The Chemical Conversion of Trichokaurin into (—)-Kaurene, Atisine, Garryine, and Veatchine

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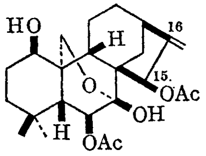
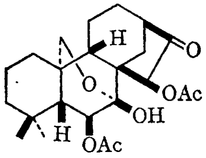
THIS Communication deals with the chemical conversion of trichokaurin (I)[1] into the keto-carboxylic acid (VIII).[2,3]

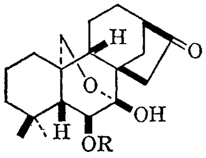
The keto-diacetate (II) [$C_{23}H_{32}O_7$, m.p. 186—187° (decomp.), ν_{max} (KBr) 3450, 1750, and 1735 cm.$^{-1}$, δ 5·45 (1H, doublet, J = 1·0 c./sec., C-15–*H*) and 5·20 p.p.m. ($CDCl_3$) (1H, doublet, J = 7·5 c./sec., C-6–*H*)] which was derived from trichokaurin (I) through the route described in the preceding Communication,[1] was allowed to react with calcium in liquid ammonia[4] to afford the alcohol (III) [ν_{max} ($CHCl_3$) 3400 and 1735 cm.$^{-1}$, δ 3·77 p.p.m. ($CDCl_3$) (1H, doublet, J = 5·0 c./sec., C-6–*H*)] and the triol (V) [ν_{max} (KBr) 3350 cm.$^{-1}$]. Their structures were confirmed by acetylation to (IV) [$C_{21}H_{30}O_5$, m.p. 210—215° (decomp.), ν_{max} (KBr) 3350, 1740, and 1720 cm.$^{-1}$, δ 2·06 (3H, singlet) and 5·06 p.p.m. ($CDCl_3$) (1H, doublet, J = 5·0 c./sec., C-6–*H*)] and (VI) [$C_{23}H_{34}O_6$, m.p. 194—195° (decomp.), ν_{max} (KBr) 3450, 1735, and 1710 cm.$^{-1}$, δ 2·07, 2·02 (each 3H, singlet), 4·80 (1H, quartet, J = 4·0 and 7·0 c./sec., C-16–*H*), and 5·03 p.p.m. ($CDCl_3$) (1H, doublet, J = 5·0 c./sec., C-6–*H*)] respectively.



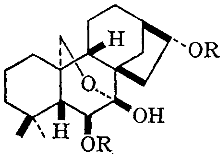
(I)



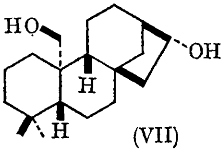
(II)



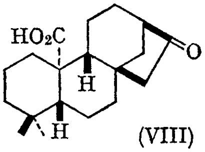
(III) R=H
(IV) R=Ac



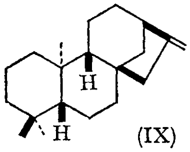
(V) R=H
(VI) R=Ac



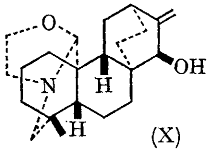
(VII)



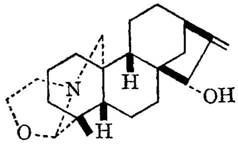
(VIII)



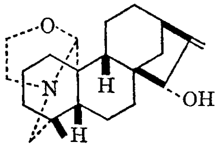
(IX)



(X)



(XI)



(XII)

Subsequently, Nagata's modification[5] of the Wolff–Kishner reduction was applied to the triol (V). The product, without purification, was hydrogenated in the presence of Adams' catalyst to yield diol (VII) [δ 1·88 (6H, singlet) and 4·09 p.p.m. ($CDCl_3$) (2H, singlet, C·C*H*$_2$·OH)]. The latter, on oxidation with Jones' reagent at room temperature, gave a keto-carboxylic acid, m.p. 238—240°, which proved to be identical with the authentic sample of the compound (VIII),[3] m.p. 240—242°,† kindly supplied by Dr. S. Masamune (University of Alberta), by mixture melting-point determination and i.r. and mass-spectral comparison.

Since the compound (VIII) has been converted into (—)-kaurene (IX),[3] atisine (X),[6] garryine (XI),[7] and veatchine (XII),[8] the present transformation means the chemical conversion of trichokaurin into (—)-kaurene and those diterpene alkaloids.

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† *cf.* m.p. 251—252·5° in ref. 3.

[1] E. Fujita, T. Fujita, and M. Shibuya, preceding Communication.
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[4] H. Vorbrueggen and C. Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 2990.
[5] W. Nagata and H. Itazaki, *Chem. and Ind.*, 1964, 1194.
[6] S. Masamune, *J. Amer. Chem. Soc.*, 1964, **86**, 291.
[7] S. Masamune, *J. Amer. Chem. Soc.*, 1964, **86**, 290.
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