spectrometry and NMR). UV (MeOH) 242 (ε 14.900) nm; IR ($CHCl_3$) 3450, 1660, 1610 cm^{-1}; PMR ($CDCl_3$) 5.70 (H-4, 1H, s), 4.55 (H-16, 1H, m, w/2 15 Hz), 1.26 (H-19, 3H, s), 1.13 (H-21, 3H, s), 0.84 (H-26 and H-27, 6H, d, J=6.2 Hz), 0.77 (H-18, 3H, s) δ. MS: 398 (3%, $M^+ - H_2O$), 383 (5%), 331 (10%), 313 (50%), 295 (23%), 271 (100%) m/z; CMR (table).

The comparison of the above spectral data with those of **1** revealed a strong structural analogy between the 2 steroids, with changes mainly due to the conformational difference that results from a different localization, in **3**, of the β-oriented hydroxy group at C-16 of **1**. This group in **3** can be located only on the D ring and has to show an α orientation. In fact the comparison of the MS- and CMR-data of **3** with those of model compounds[3,6] excludes the localization of the hydroxy group either on the side chain or on the rings A, B and C. In addition the PMR-spectrum of **3**, compared with that of **1**, showed a strongly upshifted resonance of the C-18 methyl, 0.77 δ, justificable[7] only with an α orientation of the hydroxy group at C-15 or at C-16. The definitive assignment at C-16 arised from the oxidation, as seen for **1**, of **3** to **2**.

During this structural work we have observed that, in **1** and **3**, the ^{13}C chemical shift of C-17 is strongly influenced by the stereochemistry of the hydroxy group at C-16. In fact the CMR-spectrum of **3** shows for C-17 a shielding (68.1 ppm) in agreement with the predicted values, while in **1** the value for C-17 is strongly upshifted (60.1 ppm). The observed anomaly may be due to the possibility that in **1** a hydrogen linkage may be formed between the hydroxy groups at C-20 and C-16.

The acetylation at room temperature of **1** and **3** confirmed this hypothesis. In fact the CMR-spectra of both the acetyl derivatives, **5** and **6**, besides allowing the assigning of the chemical shifts to all the D ring carbons, showed significant resonances for C-17 (60.4 and 62.8 ppm, respectively). The 1st value was particularly informative; in disagreement with the expected upshift due to the acetylation it was weekly downshifted. This unusual shift can be well justified by the above suggested intramolecular interaction.

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A new furanoterpene from a *Spongia* sp.

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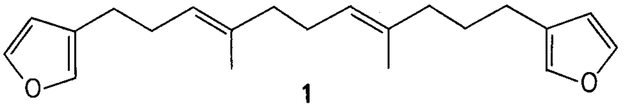
Summary. A new C21 furanoterpene, oxygenated at C(8), has been isolated from a *Spongia* sp.; its structure has been established by chemical and spectroscopic studies. The stereochemistry of tetradehydrofurospongin-1 is discussed.

A number of C21 furanoterpenes have been isolated from sponges of the family Spongiidae (order Dictyoceratida)[1]. Most have been obtained from 3 related Mediterranean sponges, *Spongia officinalis, S. nitens* and *Hippospongia communis* and can be considered to be based on anhydrofurospongin-1 (**1**) with oxygenation at the center of the prenyl chain and varying degrees of unsaturation e.g. furospongin-1 (**2**) and nitenin (**3**)[2]. Some Australian *Spongia* species have been shown to contain C21 furanoterpenes, in particular tetradehydrofurospongin-1 (**4**)[3] and the unsymmetrically oxygenated furospongenol (**5**)[4].

We now wish to report the isolation and structural elucidation of a new C21 furanoterpene isolated from a *Spongia* sp. found off the Western Australian coast.

A specimen of the sponge (found at a depth of 15 m east of Gun Island, Southern Abrolhos Group, Western Australia)[5] was collected and frozen for transport. On thawing the diced sponge was extracted twice with CH_2Cl_2: MeOH (1:1) and the extract was partitioned by the addition of H_2O. Fractionation of the CH_2Cl_2 soluble extract on silica gel afforded, in the CH_2Cl_2: AcOEt (3:1) fraction, **6** (1.3% yield based on wet weight of sponge) as an unstable oil, $[\alpha]_D^{20} - 10°$ (c=0.4, $CHCl_3$), $C_{21}H_{26}O_3$ (elemental analysis).

