Synthesis of Abietane and Transformation of Enmein into Enantioabietane

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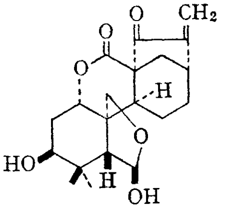
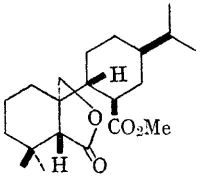
RECENTLY, we reported[1] that the acyloin condensation of the lactone ester (II) derived from enmein (I), a diterpene from *Isodon trichocarpus* Kudo, gave an oily 6-hemiketal-7-ol derivative (III) as a major product. We report the isolation of a new 7-hemiketal (IV) from the reaction mixture of the same acyloin condensation, and the transformation of the acyloin mixture into (+)-abietane, and also the conversion of abietic acid into (−)-abietane.

The reaction of the lactone ester (II) with 1·3 equiv. of sodium in liquid ammonia gave a mixture of acyloins, from which a new 7-hemiketal (IV) [$C_{20}H_{34}O_3$, m.p. 165—167°, and 179—183°, ν_{max} (KBr) 3365 and 3305 (infl.) cm.$^{-1}$, δ 0·87 (6H, doublet, *J* 5·0 c./sec., isopropyl), 1·10 (3H, singlet), 1·26 (3H, singlet), 3·35 (1H, singlet, H-6, $W_{\frac{1}{2}}$ 2·0 c./sec.), 3·48 (1H, singlet, O*H*), and 3·77 p.p.m. ($CDCl_3$) (2H, singlet, CH_2–O)] could be isolated. On acetylation, it afforded a monoacetate (V) [m.p. 161—162°, ν_{max} (KBr) 3340, 1737, and 1245 cm.$^{-1}$, δ 0·82 (6H, doublet, *J* 5·0 c./sec., isopropyl), 0·96 (3H, singlet), 1·13 (3H, singlet), 1·95 (3H, singlet, O·CO·CH_3), 3·27 (1H, singlet, O*H*), 3·66 (2H, singlet, CH_2–O), and 4·45 p.p.m. ($CDCl_3$) (1H, singlet, H-6)].

The mixture of acyloins, without purification, was subjected to the Nagata modification[2] of the Wolff–Kishner reduction to give an unsaturated alcohol (VI) [$C_{20}H_{34}O$, M^+ 290, m.p. 114—115°, ν_{max} (KBr) 3330, 1640, and 777 cm.$^{-1}$, δ 0·82 (6H, doublet, *J* 5·0 c./sec., isopropyl), 0·87 (3H, singlet), 0·92 (3H, singlet), 3·88 (2H, singlet, CH_2–OH), and 5·59 p.p.m. ($CDCl_3$) (2H, broad,


(I)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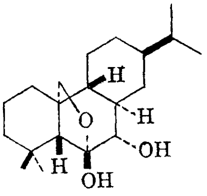
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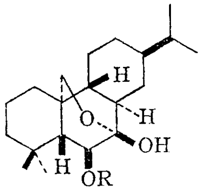
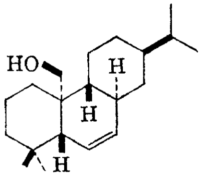
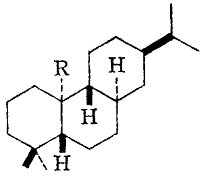
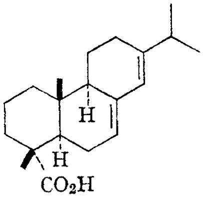
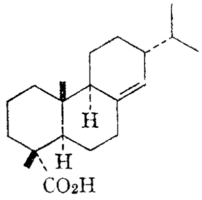
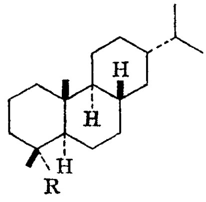

(IV) R=H
(V) R=Ac


(VI)


(VII) R=CH₂OH
(VIII) R=CHO
(IX) R=Me


(X)


(XI)


