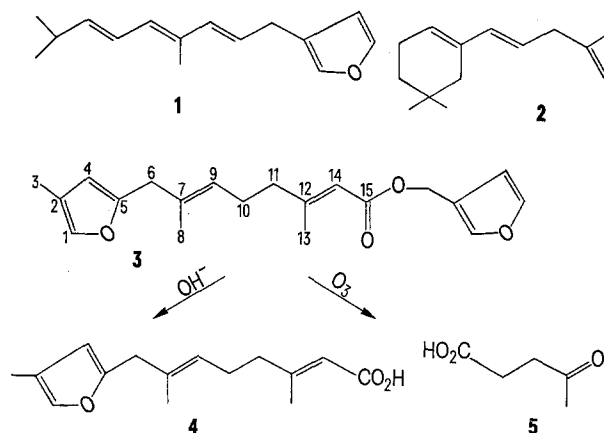


Pleraplysillin-2, a Further Furanosesquiterpenoid from the Sponge *Pleraplysilla spinifera*

Sponges of the family Spongidae (genus *Spongia*, *Hippospongia* and *Ircinia*) were previously shown to contain a number of closely related linear furanoterpenes containing 21¹ and 25 carbon atoms², all of which are characterized by terminal β -mono-substituted furan rings.

More recently *Pleraplysilla spinifera* (family Aplysillidae belonging to the same order of Dictiocerata as the family Spongidae) has provided 2 furanosesquiterpenes, **1** and **2**, both with the feature of a terminal β -mono-substituted furan ring³.

Examination of the more polar fractions eluted with benzen-petrol (1:1) from the SiO₂ column of the solvent extracts of this sponge has now led to the isolation (0.5% of the dry sponge) of an ester, **3**, with a sesquiterpenoid acidic moiety including a 4-methyl-2-substituted furan ring and an hemiterpene alcoholic part characterized as 3-hydroxymethylfuran. Here we report structural determination of this novel substance, which we called pleraplysillin-2.



Pleraplysillin-2, C₂₀H₂₄O₄, gives a positive Ehrlich test for furans and shows ν_{max} (liquid film) 1715 and 1635 (α , β -unsaturated ester) and 1030, 880 and 765 (furan) cm⁻¹ and λ_{max} 222 nm (ϵ = 14,400 in CH₃OH). The NMR-spectrum (100 MHz, CCl₄, δ -scale) with decoupling experiments indicated the presence of a 4-methyl-2-methylene substituted furan: 1.95 (3H, s), 3.17 (2H, s), 5.76 and 6.95 (1H each, bs); irradiation at 6.95 (furan- α -H; H-1) caused a sharpening of both the furan- β -H (5.76, H-4) and the methyl at 1.95 (CH₃ on C-2)⁴; in the reverse experiment irradiation at 1.95 resulted in a distinct sharpening of the furan- α -H signal only, while the furan- β -H broad singlet has been simplified by irradiation on the methylene at 3.17 (H₆, H₆). The Me-C=CH-CO₂-part structure

(Me/CO₂-*cis*)⁵ was derived from signals at 2.15 (3H, d, J = 1Hz) and 5.61 (1H, bs) with mutual coupling, while the β -methylene-substituted furan was indicated by the presence of signals at 7.40, 7.32, 6.38 (1H, each, bs) and 4.93 (2H, s). Two peaks at 2.20 (4H, =C-CH₂CH₂-C=) and 5.17 (1H, t, J = 4Hz, CH = C) and a *trans* vinyl methyl at 1.59⁶ are the remaining signal in the spectrum.

Treatment of pleraplysillin-2 with alkali yielded an α , β -unsaturated carboxylic acid, **4**, C₁₅H₂₀O₃ (M⁺/e 248), ν_{max} 3300–2500 (b), 1680 and 1635 cm⁻¹, whose NMR-spectrum was almost identical to that of the parent compound, apart from the signals for the β -methylene-substituted furan. Oxidative ozonolysis of the natural ester afforded levulinic acid (**5**).

Consequently the spectral and chemical evidence leads to the conclusion that pleraplysillin-2 has the structure **3**, which is also supported by the fragmentation pattern in the MS, which, besides M⁺ (m/e 328, 65%), includes peaks for M⁺-CH₂C₄H₈O (m/e 247, 60%), M⁺-OCH₂C₄H₈O (m/e 231, 33%), (CH₃)C₄H₇OCH₂⁺ (m/e 95, 90%), C₄H₇OCH₂⁺ (m/e 81, 92%) and the base peak at m/e 149, corresponding to the fragment (CH₃)C₄H₇OCH₂C(CH₃) = CHCH₂⁺, originating from the expected allylic cleavage of the 10, 11 bond.

Riassunto. Si riporta l'isolamento dalla spugna *Pleraplysilla spinifera* di un ulteriore furanosesquiterpenoide pleraplysillina-2 per il quale si dimostra la struttura **3**.

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Scalaradial, a Third Sesterterpene with the Tetracarbocyclic Skeleton of Sclarin, from the Sponge *Cacospongia mollior*

Recent chemical interest in the sponges metabolites has led, inter alia, to the isolation of the 2 related tetracarbocyclic sesterterpenes, sclarin (**1**)¹ and deoxosclarin (**2**)², from *Cacospongia scalaris* and the taxonomically related *Spongia officinalis*, respectively. They are members of a new class of sesterterpenes, originating from generanylfarnesol by a cyclization initiated at the isopropylidene group, which is typical of triterpenes. Of interest is the close biogenetic relationship of the sponges sester-

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