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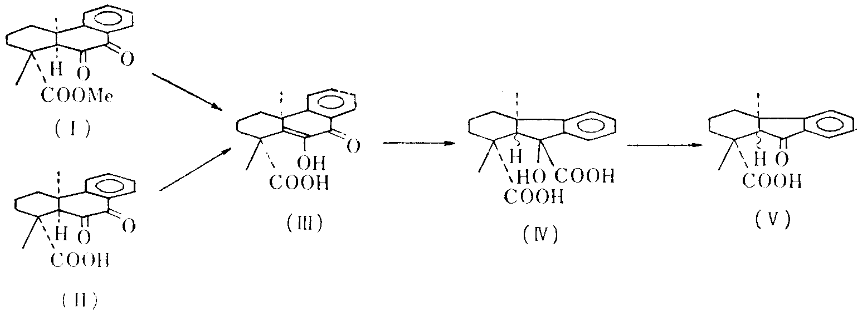
Transformation of Abietic Acid to the Hydrofluorene Derivatives[*1]

Interest in the biosynthetical correlation[1] between resin acids and gibberellins,[2,3][*2] the plant growth-promoting substance obtained from *Gibberella fujikuroi*,[4] prompted the present work on the transformation of abietic acid to the hexahydrofluorene derivative, which is a skeleton of gibberellins. Recent work on the same reaction by Grove and Riley accelerated the publication of the result of this work obtained to date.



Methyl 9,10-dioxo-deisopropyl-allodehydroabietate[5] (I) and 9,10-dioxo-deisopropyl-allodehydroabietic acid (II), yellow prisms, m.p. 147~149° (decomp.) (*Anal.* Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.18; H, 6.44), obtained from abietic acid, gave the same α,β-keto-enol (III), colorless prisms, m.p. 133~134° (decomp.), from methanol with addition of water, which gives violet color with ferric chloride; $[\alpha]_D^{8.5}$ $-34.1°$ (EtOH); UV λ_{max}^{EtOH} mμ (log ε): 259.5 (3.928), 304.5 (3.931). IR ν_{max}^{KBr} cm^{-1}: 1709, 1633, 1598 (*Anal.* Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.29; H, 6.44) by treatments with alkaline solution such as 8.5% methanolic potassium hydroxide solution at room temperature for 2 days, 8.5% potassium hydroxide solution in a boiling water bath for a few minutes, or 20% potassium hydroxide solution in a boiling water bath for 2 hours.

[*1] This communication will be published in detail as Diterpenoids (I) by this author.
[*2] Gibberellin A_3 was named gibberellic acid by the ICI research group.
1) A. J. Birch, R. W. Rickards, H. Smith: Proc. Chem. Soc., **1958**, 192.
2) B. E. Cross, J. F. Grove, P. McCloskey, T. P. C. Mulholland, W. Klyne: Chem. & Ind. (London), **1959**, 1345; N. Sheppard: J. Chem. Soc., **1960**, 3040.
3) N. Takahashi, Y. Seta, H. Kitamura, Y. Sumiki: Bull. Agr. Chem. Soc. Japan, **23**, 509 (1959); H. Kitamura, N. Takahashi, Y. Seta, A. Kawarada, Y. Sumiki: *Ibid.*, **23**, 344 (1959).
4) T. Yabuta, Y. Sumiki: *Ibid.*, **14**, 1526 (1938).
5) M. Ohta, L. Ohmori: This Bulletin, **5**, 91 (1957); cf. E. Wenkert, B. G. Jackson: J. Am. Chem. Soc., **80**, 211 (1958).

Treatment of the diketo-ester (I) or α,β-keto-enol (III) with 20% potassium hydroxide solution in the boiling water bath for 10~11 hours afforded 1,9-dicarboxy-1,11-dimethyl-1,2,3,4,10,11-hexahydrofluoren-9-ol (IV) as colorless prisms, m.p. 131~134°, from methanol with addition of water, $[\alpha]_D^{8.5}$ -32.0(EtOH). UV λ_{max}^{EtOH} mμ(log ε): 264(2.84), 272(2.87). IR ν_{max}^{KBr} 1710 cm^{-1} (*Anal.* Calcd. for $C_{17}H_{20}O_5 \cdot H_2O$: C, 63.34; H, 6.88. Found: C, 63.45; H, 7.11).

Proof of the structure of (IV) was obtained by the oxidation of (IV) with chromic acid under a mild condition to 1,11-dimethyl-1-carboxy-1,2,3,4,10,11-hexahydrofluorenone (V), whose melting point, mixed melting point, and infrared spectrum were identical with those of Ohta's authentic sample.[6]

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[6] M. Ohta: This Bulletin, **5**, 256 (1957).

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On the Alkaloid of *Fritillaria verticillata* WILLD. VAR. *Thunbergii* BAKER. (I). On the Position of the Secondary Hydroxyls and Skeleton of Verticine*[1]

Investigation by Fukuda[1] on the alkaloidal constituents of corms of *Fritillaria verticillata* WILLD. VAR. *Thunbergii* BAKER has resulted in isolation of four alkaloids; verticine, m.p. 224~224.5°, fritillarine, m.p. 130~131°, verticilline, m.p. 148~150°, and another amorphous base. Some preliminary structural survey was later reported on the principal constituent, verticine.[2] Attention to these alkaloids was directed by Dr. Fukuda who very kindly provided his specimens for the first two of the alkaloids isolated in 1931, together with some crude material.

Verticine (I), $C_{27}H_{45}O_3N$,*[2] m.p. 223~224°, purified by counter-current distribution (pH 5.4, phosphate buffer), is a saturated (UV $\lambda_{max}^{HCl-EtOH}$ 215 mμ(ε 10)) tertiary amine (complete recovery on nitrosation) of pKa′ 9.5, with no carbonyl group. Thiocyanate, m.p. 263~265° (decomp.). Hydrochloride, m.p. 310~312° (decomp.). Perchlorate, m.p. 279° (decomp.).

Hydroxylic nature of the oxygen functions was indicated by the following experiments. Chromic acid oxidation of (I) at 60° affords, after counter-current distribution (pH 3.8), two ketones, verticinone (II), $C_{27}H_{43}O_3N$, m.p. 212~213° (UV λ_{max}^{EtOH} 288 mμ(ε 38). IR ν_{max}^{KBr} 1705, 1425 cm^{-1} (sh)) (Periodate, m.p. 199° (decomp.)), and verticinedione (III), $C_{27}H_{41}O_3N$, m.p.

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*[1] Presented at the Ibaragi District Meeting of the Chemical Society of Japan, at Hitachi, October 10, 1960.

*[2] All analytical values are in good agreement with the molecular formula shown. Reported formula,[2] $C_{18}H_{33}O_2N$ or $C_{19}H_{35}O_2N$.

[1] M. Fukuda: Nippon Kagaku Zasshi, **50**, 74 (1929); Sci. Repts. Tohoku Univ., Ser. A, **18**, 323 (1929).

[2] *Idem*: Nippon Kagaku Zasshi, **69**, 165, 167 (1948).