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CHEMISTRY OF SPONGES, II.[1] PALLESCENSONE, A FURANOSESQUITERPENOID FROM *DICTYODENDRILLA CAVERNOSA*

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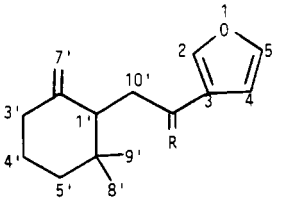
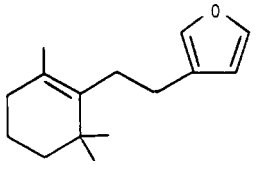
We describe here the isolation and structure elucidation of a new furanosesquiterpenoid pallescensone [**1**] which was obtained from the sponge *Dictyodendrilla cavernosa* Lendenfeld (Order Dendroceratida) collected from New Zealand coastal waters.

Pallescensone [**1**] was obtained in ca. 0.3% yield as a crystalline compound, mp 42.5-43°, $[\alpha]_D$+36° (*c* 1.0, $CHCl_3$), from a CH_2Cl_2 extract of a freeze-dried sample of *D. cavernosa*. Hrms established a molecular formula of $C_{15}H_{20}O_2$ for **1** while the presence of $C_{10}H_{17}$ and carboxyfuranyl moieties was suggested by fragment ions at *m/z* 137 and *m/z* 95, respectively, in the low resolution mass spectrum. Further fragmentation of the ion at *m/z* 137 to give ions at *m/z* 123, 122, and 107, and the presence of signals attributable to an exocyclic methylene group in the ^{1}H-nmr spectrum confirmed that pallescensone [**1**] contained a (2,2-dimethyl-6-methylidenecyclohexyl)methyl unit. The ^{1}H-nmr spectrum of **1** also exhibited three further downfield multiplets at δ 6.77, 7.43, and 8.06 which are typical of a 3-alkylfuranyl moiety. Since analogous mass spectral fragment ions and ^{1}H-nmr resonances have been reported for the related furanosesquiterpenoid penlapallascensin [**2**] (1,2), it was apparent that pallescensone [**1**] differed from structure [**2**] by the presence of a keto-group which was conjugated with the



1 R=O
2 R=H_2



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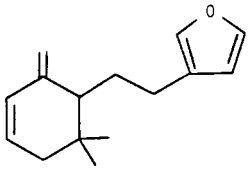

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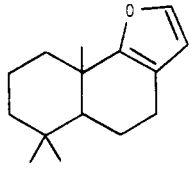

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furanyl moiety. The chemical shift of the carbonyl resonance (δ 194.2) in the ^{13}C-nmr spectrum of pallescensone [**1**] and the presence of a conjugated carbonyl

[1]For Part 1, see P. Karuso, P.R. Bergquist, R.C. Cambie, J.S. Buckleton, G.R. Clark, and C.E.F. Rickard, *Aust. J. Chem.*, **39**, 1643 (1986).

stretching band at 1683 cm^{-1} in the ir spectrum are fully consistent with the structure assigned to this compound.

The close structural similarity of pallescensone [**1**] to several furanosesquiterpenoids which have been isolated from *Dysidea pallescens* (e.g., pallescensins-1 [**3**], and -2 [**4**] and the cyclized analog pallescensin-A [**5**]) (3) and *Dysidea fragilis* (e.g., penlapallescensin [**2**]) (1), which are members of the family Dysideidae (order Dictyoceratida), further emphasizes the close relationship between the Dysideidae and members of the order Dendroceratida (4).

EXPERIMENTAL

ISOLATION OF PALLESCENSONE.—A freeze-dried sample of *D. cavernosa* (IV Station 134 Terra Nova, Brit. Mus. Nat. Hist.) (P.R.B. L.R. 7/29/72) (15.5 g), collected from Leigh, New Zealand, was extracted (Soxhlet) with CH_2Cl_2 for 6 h. Si gel chromatography (hexanes) of the crude extract gave an oil (0.16 g, 1.0% dry weight) which was purified by reverse-phase hplc (80% MeOH-H_2O) to give 2-(2,2-dimethyl-6-methylideneclohexyl)-1-(3-furanyl) ethanone [**1**] (pallescensone) as a clear oil (50 mg) which crystallized on standing, mp 42.5-43°, $[\alpha]^{20}+36°$ (*c* 1.0, $CHCl_3$) (Found: M^+ 232.1465. $C_{15}H_{20}O_2$ requires 232.1463); ir *v* max (CCl_4) 2950, 1683 (conj. CO), 1560, 1510, 1209, 1152, 868 cm^{-1}; uv λ max ($CHCl_3$) 252 nm (ε, 5100); ^1H nmr δ_H ($CDCl_3$) 0.88, 0.98, 2s, 8′, 9′-CH_3; 1.20-1.90, m, 4H, H4′, 5′; 2.07, 2.20, 2m, 1H each, H3′; 2.66, dd, *J* 9.5, *J′* 4.15, H1′; 2.80, dd, *J* 15.9, *J′* 4.4, 1H, H10′; 2.92, dd, *J* 15.9, *J′* 9.5, 1H, H10′; 4.44, br s, H7′a; 4.71, br s, H7′b; 6.77, dd, *J* 1.95, *J′* 0.74, H4; 7.43, dd, *J* 1.95, *J′* 1.47, H5; 8.06 dd, *J* 1.47, *J′* 0.98, H2; ^{13}C nmr δ_C ($CDCl_3$) 23.4, 28.7, 2q, C8′, 9′; 23.6, t, C4′; 34.2, t, C5′; 34.8, s, C6′; 38.4, 38.6, 2t, C3′, 10′; 48.4, d, C1′; 108.3, t, C7′; 108.5, d, C4; 127.9, s, C3; 143.9, d, C5; 146.6, d, C2; 148.6, s, C2′; 194.2, s, CO; ms *m/z* 232 (M^+, 14%), 217 (M^+-CH_3, 6), 189 (4), 176 (4), 163 (3), 137 ($C_{10}H_{17}^+$, 5), 123 (C_9H_{15}, 10), 122 (C_9H_{14}, 27), 107 (C_8H_{11}, 25), 95 ($C_5H_3O_2$ and C_7H_{11}, 100%), 81 (13), 69 (16), 67 (10). Attempts to form a 2,4-dinitrophenylhydrazone or a *p*-bromophenylhydrazone were unsuccessful.

ACKNOWLEDGMENTS

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