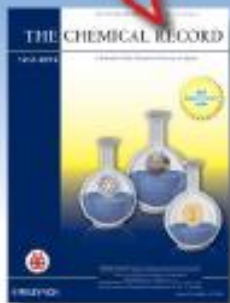
→ Non-benzenoid chemistry is started by Prof. Nozoe in Taiwan !!



Tetsuo Nozoe with colleagues and students from the chemistry department at Taihoku Imperial University in Taipei, 1935. Front row from left: Y. Nakatsuka (assistant professor, inorganic chemistry), T. Watase (professor, analytical chemistry and a guest from Osaka University), K. Matsuno (professor, theoretical chemistry), and Tetsuo Nozoe (assistant professor, organic chemistry). Back row from left: K. Nakagawa, A. Tachiiri, T. Kinugasa (assistant, organic chemistry), K. Pan (assistant, theoretical chemistry), T. Matsumoto, S.-L. Liu, H. Matsumura, S. Ogawa, P.-Y. Yeh, Y. N. So, S. Katsura (assistant, organic chemistry), and H. Imuma (assistant, inorganic chemistry).



You Are Invited!



Eight times by E. J. Corey. Five times by Ryoji Noyori. Ten by Prelog, five by Woodward, almost countless times by Eschenmoser. Grubbs and Lehn, Hoffmann and Herschbach, Wittig and Brown.

All these and thousands of other chemists signed Tetsuo Nozoe's autograph books – almost 1200 pages in all – between 1953 and 1994. They wrote poems, drew artistic sketches and their favorite molecules and reactions, all with collegial friendship and good-natured humor.

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by Prof. T. Nozoe in
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Makiko KAWASU **川合眞紀** 東京大学大学院新領域創成科学研究科 教授-理化学研究所 理事

2010年のノーベル化学賞は Richard H. Heck, 鈴木章、根岸英一の3氏が受賞しました。有機合成で工業的にも重要な反応の開発に対する貢献が受賞理由です。バ

淑典に一個人の枠を越えた貢献をされました。物理学の分野では今日でも美しい時期から本音が太鼓鼓る場さる

米国への頭脳流出

これらの先生方の多くは第二次世界大戦後の困難な時期に研究者としてのキャリアーを開始し、自らの意思でよりよい研究環境を求めて米国へ渡った、いわゆる米国への「頭脳流出」のさきがけです。頭脳流出というといささかネガティブな響きがありますが、この時代に渡来された方々は我が国の科学の国際化に大変貢献されています。数年間の留学とは異なり、海外の大学や研究機関で研究室を主宰してこられた先生方のもとには、多くの若い日本人研究者が集い、留学生活を通じて国外の研究者との親交を深めてきました。実際

ます。化学分野でも、定年を迎えるに当たり、研究のアクティビティの確保を目的として海外の大学や研

新しいタイプの国際流出

がん遺伝子研究の世界的権威で、京都大学ウイルス研究所長だった伊藤嘉明教授が63歳の定年を迎えた2002年、シンガポール政府の招きで、自らの研究室のスタッフ9人を引き連れシンガポールに移住し、日本では異例の「研究室ごとの国際流出」として、学界を騒然とさせました。定年後に研究グループのサイズを縮小するなど、日本では研究活動を縮小せざるを得ないのに対し、伊藤氏はシンガポール国立大医学部腫瘍学研究所長で、シンガポール分子細胞生物学研究所教授を兼ね、シンガポール政府から研究に専念できる環境が与えられ、ますます発展することを期待されています。化学分野でも、定年を迎えるに当たり、研究のアクティビティーの確保を目的として海外の大学や研

究所に移籍するケースが増えています。奈良教授一氏も2007年東大定年後にシンガポール南洋理工大学教授になり引き続き研究の第一線で活躍しています。一緒に移動された山根基氏と千葉俊介氏は現在助教授として奈良教授ともども、南洋理工大学の合成化学の強化に尽力されています。2002年に山本尚氏は60歳を目前にして名古屋大学からシカゴ大学へと移籍しました。山本氏はハーバード大学のE. J. Coreyの下でPhDを取り、東レ研究所や京大で勤務の後、1977年から数年ハワイ大学で教鞭をとっていた国際派ですので、画一的な日本の雇用システムの中には納まらなかったのでしょうか。

物理化学の分野では、台湾の国立交通大学理学院に分子科学の研究者が集結しています。増原宏氏（奈良先端大特任教授）が応用化学科の栄誉教授として教育にも関与される傍ら、Center for interdisciplinary scienceの増原研究室ではBiomolecular probeの研究を推進しています。応用化学科には分子科学研究所の前所長の中村宏樹氏や東北大から藤村勇一氏が加わっており、1つの分野を担っています。東大理学部物理学科の元教授小林孝嘉氏もQuantum Science分野で活躍しています。グローバル化の新しいパターンは、アジア諸国の急激な研究市場拡大を支援する意味でも重要な役割を担っていると言えます。



海外で活躍する若手研究者 4

私が見た台湾の大学における 教育・研究環境

キャリアパスとしての台湾

三浦篤志 Atsushi MIURA

急速に進むグローバル化、ボーダレス化、さらに国内におけるポストの減少。若手研究者には厳しいジョブハンティングの状況が続いている。そこでアジアの近隣諸国にポジション探しの目を向けてみてはいかがだろうか。キャリアパスの1つとして台湾の大学での教育・研究を選択した筆者の経験をご紹介します。

はじめに

読者の皆さんは“台湾”と聞いて何を思い浮かべるだろう？ 手近な海外旅行先としてはよく知られた国と思われるが、台湾の大学における研究・教育の現状に関して詳しい状況を説明できる方は少ないのではないだろうか。筆者は2008年4月から台湾に住んでい

動、2009年8月より同学科で助理教授として採用していただき現在に至る。

こちらに来たきっかけは、現在研究室を共同主宰させていただいている増原宏先生に台湾の大学で新しく開く研究室と一緒に研究をしてみないかと誘っていただいたことによる。増原先生から“台湾へ...”とお誘いいただいたのが2007年12月で、初めて交通大学を

Hiroshi Masuhara believes that

**This 7th Taiwan-Japan Bilateral Symposium on
Architecture of Functional Organic Molecules**

**is surely one of milestones for the next fruitful
collaborations between Taiwan-Japan in Chemistry**

Thank you very much for your kind attention.