

SPECIALIA

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Furocaulerpin, a new acetylenic sesquiterpenoid from the green alga *Caulerpa prolifera*¹

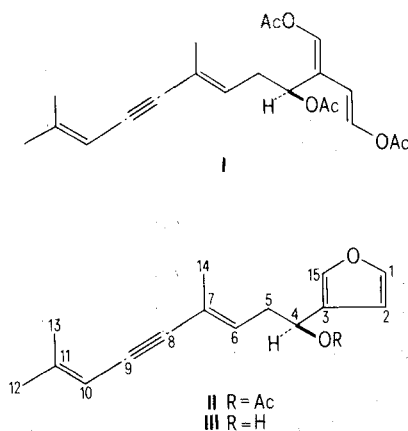
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Summary. Furocaulerpin, an acetylenic sesquiterpenoid possessing a furan ring, has been isolated from the marine alga *Caulerpa prolifera*, and its stereostructure elucidated mainly on the basis of physico-chemical data.

In 1978 we reported the isolation from the green alga *Caulerpa prolifera* of Caulerpenyne (**I**), a sesquiterpenoid possessing a 1,4-diacetoxybuta-1,3-diene moiety². Metabolites containing this functionality are very rare in nature and seem to be peculiar to the green algae of the family Caulerpaceae³ and Codiaceae⁴ (Siphonales).

We wish to report here that *Caulerpa prolifera* also produces Furocaulerpin (**II**), structurally related to **I** and containing a monosubstituted furan ring. The co-occurrence of **I** and **II** in the same organism could be of biogenetic interest as far as the formation of furan rings in natural compounds is concerned.



Fresh material (collected in the Bay of Salerno, Italy, September 1979) was freeze-dried and repeatedly extracted with chloroform. Fractionation on silica gel, using increasing amounts of diethyl ether in light petroleum as eluent, afforded crude **II**, which was purified by HPLC (μ -porasil column, Waters Ass., eluent n-hexane-AcOEt 97:3), 0.03% yield based on fresh seaweed weight, $[\alpha]_D^{20} -15.0^\circ$ ($c=1$ CHCl₃), oily.

Alkaline hydrolysis of **II** was performed in 10% KOH in ethanol-water (80:20) under reflux for 1 h giving crude **III**, which was purified by PLC (eluent light petroleum-Et₂O 6:4).

High resolution mass spectroscopy established the elemental composition of **II** as C₁₇H₂₀O₃. The positive Ehrlich test and the NMR-spectrum [270 MHz, CDCl₃, 3 narrow 1-H multiplets, mutually coupled, at δ 6.41 (β -furan proton), 7.38 and 7.43 (α -furan protons)] pointed to the presence of a β -substituted furan ring.

The presence of an acetoxymethyne group was deduced from IR ($\nu_{\text{max}}^{\text{CCl}_4}$ 1740 and 1235 cm⁻¹) and NMR [δ 2.06 (3H, s, CH₃CO) and 5.80 (1H, broad t, J=6.6 Hz, >CHOAc)] spectra and confirmed by alkaline hydrolysis of **II** which afforded **III**, $[\alpha]_D^{20} -24.4^\circ$ ($c=1$ CHCl₃), oily, M⁺ = 230, $\nu_{\text{max}}^{\text{CCl}_4}$ 3600 cm⁻¹, δ 4.75 (1H, broad t, J=6.5 Hz, >CHOH) from which **II** could be regenerated by acetylation (Ac₂O/Py). Spin decoupling experiments indicated that this group must be linked to the furan ring, since the signal at δ 5.80 resulted long range coupled with the signals of the furan protons.

Further analysis of the PMR-spectrum and extensive spin decoupling experiments allowed us to expand the above partial structure to the sequence C(1)–C(7). In fact the methylene protons resonate as 2 symmetrical double doublets (J = 14.5, 6.6 and 7.0 Hz) at δ 2.71 and 2.57, coupled with the triplet at δ 5.80 and with the triplet at δ 5.72 (1H, 6-H) broadened by long range coupling with 7-Me (δ 1.82). The sequence of the remaining 6 carbon atoms implied by the molecular formula of **II** was clarified on the basis of IR ($\nu_{\text{max}}^{\text{CCl}_4}$ 2185 cm⁻¹, –C≡C–) and NMR [singlet at δ 5.36 (1H, 10-H) broadened by long range coupling with the 11-Me groups resonating at δ 1.89 (cis) and 1.82 (trans, superimposed to the signal of 7-Me)] spectra.

At this juncture it became apparent that the new compound must be represented by the formula **II**, which is also supported by the UV-spectrum [$\lambda_{\text{max}}^{\text{n-hexane}}$ 242 (sh), 256, 269 and 283 nm with ϵ 8820, 12500, 15450 and 11030] and the fragmentation pattern in the mass spectrum which, besides M⁺ (m/e 272), includes diagnostically important peaks for M⁺ – AcOH (m/e 212), M⁺ – C₁₀H₁₃ (m/e 139), M⁺ – C₇H₇O₃ (m/e 133) and M⁺ – C₁₀H₁₃ – CH₂CO (m/e 97).

The E-configuration of the double bond was assigned by application of the nuclear Overhauser effect; irradiation at the frequency of 7-Me resulted in a 16% enhancement of the integrated absorption of the methylene signal whereas the signal of 6-H was not significantly affected. The chirality of C(4) was established applying the Horeau method⁵ on **III**, which gave a preponderance of (–)-*a*-phenylbutyric acid (optical yield 7%).

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