Vinylfurans Revisited: A New Sesquiterpene from *Euryspongia deliculata*

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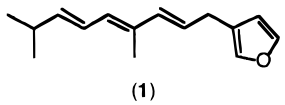
A novel furanoterpene (**2**), *iso*-dehydrodendrolasin, has been isolated from the tropical marine sponge *Euryspongia deliculata* and characterized by 2D NMR.

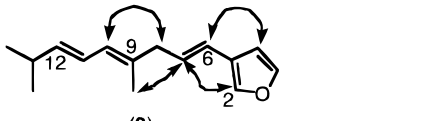
Sponges of the genus *Euryspongia* have been shown to contain furanoterpenes[1,2] and a number of other compounds, including sesquiterpene quinones,[3] hydroquinones,[4] and secosteroids.[5] A sponge identified as *Euryspongia deliculata* Bergquist,[6] was collected at Heron Island on the Great Barrier Reef at a depth of approximately 16 m. The CH_2Cl_2−MeOH (1:1) extract of this sponge was partitioned between hexane and water to give a major UV-active component that eluted with hexane on a normal-phase flash column. This component was shown to consist of two compounds by GC−MS and NMR analysis at a ratio of approximately 10:1. The minor component was identified as dehydrodendrolasin (**1**)[7] by comparison of the ^{1}H and ^{13}C NMR data with literature values.[8]

The molecular formula of the major component **2**, named by us as *iso*-dehydrodendrolasin, was determined as $C_{15}H_{20}O$ by HREIMS. The ^{1}H NMR spectrum (Table 1) indicated the presence of a β-substituted furan ring (two α protons at δ 7.35 and 7.32; β proton at δ 6.49); an isopropyl group (6H doublet at δ 1.01; 1H multiplet at δ 2.35); a 1,1,4-trisubstituted diene (1H multiplets at δ 6.21, 5.59 and 5.85); a disubstituted double bond (1H multiplets at δ 6.24 and 5.90); a methylene (2H doublet at δ 2.85); and a vinyl methyl (3H singlet at δ 1.75). The structure of **2** was assigned as shown with the use of DQF COSY, TOCSY, geHSQC, and geHMBC data. The 6*E*,9*E*,11*E* stereochemistry was assigned on the basis of coupling constants (J = 16 Hz for H6−H7 and J = 15 Hz for H11−H12), the ^{13}C chemical shift of the vinyl methyl (16.7 ppm),[9] and NOESY data (Table 1; shown on **2**).

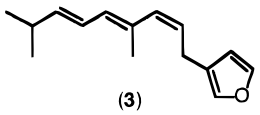
A review of the marine furanoterpene literature revealed that the spectroscopic data of **2** was identical to the compound designated as (7*Z*,9*E*,11*E*)-3-(4,8-dimethylnona-2,4,6-trienyl)furan (**3**) by Dunlop et al.,[10] except for two differences. First, the coupling constant between H6 and H7 is 16 Hz in **2** but is 10 Hz in **3**, which implies these compounds may be double-bond isomers. Second, the UV data for **2**, which exhibits a broad band of absorption between 220 and 260 nm with a λ_{max} of 242 nm, does not match that of **3** (λ_{max} 252, 270 nm). The band of absorption observed for **2** can be explained as a combination of a vinylfuran (207, 225, 231, and 239 nm)[1] and a trisubstituted diene (230 nm) absorbance. Van Altena and Miller have queried the UV data for **3** and have identified anomalies in the ^{13}C NMR data of **3** compared to dehydrodendrolasin (**1**).[1] From a comparison of literature data together with synthesis of analogues, they proposed that a methylene carbon should have a chemical shift of approximately 28 ppm when α to the furan ring of an allyl furan, but a shift of approximately 40 ppm when in the γ position of a vinyl furan. On this basis they suggested that **3**, with a methylene carbon at 43.2 ppm, was better described as a vinylfuran rather than an allylfuran. Because of the literature ambiguity, a 1D INADEQUATE experiment[11] was employed; selective excitation (20 ms Gaussian pulse) of the methylene carbon at 43.1 ppm resulted in INADEQUATE correlations to C7 and C9, rather than signals assigned to C3 and C7, unambiguously confirming the structure of *iso*-dehydrodendrolasin (**2**). These data further support the revised structure proposed for **3** by van Altena and Miller.