(XII) R=CO₂H
(XIII) R=CO₂Me
(XIV) R=CH₂OH
(XV) R=CHO
(XVI) R=Me

$W_{\frac{1}{2}}$ 4·5 c./sec.)], which was hydrogenated on Adams' catalyst to yield a saturated alcohol (VII) [m.p. 109—109·5°, $[\alpha]_D^{29}$ + 9·3° (*c* 0·58, n-hexane), ν_{max} (KBr) 3345 cm.$^{-1}$, δ 0·84 (6H, doublet, *J* 5·0 c./sec.), 0·89 (6H, singlet), and 3·91 p.p.m. ($CDCl_3$) (2H, singlet, CH_2–OH)]. The latter, on oxidation with Jones' reagent at 0°,[3] gave an aldehyde (VIII) [$C_{20}H_{34}O$, m.p. 78—79°, ν_{max} (KBr) 2750 and 1708 cm.$^{-1}$, δ 0·70 (3H, singlet), 0·82 (6H, doublet, *J* 5·0 c./sec., isopropyl) 0·90 (3H, singlet), and 10·10 p.p.m. ($CDCl_3$ + D_2O) (1H, doublet, *J* 2·0 c./sec., C*H*O)], which was reduced by the modified Wolff–Kischner reaction to afford (+)-abietane (IX) [M^+ 276, m.p. 38°, $[\alpha]_D^{25}$ + 5° (*c* 0·366, n-hexane), ν_{max} (KBr) 1467, 1453, 1389, and 1369 cm.$^{-1}$, o.r.d. plain positive curve (*c* 0·366, n-hexane)].

Catalytic hydrogenation (PtO_2–AcOH)[4] of abietic acid (X) or dihydroabietic acid (XI)† gave all-*trans*-tetrahydroabietic acid (XII), whose methyl ester (XIII) was reduced to alcohol (XIV),[5] $C_{20}H_{36}O$, m.p. 33—34°, $[\alpha]_D^{29}$ + 7° (*c* 1·087, n-hexane), with $LiAlH_4$. The alcohol, on oxidation with Jones' reagent at 0°, gave an oily aldehyde (XV) [ν_{max} (CCl_4) 2690 and 1726 cm.$^{-1}$, δ 0·82 (6H, doublet, *J* 5·0 c./sec., isopropyl), 0·88 (3H, singlet), 1·06 (3H, singlet), and 9·23 p.p.m. ($CDCl_3$) (1H, singlet, C*H*O)], which was subjected to a modified Wolff–Kischner reduction to give (−)-abietane (XVI) [$C_{20}H_{36}$, M^+ 276, m.p. 37—38°, $[\alpha]_D^{25}$ − 5° (*c* 0·285, n-hexane), o.r.d. plain negative curve (*c* 0·285, n-hexane)].

The abietanes (IX) and (XVI) were shown to be enantiomeric by the following data: the same melting points, the same retention times on the vapour-phase chromatograms (SE-30, capillary column, 45 m.), the identity of their mass spectra, their superimposable i.r. spectra, the same values (but with the opposite signs) of their specific rotations, and the opposite signs of their o.r.d. plain curves.

These hydrocarbons are the first abietanes. We propose the name "abietane" for compound (XVI), and "enantioabietane" for compound (IX). Since (−)-abietic acid (X) has already been synthesized,[6] its conversion into abietane constitutes the total synthesis of the latter.

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[1] E. Fujita, T. Fujita, H. Katayama, and S. Kunishima, *Chem. Comm.*, 1967, 258.
[2] W. Nagata and H. Itazaki, *Chem. and Ind.*, 1964, 1194.
[3] W. Herz and R. N. Mirrington, *J. Org. Chem.*, 1965, **30**, 3198.
[4] L. Ruzicka and J. Meyer, *Helv. Chim. Acta*, 1922, **5**, 343.
[5] This alcohol was previously known, but had not been obtained crystalline. J. W. Huffman, T. Kamiya, L. H. Wright, J. J. Schmid, and W. Herz, *J. Org. Chem.*, 1966, **31**, 4128.
[6] E. Wenkert, A. Afonso, J. B. Bredenberg, C. Kaneko, and A. Tahara, *J. Amer. Chem. Soc.*, 1964, **86**, 2038.