

Recently, Hartshern, *et al.*,¹¹⁾ on comparing the optical rotatory dispersion curve of valeranone with those of 5-methylcoprostan-4-one (α , -75) and methyl 1-oxo-5 β -etianate (α , -136),¹⁰⁾ suggested that the preferred conformation of valeranone is related to projection Ia (R=H, X=H); an assumption which is in agreement with the present conclusion.

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Structure of Cyperotundone

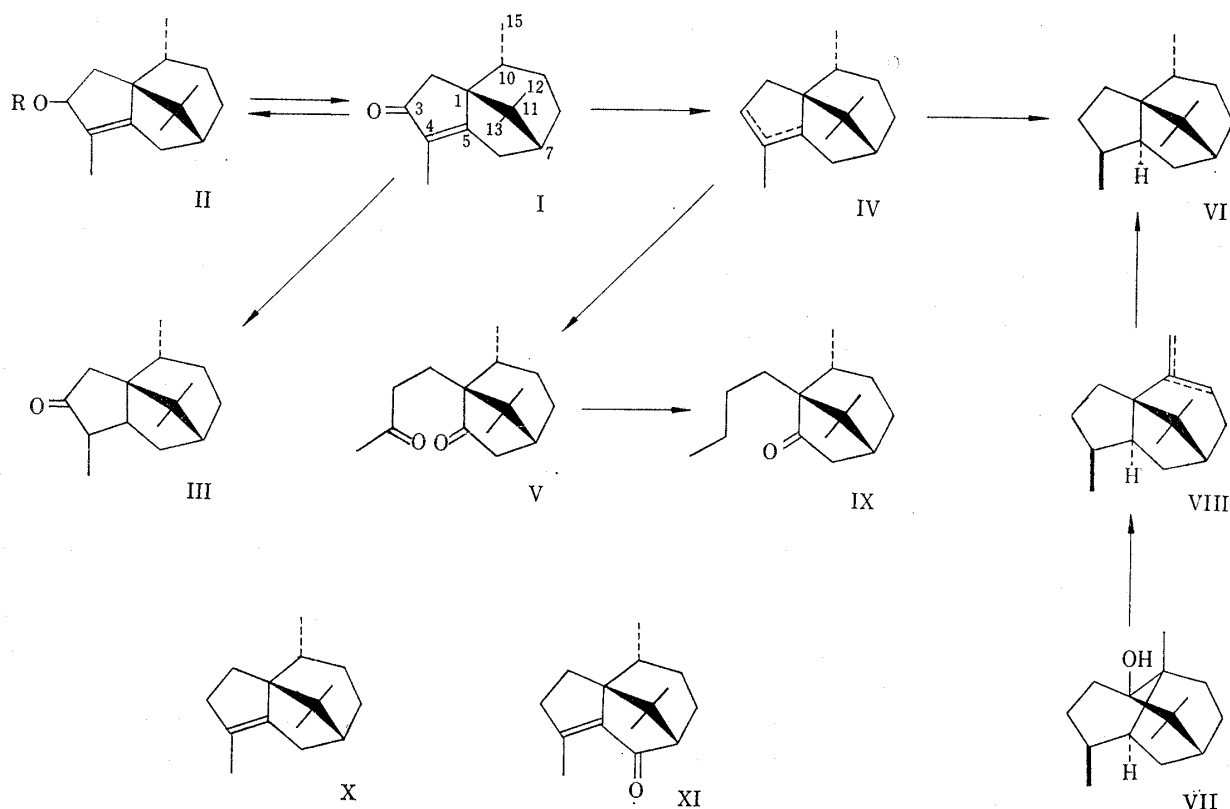
From the tuber of nutgrass (*Cyperus rotundus* LINNÉ) of Japanese origin, a new sesquiterpenoid ketone has been isolated for which the name cyperotundone is proposed.*¹ The present communication provides evidence that cyperotundone is represented by formula I.

Cyperotundone (I), C₁₅H₂₂O, m.p. 46~47.5°, $[\alpha]_D +40.4^\circ$,*² was characterized as the 2,4-dinitrophenylhydrazone, C₂₁H₂₆O₄N₄, m.p. 224~225°. The spectral properties [$\lambda_{\max}^{\text{EtOH}}$ 245 m μ (log ϵ 3.96), ν_{\max} 1706, 1667 cm⁻¹, no vinyl proton signal in the ketone (I) and $\lambda_{\max}^{\text{EtOH}}$ 396 m μ (log ϵ 4.76) in its 2,4-dinitrophenylhydrazone] are those of a fully-substituted α,β -unsaturated ketone in a five-membered ring. The presence of a methyl group at the α -position on the double bond in cyperotundone is indicated by a vinyl methyl signal at 8.33 τ in the nuclear magnetic resonance spectrum. A band at 1412 cm⁻¹ in the infrared spectrum of the ketone (I) suggests the presence of a methylene grouping adjacent to carbonyl. This is confirmed by the following evidence. Lithium aluminum hydride reduction of the ketone (I) gave the alcohol (II; R=H), C₁₅H₂₄O, m.p. 136°, $[\alpha]_D -37.7^\circ$, ν_{\max} 3205 cm⁻¹ (hydroxyl), which on manganese dioxide oxidation regenerated the ketone (I). The nuclear magnetic resonance spectra of the alcohol (II; R=H) and its acetate (II; R=Ac), C₁₇H₂₆O₂, n_D^{25} 1.508, $[\alpha]_D -28.3^\circ$, show that the proton in the -CH(OR)- moiety is coupled with a pair of the adjacent methylenic protons.

