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Transformation of Abietic Acid to Hydrofluorene Derivative (Part II)*1,*2

In continuation of previous work,[1,2] the authors report herein the transformation of abietic acid to the 7-substituted perhydrofluorene derivatives, which have a skeleton of biologically attractive gibberellins.[3]

Treatment of methyl 9,10-dioxodeisopropylallodehydroabietate[4] (II) with sulfuric acid-nitric acid[5] led to a nitro compound[6],*3 (III) as yellow prisms, m.p. 217~223° (from methanol); $[\alpha]_D^{29.5}$ −204° (EtOH); IR ν_{max}^{KBr} cm^{-1} : 1728, 1690, 1603, 1522, 1342 (*Anal.* Calcd. for $C_{18}H_{19}O_6N$: C, 62.60; H, 5.55; N, 4.06. Found : C, 62.78; H, 5.42; N, 4.04) in 45% yield and its corresponding α,β-keto-enol compound (IV), colorless prisms, m.p. 166~168° (from methanol), which gave dark violet color with ferric chloride; UV λ_{max}^{EtOH} mμ (log ε): 250 (4.26), 315 (3.13). IR ν_{max}^{KBr} cm^{-1} : 1726, 1636, 1606, 1516, 1344 (*Anal.* Calcd. for $C_{18}H_{19}O_6N$: C, 62.60; H, 5.55; N, 4.06. Found : C, 62.52; H, 5.45; N, 4.18) in 5.8% yield.

The benzilic acid rearrangement[1,2] of the diketo compound (III) with dilute potassium hydroxide solution on a boiling water bath for 20 minutes gave 1,9-dicarboxy-1,11-dimethyl-7-nitro-1,2,3,4,10,11-hexahydrofluoren-9-ol (V), clusters, m.p. 206~207.5° (decomp.), from methanol-water; $[\alpha]_D^{30}$ −51.2° (EtOH); UV λ_{max}^{EtOH} mμ (log ε) : 282 (3.97); IR ν_{max}^{KBr} cm^{-1}: 1722, 1594, 1508, 1344 (*Anal.* Calcd. for $C_{17}H_{19}O_7N \cdot H_2O$: C, 55.58; H, 5.76; N, 3.81. Found: C, 55.62; H, 5.91; N, 4.41) in 28% yield and α,β-keto-enol compound (VII) as plates, m.p. 138~141° (strongly decomp.) from methanol-water, which gave a dark violet color with ferric chloride; UV λ_{max}^{EtOH} mμ (log ε) : 249.5 (4.24), 317.5 (3.44); IR ν_{max}^{KBr} cm^{-1} : 1711, 1645, 1609, 1528, 1353 (*Anal.* Calcd. for $C_{17}H_{17}O_6N$: C, 61.63; H, 5.17; N, 4.23. Found : C, 61.29; H, 5.15; N, 4.46) in 8% yield, and the same treatment for 2 hours gave (V) in 47% yield.

Proof of the hydrofluorene skeleton of (V) was obtained by the oxidation of (V) with chromic acid to 1-carboxy-1,11-dimethyl-7-nitro-1,2,3,4,10,11-hexahydrofluoren-9-one (IX) as plates, m.p. 188~189° (from methanol-water); IR ν_{max}^{KBr} cm^{-1} : 1710, 1702, 1603, 1529, 1347 (*Anal.* Calcd. for $C_{16}H_{17}O_5N$: C, 63.36; H, 5.65; N, 4.62. Found : C, 63.45; H, 5.56; N, 5.15), which could be derived from an authentic sample[1,2,7] (VIII) by sulfuric acid-nitric acid nitration.

Catalytic hydrogenation of the methyl ester (VI), plates, m.p. 152~153.5° (from ether-petr. ether); IR ν_{max}^{KBr} cm^{-1} : 1730, 1591, 1529, 1340 (*Anal.* Caled. for $C_{19}H_{23}O_7N$: C, 60.47; H, 6.14; N, 3.71. Found : C, 60.96; H, 6.18; N, 4.18) obtained from (V) with diazomethane, afforded the corresponding amine (X) as plates, m.p. 156~157° (from ether-petr. ether); IR ν_{max}^{KBr} cm^{-1} : 1727, 1616 (*Anal.* Calcd. for $C_{19}H_{25}O_5N$: C, 65.69; H, 7.25; N, 4.03. Found: C, 66.21; H, 7.25; N, 4.25).