(**1**)



(**2**) ⟷ NOESY correlations



(**3**)

Experimental Section

General Experimental Procedures. These have been reported previously.[12]

Animal Material. The bright violet-purple sponge *Euryspongia deliculata* Bergquist (order Dendroceratida, family Dysideidae)[6] was collected at approximately 16-m depth at Heron Island (23°27′ S, 151°55′ E) on the Great Barrier Reef. The sponge is massive in shape, has a broad base, and grows on coral boulders. In life, its color is a striking violet, one of the distinguishing features of this species. Its tissue is soft, spongy, and very compressible. The surface has low rounded conules with a fine cobweblike tracery in between. Oscules occur singly or in aggregations over the entire surface. Primary fibers of the skeleton are cored by detritus and become fasciculate near the surface, with these fasciculations being another distinguishing feature of this species. Secondary fibers are clear of detritus. All fibers are stratified and pithed. Voucher specimens (G314225 and G314226) are held at the Queensland Museum, Brisbane.

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Table 1. ^{1}H and ^{13}C NMR Data for Deliculatafuran (2)

position	δ^{13}C[a]	δ^1H[b]	COSY[c]	HMBC[d]	NOESY[b]
2	143.3 (d)	7.35 (1H, s)	H1	H4, H5	H6, H7, H14/15, H16
3	124.3 (s)			H2, H4, H5, H6, H7	
4	107.5 (d)	6.49 (1H, d, <0.5)	H5	H2, H5, H6	H5, H6, H7, H14/15, H16
5	139.1 (d)	7.32 (1H, d, <0.5)	H4	H2, H4, H6	H4, H14/15, H16
6	120.9 (d)	6.24 (1H, d, 16)	H7, *H8*	H8	H2, H4, H7, H8
7	127.9 (d)	5.90 (1H, dt, 8, 16)	H6, H8	H8	H2, H4, H6, H8, H16
8	43.1 (t)	2.85 (2H, d, 8)	H7, *H6*	H6, H7, H16	H6, H7, H10, H16
9	135.9 (s)			H7, H8, H11, H16	
10	125.7 (d)	5.85 (1H, d, 11 Hz)	H11, *H12*, *H13*, *H14/15*	H8, H11, H12, H16	H8, H11, H12
11	123.5 (d)	6.21 (1H, dd, 11, 15)	H10, H12, *H14/15*	H10, H13, H16	H10, H12, H13, H14/15
12	140.4 (d)	5.59 (1H, dd, 7, 15)	H11, H13, *H10*, *H14/15*	H10, H13, H14/H15 H16	H10, H11, H13, H14/15
13	31.4 (d)	2.35 (1H, dsept, 7, 7)	H12, H14/15, *H10*	H11, H14/15	H11, H12, H14/15
14	22.5 (q)	1.01 (3H, d, 7)	H13, *H10*, *H11*, *H12*	H12, H13, H14/15	H4, H5, H11, H12, H13
15	22.5 (q)	1.01 (3H, d, 7)	H13, *H10*, *H11*, *H12*	H12, H13, H14/15	H4, H5, H11, H12, H13
16	16.7 (q)	1.75 (3H, s)		H8, H10	H2, H4, H5, H7, H8

[a] Inverse detection at 500 MHz (geHSQC); solution in $CDCl_3$; $^{13}C = 77.0$ ppm. [b] 500 MHz; solution in $CDCl_3$ referenced at $^1H = \delta$ 7.25; brackets contain integration, multiplicity, and J values (Hz). [c] Correlations in italics are HOHAHA correlations. [d] Inverse detection at 500 MHz; correlations observed when $^1J_{^{13}C-^1H} = 135$ Hz and long range $^nJ_{^{13}C-^1H} = 8$ Hz.

Extraction and Isolation. The wet sponge (450 g) was extracted with 1:1 CH_2Cl_2−MeOH (4 × 400 mL). After filtration and concentration in vacuo, the residue was partitioned between hexane (3 × 200 mL) and H_2O (500 mL). The organic extract was then dried with $MgSO_4$ and evaporated to give an orange oil (0.6 g) that did not show P_{388}, antibacterial, or antifungal activity. Filtration through silica with 100% hexane afforded *iso*-dehydrodendrolasin **2**, together with a small amount (<10%) of dehydrodendrolasin (**1**) as a pale yellow oil (0.21 g, 0.05% of wet wt). Further purification through silica gave *iso*-dehydrodendrolasin (**2**) as a pale yellow oil: UV (hexane) λ_{max} (log ϵ) 221 (sh), 242 (4.47); IR (film) ν_{max} 2959, 2868, 1571, 1508, 1466, 1072, 1025, 964, 872 cm^{-1}; ^{1}H and ^{13}C NMR, see Table 1; HREIMS m/z 216.1511 (calcd for $C_{15}H_{20}O$, 216.1509); EIMS m/z $[M]^+$ 216 (100), 173 (28), 147 (36), 105 (32), 83 (82).

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