The ^1H-NMR-spectrum (270 MHz, $CDCl_3$) suggested the presence of 2 β-substituted furan rings [4 multiplets at δ 7.30 (3H), 7.20 (1H), 6.49 (1H), 6.27 (1H)]. This was supported by the ^{13}C-NMR-spectrum (20.1 MHz, $CDCl_3$) (table) which showed signals for 4 furan α-carbons (doublets at δ 139.0, 140.0, 142.7, 143.5) and 4 furan β-carbons (doublets at δ 107.7, 112.2; singlets at δ 124.5, 125.0). The ^1H-NMR-spectrum included a broad signal at δ 2.70 for a doubly allylic mehtylene which was shown to be coupled (J 7 Hz) to 2 vinylic protons resonating at δ 5.58 and with long-range coupling to the furan protons at δ 7.30. 7.20 and 6.27. The presence of a tertiary carbinol system was deduced from IR (ν_{max}^{film} 3400 cm^{-1}), ^1H-HMR [δ 1.86 (D_2O exchangeable), 1.29 (3H, s)] and ^{13}C-NMR evidence (δ 72.6, C-OH). Significant downfield shifts were observed for the vinyl multiplet (δ 5.58 to 6.0) and the methyl singlet (δ 1.29 to 1.8) when the ^1H-NMR-spectrum was recorded in the presence of Tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium (III). The CI_{CH_4} mass spectrum of **6** showed, besides the $M^+ + 1$ ion, significant peaks at m/z 309 ($M^+ + 1 - H_2O$) and 175 ($M^+ - C_9H_{11}O_2$), the latter arising from fragmentation α to the tertiary hydroxyl group. The EI mass-spectrum did not show an M^+, the highest



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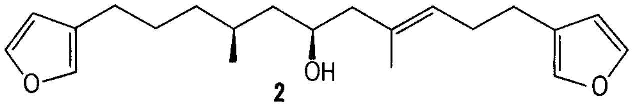

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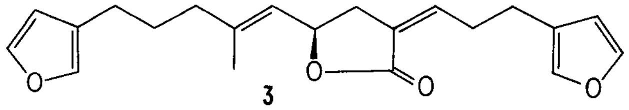

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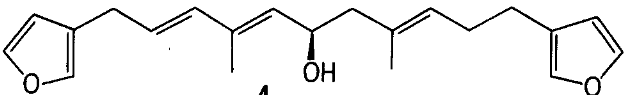

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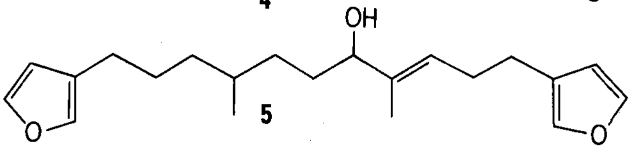

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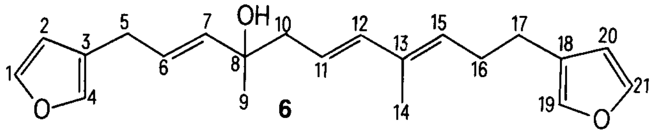

6

mass ion appearing at m/z 219 ($M^+ - C_7H_7O$) probably arising from fragmentation of the C(7), C(8) bond. The evidence so far supports sequence C(1)-C(9) for compound **6**. Further examination of the ^{1}H-HMR-spectrum revealed the presence of a disubstituted double bond (δ 6.30, d, J 16.0 Hz; δ 5.90, dt, J 16.0, 7.0 Hz) conjugated to a trisubstituted double bond [UV: $\lambda_{max}^{pentane}$ 227 nm (ε 2300); δ 5.18, brt, J 6.5 Hz, vinyl proton; δ 1.57, s, vinyl methyl] the proton of which showed coupling to a vinyl methyl and a allylic methylene (δ 2.1-2.6). These observations can be accommodated by the sequence C(10)-C(16) and the requirement for the incorporation of a methylene and a β-substituted furan into the structure leads to structure **6** for the C21 furanoterpene metabolite.

