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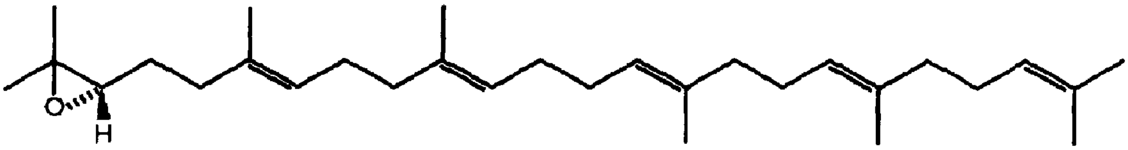
THE OCCURRENCE OF (S)-(-)-SQUALENE-2,3-EPOXIDE IN NATURE: ISOLATION FROM THE GREEN ALGA CAULERPA PROLIFERA.

L. De Napoli, E. Fattorusso, S. Magno and L. Mayol,
Istituto di Chimica Organica e Biologica dell'Università di Napoli
via Mezzocannone 16, 80134 Napoli.

Summary.- The unprecedented isolation of (S)-(-)-squalene-2,3-epoxide (1) from a natural source (green alga Caulerpa prolifera) is reported.

Squalene-2,3-epoxide is considered as the immediate precursor of triterpenes and sterols in Nature. Although its important role in the terpenoid biosynthesis has been unequivocally established[1], its isolation from a natural source has not been reported so far: only its 10,11-isomer has been found in the micelia of Sclerotinia fructicola[2].



1

In the course of our studies on the chemistry of marine organisms, we found that the green alga Caulerpa prolifera, from which we isolated the acetylenic sesquiterpene caulerpenyne[3], also produces relatively large amounts of squalene and minor quantities of (S)-(-)-squalene-2,3-epoxide.

The less polar fraction of the chloroform extracts of the green alga Caulerpa prolifera (collected near the coasts of the Bay of Naples) upon chromatography on silica gel (elution with Et_2O in n-hexane) afforded squalene (0.03 % of fresh seaweed weight) as well as crude 1. The latter was further purified by SiO_2 TLC using *n*-hexane-ethyl acetate (85:15) as the eluent, thus obtaining **1** as a pure compound (0.005% of fresh weight; $[\alpha]_D$ −1.7°, c=1 in $CHCl_3$). Its spectral data (PMR, CMR, MS and IR) clearly indicated it to be an acyclic triterpeno having an oxirane ring, most probably the all *trans*-2,3-epoxysqualene: the stere chemistry of double bonds resulted from the chemical shifts of the vinylic methy groups on C_6, C_{10}, C_{15} and C_{19} , which resonate at δ 1.61[4]. The identification confirmed by comparison of **1** with a synthetic sample of (±)-squalene-2,3-epoxide prepared from all *trans*-squalene,with N-bromosuccinimide according to van Tamele and Curphey[5].

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