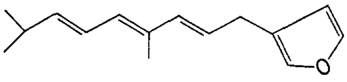
Pleraplysillin-2, a Further Furanosesquiterpenoid from the Sponge *Pleraplysilla spinifera*

Sponges of the family Spongidae (genus *Spongia*, *Hippospongia* and *Ircinia*) were previously shown to contain a number of closely related linear furanoterpenes containing 21[1] and 25 carbon atoms[2], all of which are characterized by terminal β-mono-substituted furan rings.

More recently *Pleraplysilla spinifera* (family Aplysillidae belonging to the same order of Dictioceratida as the family Spongidae) has provided 2 furanosesquiterpenes, **1** and **2**, both with the feature of a terminal β-mono-substituted furan ring[3].

Examination of the more polar fractions eluted with benzen-petrol (1 :1) from the SiO_2 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.



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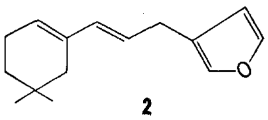

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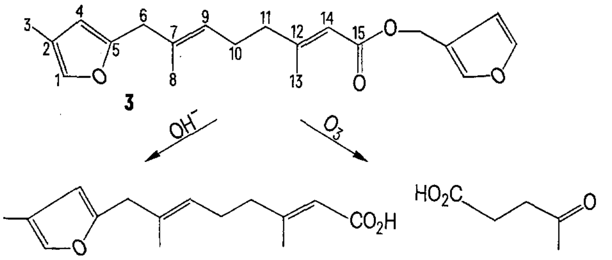

3 **4** **5**

Pleraplysillin-2, $C_{20}H_{24}O_4$, 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 CH_3OH). The NMR-spectrum (100 MHz, CCl_4, 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 (CH_3 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 (H_6, H_6). The Me–C=CH–CO_2–part structure (Me/CO_2-*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, $=C\text{–}CH_2CH_2\text{–}C=$) and 5.17 (1H, t, J = 4Hz, CH = C) and a *trans* vinyl methyl at 1.59[6] are the remaining signal in the spectrum.

Treatment of pleraplysillin-2 with alkali yielded an α,β-unsaturated carboxylic acid, **4**, $C_{15}H_{20}O_3$ (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 $M^+\text{-}CH_2C_4H_3O$ (m/e 247, 60%), $M^+\text{-}OCH_2C_4H_3O$ (*m/e* 231, 33%), $(CH_3)C_4H_2OCH_2^+$ (*m/e* 95, 90%), $C_4H_3OCH_2^+$ (*m/e* 81, 92%) and the base peak at *m/e* 149, corresponding to the fragment $(CH_3)C_4H_2OCH_2C(CH_3)$ = $CHCH_2^+$, 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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18 February 1974.

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[1] E. FATTORUSSO, L. MINALE, G. SODANO and E. TRIVELLONE, Tetrahedron *27*, 3909 (1971); G. CIMINO, S. DE STEFANO, L. MINALE and E. FATTORUSSO, *27*, 4673 (1971); *28*, 267 (1972); G. CIMINO, S. DE STEFANO and L. MINALE, *28*, 5983 (1972).

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

Recent chemical interest in the sponges metabolites has led, inter alia, to the isolation of the 2 related tetracarbocylic sesterterpenes, scalarin (**1**)[1] and deoxoscalarin (**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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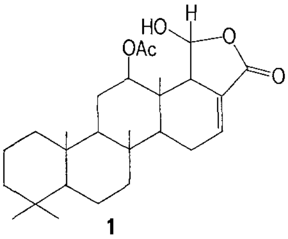
terpenes **1** and **2** with the fern sesterterpene, cheilanthatriol (**3**), recently isolated by HAFIZULLAH et al.[3].

In our further search for constituents of marine sponges, we have now isolated a third tetracarbocyclic sesterterpene from *Cacospongia mollior*, which proved to have the structure **4**, closely related to scalarin (**1**) and deoxoscalarin (**2**) and accordingly named scalaradial.



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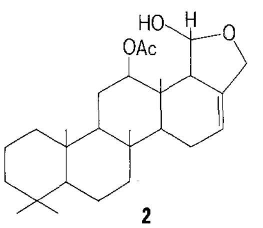

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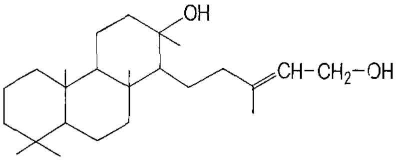

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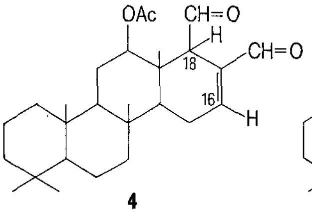

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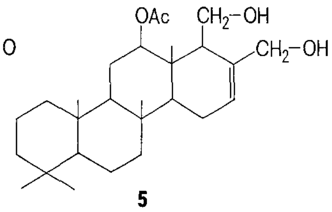

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By essentially the same procedure as reported in previous papers[4], the fresh tissues (300 g, dry weight) of *Cacospongia mollior*[5] were extracted with acetone to give a brown oil (7 g), which was directly chromatographed on silica gel. Elution with 40–70°-light petroleum and increasing amounts of ether afforded the crystalline scalaradial (200 mg), which was recrystallized from ethanol, m.p. 111–113°; $[\alpha]_D$ + 47.3° (c, 0.9; CH_3OH). The physical properties of scalaradial thus obtained are listed below[6].

