Tetrahedron Letters No.32, pp. 2741-2742, 1969. Pergamon Press. Printed in Great Britain.

STRUCTURE OF α-ROTUNOL AND β-ROTUNOL

H. Hikino, K. Aota, D. Kuwano, and T. Takemoto

Pharmaceutical Institute, Tohoku University, Sendai, Japan.

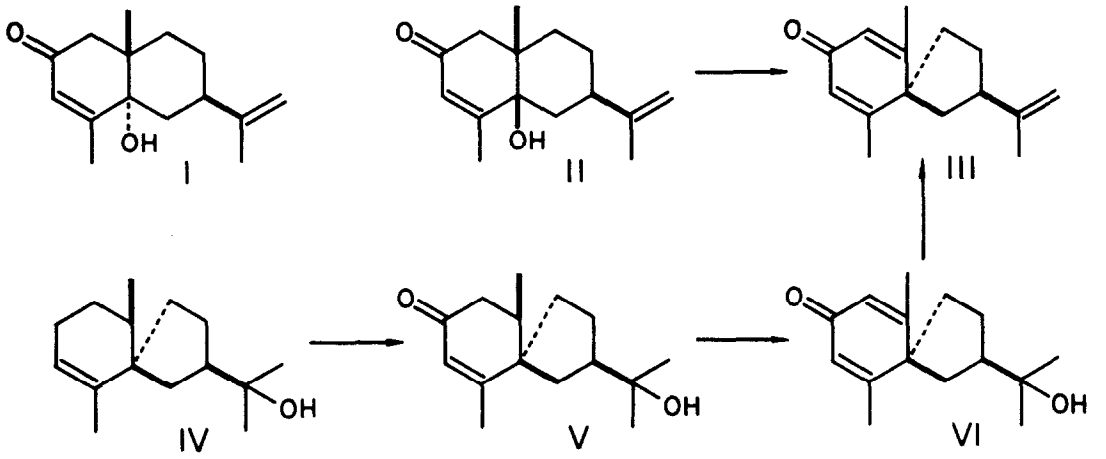
(Received in Japan 14 May 1969; received in UK for publication 5 June 1969)

The present communication deals with evidence for the stereostructures (I and II) of two new sesquiterpenic keto-alcohols α-rotunol and β-rotunol which have been recently isolated from the tuber of nutgrass, Cyperus rotundus Linné (Cyperaceae), of Japanese origin.

β-Rotunol, $C_{15}H_{22}O_2$, m.p. 118~119°, is shown by its spectral properties to have a tertiary methyl (1.15 ppm (3H)), an isopropenyl (890 cm^{-1}, 1.74 (3H), 4.75 ppm (2H)), a β-methyl-β-substituted α,β-unsaturated ketone in a six-membered or larger ring (232 nm (log ε 4.11), 1640 cm^{-1}, 1.99 (3H), 5.89 ppm (1H)), and a tertiary hydroxyl (3450 cm^{-1}). β-Rotunol was treated with phosphorus oxychloride in pyridine to give a dehydration product which was shown by its spectral properties to have a β,β'-dimethyl cross-conjugated dienone (1660, 1630 cm^{-1}, 2.04 (6H), 5.84 ppm (2H)) and an isopropenyl (890 cm^{-1}, 1.77 (3H), 4.71 ppm (2H)). Based on the above facts, we formulated the dehydration product as III and, consequently, β-rotunol as II, the location of the isopropenyl being tentatively assigned on the assumption that β-rotunol follows the isoprene rule.

To prepare the dienone (III), hinesol (IV)[1,2] was oxidized with t-butyl chromate to give the enone (V) which on oxidation with 2,3-dichloro-5,6-dicyano-benzoquinone afforded the dienone (VI). On treatment with phosphorus oxychloride in pyridine the hydroxy-dienone (VI) gave a mixture of the isopropenyl and isopropylidene derivatives. The former was identified as the dienone (III), establishing the stereostructure of β-rotunol except the configuration at the ring junction.

Mechanistic considerations of the rearrangement of β-rotunol to the dienone (III) indicate that the C-5 hydroxyl and the C-10 methyl are β-cis. This was further confirmed by the CD curve of β-rotunol which shows a negative Cotton effect for the n-π^* transition ($[\theta]_{334}$ -4560) being almost identical with that of the reference substance, 5β-spirost-3-en-2-one.[3] It is worthy to note that the CD curve exhibits a positive Cotton effect for the π-π^* transition ($[\theta]_{236}$ +51200) whose sign is opposite to that of the reference substance, the reversion being due to the hydroxyl function at the γ-position of the α,β-unsaturated ketone.[3]



On the basis of the above evidence, β-rotunol is concluded to have the stereostructure II.

α-Rotunol, $C_{15}H_{22}O_2$, m.p. 87.5~88.5°, is also shown by its spectral properties to possess the same structural features as β-rotunol, a tertiary methyl (1.04 ppm (3H)), an isopropenyl (891 cm^{-1}, 1.76 (3H), 4.77 ppm (2H)), a β-methyl-β-substituted α,β-unsaturated ketone in a six-membered or larger ring (235 nm (log ε 4.03), 1663, 1623 cm^{-1}, 1.95 (3H), 5.83 ppm (1H)), and a tertiary hydroxyl (3450 cm^{-1}). The mass spectrum of α-rotunol is also identical with that of β-rotunol but there are differences in the intensities in certain peaks, indicating that both the ketols have the same gross structure. The stereochemistry of α-rotunol was shown by its CD curve exhibiting a negative Cotton effect for the n-π^* transition ($[\theta]_{361}$ -530) which is essentially superimposable, including the fine structure, on that of the reference substance, 17β-acetoxy-5α-androst-3-en-2-one.[3] The change in sign of the Cotton effect for the π-π^* transition due to the difference of the γ-functions was again observed in α-rotunol and the reference substance.

The above evidence leads to the conclusion that α-rotunol is represented by stereoformula I.

We thank Dr. K. Kuriyama, Shionogi Research Laboratory, for helpful advice on the CD curves.

REFERENCES

1) J. A. Marshall and P. C. Johnson, J. Amer. Chem. Soc., 89, 2750 (1967).

2) T. Kimura and I. Yosioka, Chem. Pharm. Bull. (Tokyo), in press.

3) K. Kuriyama, personal communication.