Hydrogenation of the ketone (I) over palladized carbon in ethanol yielded the saturated dihydro-derivative (III), mol. wt. 220 (mass spec.), C₁₅H₂₄O, m.p. 83~84°, $[\alpha]_D -9.9^\circ$. The infrared spectrum shows the presence of a cyclopentanone (1736 cm⁻¹) and a methylene adjacent to carbonyl (1412 cm⁻¹). Base-catalyzed deuteration of the ketone (III)

*¹ Details of the isolation will be published elsewhere.

*² All compounds analyzed correctly. Rotations were measured in CHCl₃ solution and IR spectra in KBr disk unless noted otherwise. NMR spectra were determined in CCl₄ solution with (CH₃)₄Si as internal standard.



afforded the trideuterio-derivative, mol. wt. 223 (mass spec.), with no infrared absorption attributable to an active methylene.

The combined evidence points to the presence of the partial structure of a 2-methyl-3-substituted-2-cyclopentenone system with a methylene grouping adjacent to the carbonyl in cyperotundone.

On Huang-Minlon reduction, the ketone (I) gave the hydrocarbon, $C_{15}H_{24}$, n_D^{25} 1.499, $[\alpha]_D -22.2^\circ$, which was shown by the nuclear magnetic resonance spectrum to be a mixture (IV) of cyperene¹⁾ and its isomer. The hydrocarbon (IV) was oxidised with ozone to yield, besides acidic product, the diketone, $C_{15}H_{24}O_2$, m.p. $77.5\sim 78.5^\circ$, $[\alpha]_D +39.8^\circ$, infrared bands at 1727 (cyclopentanone), 1412 cm^{-1} (methylene adjacent to carbonyl), NMR: a doublet (3H) at 9.28τ ($J=6.0$ c.p.s., $\underline{CH}_3\text{-CH}\langle$), two singlets (3H, respectively) at 9.06 and 8.84τ ($(\underline{CH}_3)_2\text{C}\langle$), a singlet (3H) at 7.93τ ($\underline{CH}_3\text{-CO-}$). This diketone was identified (mixed m.p., IR, NMR) as the dione¹⁾ (V) obtained from cyperene. Hydrogenation of the hydrocarbon (IV) over Adams' catalyst in acetic acid furnished the saturated hydrocarbon, $C_{15}H_{26}$, n_D^{25} 1.496, $[\alpha]_D -57.7^\circ$, whose physical and spectral properties are essentially identical with those of isopatchoulane*³⁾ (VI), $C_{15}H_{26}$, n_D^{25} 1.498, $[\alpha]_D -49.2^\circ$, derived from patchouli alcohol (VII)²⁾ via its rearranged dehydration product, α,γ -patchoulene (VIII), $C_{15}H_{24}$, n_D^{25} 1.504, $[\alpha]_D -53.7^\circ$. On the basis of these results, cyperotundone is shown to have the isopatchoulane skeleton.

Arranging the previous partial structure (the cyclopentenone system) into the isopatchoulane skeleton gives formula I (without stereochemistry) as the structure of cyperotundone.

*³⁾ This name was adopted from the proposal made by Trivedi, *et al.*¹⁾

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2) G. Büchi, R.E. Erickson, N. Wakabayashi: *J. Am. Chem. Soc.*, **83**, 927 (1961); M. Dobler, J.D. Dunitz, B. Gubler, H.H. Weber, G. Büchi, J. Pallida O.: *Proc. Chem. Soc.*, **1963**, 383; G. Büchi, W.D. Macleod, Jr., J. Pallida, O.: *J. Am. Chem. Soc.*, **86**, 4438 (1964).

The absolute stereochemistry of patchouli alcohol has been elucidated as shown in formula VII.³⁾ Accordingly, the correlation of cyperotundone with patchouli alcohol *via* isopatchoulane (VI) fixed the absolute configuration of the C-11 carbon bridge between C-1 and C-7 as β in cyperotundone. Huang-Minlon reduction of the dione (V) gave the ketone (K), C₁₅H₂₆O, n_D^{25} 1.489, $[\alpha]_D +15.8^\circ$, infrared band (liquid) at 1736 cm⁻¹ (cyclopentanone). Optical rotatory dispersion of the ketone (K) gives a positive Cotton effect (a , +66) which confirmed the β -configuration of the C-11 carbon bridge.³⁾ The nuclear magnetic resonance spectrum of cyperotundone exhibits that the C-12 and C-13 methyl protons are nonequivalent appearing at 8.83 and 9.25 τ , respectively, as a result of anisotropy of the unsaturated system. On the other hand, the C-15 methyl protons, due to strong shielding, appear at 9.39 τ which indicates the C-10 methyl group to be situated in an α -configuration. This assignment is consistent with the justifiable assumption that catalytic addition of hydrogen to α,γ -patchoulene (VIII) takes place from the less hindered β -side of the molecule to furnish isopatchoulane (VI). Consequently, the absolute stereochemistry of cyperotundone is indicated as formula I.

Recently, from *Cyperus rotundus* LINNÉ of Chinese origin, two sesquiterpenoids, cyperene and patchoulenone, have been isolated and shown to have structures (X) and (XI), respectively (no stereochemistry indicated).^{1,4)} As the present authors have now established that both the compounds possess the same carbon skeleton as cyperotundone, it follows that the absolute stereochemistry of cyperene and patchoulenone must be as indicated in formulae X and XI, respectively. In the nuclear magnetic resonance spectra of both compounds, similar shielding of the methyl protons can be observed although the magnitudes of the shifts are relatively small: *i.e.*, 9.06 (C-12), 9.25 (C-13), and 9.20 τ (C-15 methyl protons) in cyperene and 8.97 (C-12), 9.10 (C-13), and 9.15 τ (C-15 methyl protons) in patchoulenone.⁴⁾

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