

STRUCTURES OF ROTUNDENE AND ROTUNDENOL

S.K. PAKNIKAR*

Post-graduate Centre (Bombay University), Panaji, 403 001, India

O. MOTL

Institute of Organic Chemistry and Biochemistry, 166 10, Prague, Czechoslovakia

K.K. CHAKRAVARTI

National Chemical Laboratory, Poona, 411 008, India.

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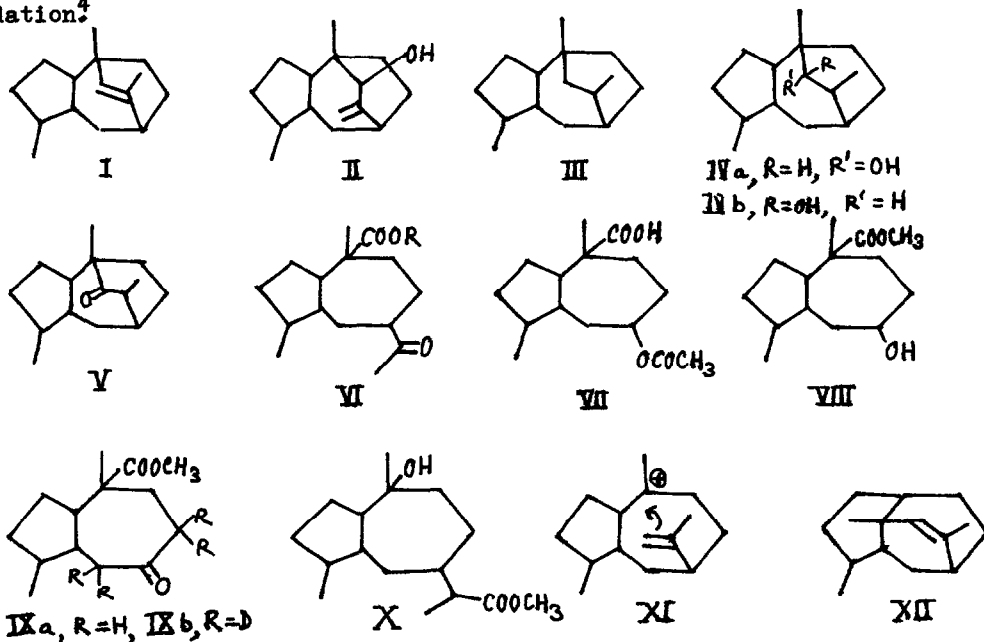
In an earlier communication¹ we described the isolation and salient structural features of two new sesquiterpenoids rotundene and rotundenol from Cyperus scariosus. We herein present evidence that they represent a new carbon framework with formulae (I) and (II).

Rotundene was isolated from the hydrocarbon fraction of C.scariosus (Indian origin) and C.rotundus (Chinese origin²). Purification was effected by a combination of preparative GLC and chromatography over $\text{AgNO}_3\text{-SiO}_2$, colourless oil, $\text{C}_{15}\text{H}_{24}$, (M^+ 204), $[\alpha]_D - 16.3^\circ$. PMR spectrum (100 MHz)³ indicated the presence of : a tertiary methyl, 0.99(3H,S), a vinyl methyl, 1.72(3H,d,J = 1.6 Hz), a secondary methyl, 0.85(3H,d,J=7 Hz) and a vinyl proton 5.45(1H, broad signal). Taken in conjunction with the presence of only three methyls, this feature suggested that the fourth methyl group of FPP(or equivalent) must have been converted to methylene or methine group during its transformation to rotundene.

Catalytic reduction of (I) produced a saturated (IR, PMR), dihydro derivative, rotundane (III) indicating its tricyclic nature. The spectral characteristics (IR, PMR) of (III) were found to be different from those of any known tricyclic skeletal types and thus rotundene belongs to a new tricyclic framework.

Hydroboration-oxidation of (I) with diborane gave a crystalline alcohol, (IVa), m.p. 95-96^o, IR ν^{max} 3350 cm^{-1} ., CrO_3 oxidation of (IVa) furnished the Ketone (V), m.p. 36^o, $[\alpha]_D - 49^\circ$, IR ν^{max} 1710 cm^{-1} ($\nu = 0$ on a

six membered ring). The Ketone (V) could also be prepared from (I) by epoxidation followed by rearrangement with BF_3 etherate. Lithium aluminium hydride reduction of (V) gave a crystalline alcohol, m.p. 61° , (IVb) epimeric with (IVa), PMR: 0.91 (3H, S), 0.85(3H,d,J = 7 Hz), 1.0(3H,d,J = 7 Hz), 3.60(1H, d, J = 9 Hz). Oxidation of (IVb) with Jones's reagent furnished Ketone (V). The Keto group of (V) appears to be hindered since it did not form any derivative (semicarbazone, oxime) and resisted Baeyer-Villiger oxidation.⁴



Ozonolysis of (I) gave a Keto-carboxylic acid (VI, R=H), characterised as its methyl ester, $\text{C}_{16}\text{H}_{22}\text{O}_3$ (VI, R= CH_3), IR ν^{max} 1728, 1712 cm^{-1} , PMR: 0.90(3H,d,J = 7 Hz), 0.99(3H,S), 2.09(3H,S), 3.69(3H,S). Reaction of (VI, R=H) with excess perbenzoic acid gave the acetoxy acid (VII) which on hydrolysis with aq. methanolic KOH, followed by esterification gave the hydroxyester (VIII). The hydroxy-ester (VIII) on oxidation with CrO_3 furnished the Keto ester (IXa), $\text{C}_{14}\text{H}_{22}\text{O}_3$, (M^+ 238), IR ν^{max} 1731, 1710, 1430 cm^{-1} , PMR: 0.93(3H,d,J = 7 Hz), 1.19(3H,S) 2.0 to 2.5(4H,m), 3.65(3H,S).