Scalaradial (**4**): $C_{27}H_{40}O_4$ [*m/e* 428 (very small, M^+)]; λ_{max} (MeOH) 231 nm (ε, 3,340); ν_{max} (nujol) 2720, 1735, 1725, 1682 and 1650 cm^{-1}; δ (C_6D_6) 0.62, 0.66, 0.70, 0.82 and 0.88 (each 3H, s), 1.91 (3H, s), 3.56 (1H, m), 4.90 (1H, m), 6.26 (1H, m), 9.20 (1H, s) and 9.60 (1H, d, J = 4Hz) ppm.

The IR- and UV-spectra of it coupled with NMR signals at δ 9.60, 9.20 and 6.26 ppm indicate the presence of a disubstituted α, β-unsaturated aldehyde, and a simple aldehyde group. The arrangement of the 2 aldehyde groups as shown in **4** can be confirmed with the aid of double resonance experiments: irradiation at the centre of the olefinic multiplet at δ 6.26 (H-16) caused the signal at δ 3.56 (H-18) to collapse to a sharp doublet (J = 4Hz); in the reverse experiment irradiation at δ 3.56 (H-18), the olefinic multiplet at δ 6.26 (H-16) collapsed to a triplet (J = 4Hz) and transformed the aldehyde doublet at δ 9.60 into a sharp singlet; finally irradiation at δ 9.60 collapsed the multiplet at δ 3.56 (H-18) to a doublet (J = 3Hz).

Furthermore, scalaradial contains an acetoxy group, as indicated by IR-(ν_{max} 1735 cm^{-1}) and NMR-(δ 1.91 and 4.90 ppm) spectra, and 5 *tert* – methyl's (NMR). This, together with above spectral evidence, suggests a close relationship with both scalarin (**1**) and deoxoscalarin (**2**).

The mass spectrum showed strong peaks at *m/e* 191 (100%) and 205 (65%) also apparent as the highest peaks in the spectra of both **1** and **2**, and corresponding to cleavage of 8–14 and 9–11 bonds and 8–14 and 11–12 bonds, respectively. All these data indicate that the new sesterterpene is most favourably represented by formula **4**, which has been confirmed by conversion of scalaradial, on sodium borohydride reduction, into the diol **5** identical (TLC, NMR, MS) with the diol derived from deoxoscalarin (**2**) on the same reaction[2].

Riassunto. Si descrive l'isolamento di un nuovo sesterterpene tetracarbociclico, scalaradiale, dalla spugna *Cacospongia mollior*, per il quale si dimostra la struttura **4**, strettamente correlata alla scalarina (**1**) e alla deoxoscalarina (**2**), precedentemente ottenute dalle spugne *Cacospongia scalaris* e *Spongia officinalis*, rispettivamente.

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[5] Sponges, collected in the Bay of Naples, were obtained from the Supply Department of the Zoological Station (Naples) and identified by Professor N. SARÀ and Dr. G. PULITZER-FINALI (University of Genova) to whom the authors express their thanks.

[6] Mass spectra were recorded on an AEI MS-30 spectrometer; NMR-spectra were taken on a Varian HA-100D spectrometer; IR- and UV-spectra were determined with a Perkin-Elmer 257 and Baush and Lomb Spectronic 505 spectrophotometers, respectively.

Tiliageine: a New *Bis*benzylisoquinoline Biphenyl Alkaloid from *Tiliacora dinklagei*[1]

Tiliacora dinklagei (Menispermaceae), a woody climber indigenous to Ghana and other parts of West Africa, has been used natively as a tie for securing house parts[2] and as a medicinal in the treatment of a variety of fevers and other conditions[3]. A number of alkaloids of the *bis*-benzylisoquinoline biphenyl type have been isolated from *Tiliacora* species in India[4–6] and Africa[7,8] as well as from other Menispermaceous species around the world[9].

Chromatography of an extract of *T. dinklagei* afforded tiliageine (*I*), mp 270°; $[\alpha]_D^{25}$ + 132.6° (c 1.43, pyr.); λ_{max}^{MeOH} 212 nm (log ε 4.83), 231 (sh) (4.60), 288 (4.03), 295 (sh) (3.96); ν_{max}^{KBr} 2960 cm^{-1}, 1610, 1585, 1500, 1450, 1435, 1420, 1325, 1305, 1267, 1240, 1225, 1115, 1050, 978, 905, 870, 815; $\delta_{60\,MHz}^{CDCl_3}$ 2.34 (s) (3H) (NCH_3), 2.60 (s) (3H) (NCH_3), 3.41 (s) (3H) (OCH_3), 3.76 (s) (3H) (OCH_3), 3.81 (s) (3H) (OCH_3), 6.25–7.18 (m) (ArH); M^+ *m/e* 608 (100%) (measured 608.2869 and calculated as 608.2886 for $C_{37}H_{40}N_2O_6$), 501 (1) (measured 501.2401 and calculated as 501.2390 for $C_{30}H_{33}N_2O_5$), 417 (2) (measured 417.1942