For the purpose of dehydration of 9-hydroxyl group of (V), the thionyl chloride-pyridine treatment was the only satisfactory method and the ester (VI) was readily derived

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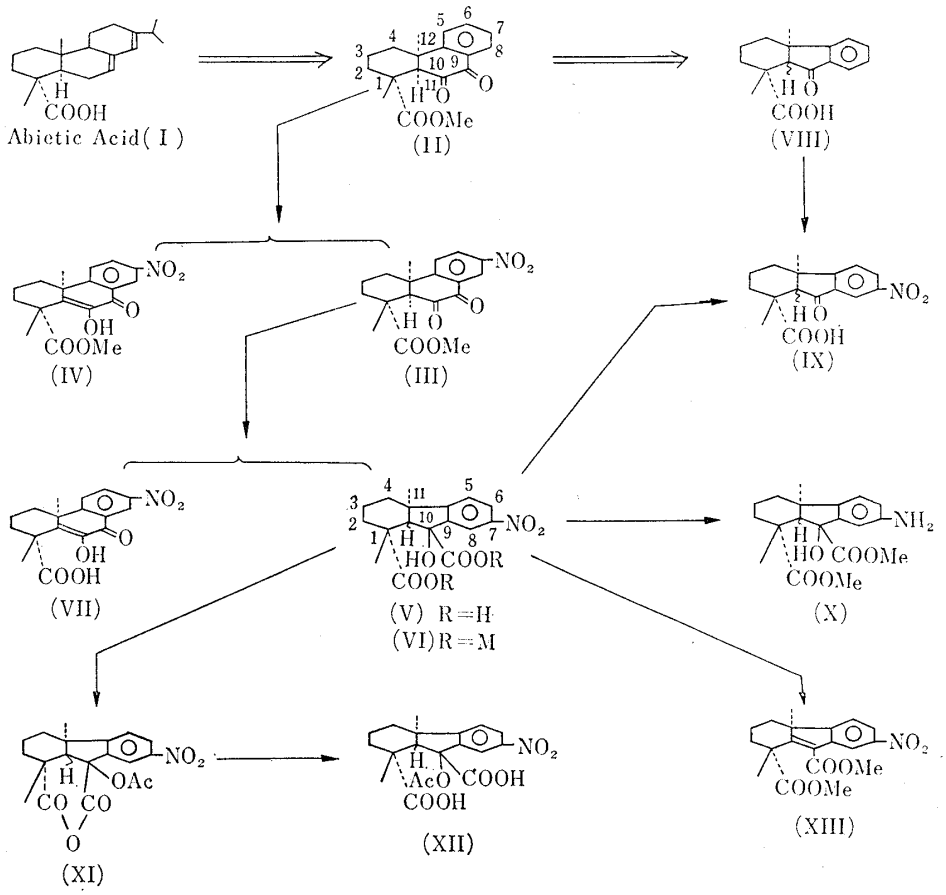
*1 This communication will be published in detail as Diterpenoids (II).

*2 Part I. A. Tahara : This Bulletin, **9**, 252 (1961).

*3 The strong probability of 7-nitro-position in the nitrated products (III) and (IV), although it has no rigid evidence yet, is offered by the effect of 9-keto group and the less steric hindrance of 7-position than 5-posion in (II).[5] The convincing proof will be given in the near future.

1) A. Tahara : *Ibid.*, **9**, 252 (1961).
2) cf. J. F. Grove, B. J. Riley : J. Chem. Soc., **1961**, 1105.
3) J. F. Grove : Quart. Revs., **15**, 56 (1961).
4) M. Ohta, L. Ohmori : This Bulletin, **5**, 91 (1957); cf. E. Wenkert, B. C. Jackson : J. Am. Chem. Soc., **80**, 211 (1958).
5) R. Hodges, R. A. Raphael : J. Chem. Soc., **1960**, 50.
6) cf. M. Ohta : Yakugaku Zasshi, **77**, 924 (1957).
7) M. Ohta : This Bulletin, **5**, 256 (1957).



to the intended compound (XIII) as plates, m.p. 125~128°(from methanol-water); $[\alpha]_D^{30}$ −130.5°(EtOH); UV λ_{max}^{EtOH} 254 mμ(log ε 4.40); IR ν_{max}^{KBr} cm^{-1} : 1731, 1721, 1591, 1527, 1344 (*Anal.* Calcd. for $C_{19}H_{21}O_5N$: C, 63.50; H, 5.89; N, 3.90. Found : C, 63.31; H, 5.83; N, 4.11) in 70% yield. However, (V) could not be dehydrated by the Grove and Riley method[2] for dehydration, and was only converted to (XII) as prisms, m.p. 209~212°(from methanol-water), IR ν_{max}^{KBr} cm^{-1} : 1720, 1710, 1595, 1530, 1341, 1240 (*Anal.* Calcd. for $C_{19}H_{21}O_8N$: C, 58.31; H, 5.41; N, 3.58. Found : C, 58.24; H, 6.19; N, 3.88) through the corresponding anhydride (XI) as prisms, m.p. 236~240°(from acetone-water); IR ν_{max}^{KBr} cm^{-1} : 1802, 1762, 1732, 1594, 1531, 1350, 1231 (*Anal.* Calcd. for $C_{19}H_{19}O_7N$: C, 61.12; H, 5.13; N, 3.75. Found : C, 61,27; H, 5.68; N, 3.72).

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