The multiplet in the region 2.0 to 2.5(4H) was attributed to

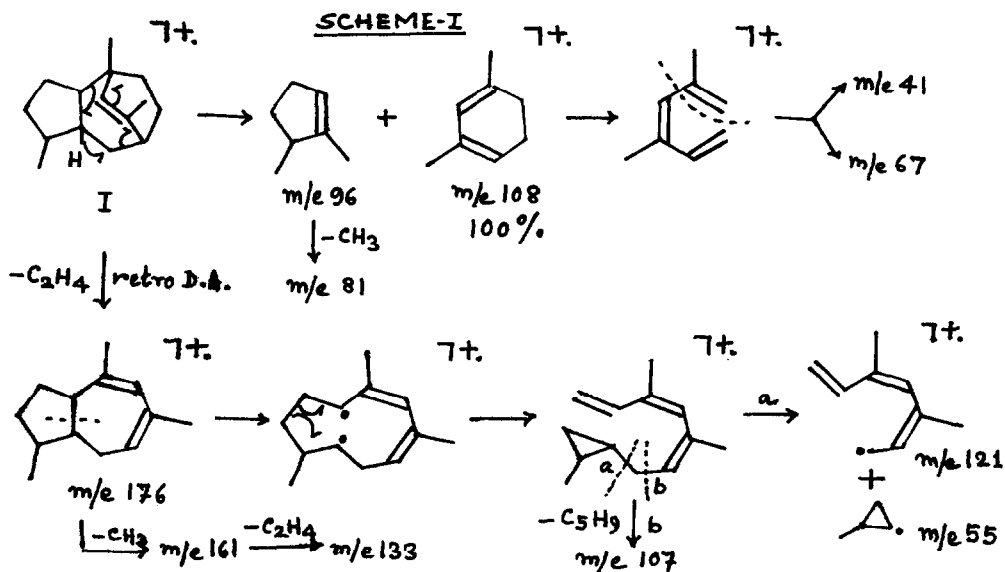
$\text{H}_2^i - \text{C}^i - \text{CH}_2^i$ protons since it disappeared in the PMR spectrum of tetradeutero derivative (M^+242) prepared by known methods. The structures were fully supported by mass spectral data, (IXa, M^+238 , m/e 206, 179, 178, 161, 153, 138, 121, 95, 81, 76, 55, 53).

Useful information regarding the position of the tertiary methyl group w.r.t. olefinic linkage could be obtained by comparing the chemical shift of the tertiary methyl group of rotundene and its derivatives not containing the unsaturated linkage. The characteristic upfield shift of the tertiary methyl singlet from 0.99 in (I) to 0.83 in (II) was found to be entirely consistent with the established trend⁵ in compounds having similar structural features. Confirmation of this was found in the properties of hydroxy-ester (X) which resulted from the performic acid oxidation of the Ketone (V) followed by hydrolysis and esterification. The PMR spectrum of (X) had its tertiary methyl signal at 1.13 characteristic of $\text{CH}_3 - \text{C}^i - \text{OH}$ grouping. The hydroxy-ester (X) resisted acetylation under normal conditions and hence the hydroxyl in (X) must be tertiary.

The experimental results and the spectral data cited above can satisfactorily be accommodated by the structure (I) for rotundene. Biogenetically, structure (I) can be derived from the cation (XI) and is expected to co-occur with cyperene and related compounds. Furthermore, the ^{13}C natural abundance NMR spectrum⁶ of rotundene showed the presence of all the structural features (3 CH_3 , 5 CH_2 , 5 CH , 2 C) supporting its formulation as (I).

The CMR shifts also fits structure (XII), but is biogenetically less likely than (I), since its biogenesis requires two extra carbonium ion shifts from the cation (XI). The mass spectral fragmentation pattern also points out structure (I) for rotundene. The intense M-96 ion (base peak) at m/e 108 is certainly due to facile loss of C_7H_{12} as shown in Scheme - I.

In view of the previously established relationship of rotundene (I) and rotundenol, the latter should be represented by (II).



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References and Notes

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2. B. Trivedi, O. Motl, V. Herout and F. Šorm, *Coll. Czech. Chem. Comm.* **29**, 1675 (1964)
3. Chemical shifts are expressed in δ' p.p.m. with internal T.M.S. as standard.
4. After initial failures with PBA and MCPBA, to obtain the desired lactone, performic acid gave some quantity of lactone.
5. R.N. Mirrington and K.J. Schmalzl, *J. Org. Chem.* **37**, 2877 (1972).
6. The detailed analysis will be published elsewhere.