Confirmation of this was obtained from ozonolysis of **6** which yielded, after oxidative work up, succinic acid and a mixture of diacids which were identified as their dimethyl esters by GC/EIMS as dimethyl succinate, dimethyl malonate and dimethyl citramalate on comparison with authentic samples. A low yield of citramalic acid, probably due to rearrangement of the ozonide[6], precluded the determination of the chirality at C(8). The *E*-configuration of the double bond at C(11) was assigned on the basis of the coupling (J 16 Hz) between 11-H and 12-H observed in the ^{1}H-NMR-spectrum of **6**. The high field resonance (δ 16.2) for the vinyl methyl group in the ^{13}C-NMR-spectrum of **6** indicates steric shielding by the *cis*-allylic methylene group and therefore an *E*-configuration for the trisubstituted double bond. The assignment of configuration of the C(6) double bond was not straightforward since the protons appeared as part of a tightly coupled system in the ^{1}H-NMR-spectrum. An expansion of this multiplet obtained at 270 MHz was generated by computer simulation (ITRCAL program)[7] and required the following parameters $J_{6,7}$ 15.6 Hz, $J_{5a,5b}$ − 12 Hz, $J_{5a,6}$ 6.9 Hz, $J_{5b,6}$ 6.8 Hz, $J_{5a,7}$ − 1.5 Hz and $J_{5b,7}$ − 1.2 Hz. The large coupling constant between 6-H and 7-H supports the assignment of an *E*-configuration for this double bond.

^{13}C-NMR chemical shifts (in ppm from internal TMS) of the furanoterpenes **4** and **6**

C	4	6	C	4	6
C(1)	142.8^a	142.7^a	C(12)	48.2	125.3^d
C(2)	107.8	107.7	C(13)	132.5	134.6
C(3)	124.5^b	124.5^b	C(14)	16.7^e	16.2
C(4)	139.0^c	139.0^c	C(15)	121.4	123.5^d
C(5)	43.0	42.5	C(16)	28.6	28.6
C(6)	128.0^d	126.6^d	C(17)	24.9	25.0
C(7)	127.8^d	138.2	C(18)	124.9^b	125.0^b
C(8)	136.9	72.6	C(19)	139.8^c	140.0^c
C(9)	16.3^e	28.0	C(20)	111.1	111.2
C(10)	128.7^d	46.5	C(21)	143.5^a	143.5^a
C(11)	66.2	125.0^d			

Spectra were obtained with a Brucker Spectrospin WP80 at 20.1 MHz for $CDCl_3$ solutions. $^{a-e}$ Assignment may be interchanged.

A collection (obtained from dredging operations off Rottnest Island, Western Australia) gave a specimen of a *Leiosella* sp.[7]. Extraction with MeOH yielded an oil which was fractionated on alumina (Act III, neutral). Elution with light petroleum:CH_2Cl_2 (1:1) gave fractions of tetradehydrofurospongin-1 **4** (0.6% of dry wt of sponge) and the corresponding ketone (0.02%), as air and light sensitive oils. Although these compounds have been isolated previously[3] from a *Spongia* sp. the stereostructure had not been completely determined.

The ^{13}C-NMR of **4** (table) shows the presence of 2 signals for vinylic methyl carbons at δ 16.3 and 16.7 allowing *E*-configurations to be assigned to both trisubstituted double bonds. The ^{1}H-NMR shows, as reported[3], J 15 Hz for the vinylic protons at C(6) and C(7) pointing to an *E*-configuration for this double bond. An attempt was made to determine the absolute configuration of **4** by application of the Horeau method[9] which gave a preponderance of (+)-phenylbutyric acid thus indicating the *R*-configuration at C(11). The low optical yield obtained (6.0%) allows only a tentative assignment[9]. In so far as this result is consistent with those obtained[10,11] for **2** and a derivative of **3**, which also returned low optical yields, the absolute stereochemistry at C(11) appears to be identical in all these compounds.

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