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STUDIES OF AUSTRALIAN SOFT CORALS. V - A NOVEL FURANO-SESQUITERPENE ACID FROM THE SOFT CORAL *SINULARIA GONATODES* (Kolonko)†

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There have been several previous reports[2] of sesquiterpenoid compounds from alcyonacean soft corals, (phylum Coelenterata, class Anthazoa, subclass Octocorallia). We wish to report the isolation of the new furano-sesquiterpenoid acid <u>1</u> from a specimen of *Sinularia gonatodes* collected in South East Bay, Great Palm Island, north of Townsville.

Extraction of a large sample of freeze dried coral followed by rapid silica gel chromatography and crystallisation from petroleum ether gave 1 as fine white crystals (m.p. 99-100°C, $C_{15}H_{18}O_3$[3], $M^{\oplus}$246.123, optically inactive) in almost 2% yield based on the dry weight of the coral.

The presence of a conjugated carboxylic function was indicated by the infra red spectrum (ν_{max}^{nujol} 3140-2780 cm^{-1}, H-bonded-O-H; 1655 cm^{-1} conjugated C=O), and supported by the presence of an exchangeable proton at δ9.85 in the proton n.m.r. spectrum. The u.v. spectrum was very complex [λ_{max}^{EtOH} 208, 236, 258 nm (log 4.23, 4.34, 4.39)] and showed only a small reversible bathochromic shift (10 nm) in the 258 nm peak on base treatment. The values were not unexpected for 1 which contains several independent chromophores.[4]

The structure however, was determined largely on the basis of the ^1H- and ^{13}C- n.m.r. values which appear in Table 1. The assignments were based on general considerations.[5,6] The ^1H- n.m.r. assignments were supported by the following double resonance experiments. Irradiation at δ2.2 (H_2 -8, H_2 -7) collapsed the triplet at δ5.30 (H -9) to a singlet, and irradiation at δ5.30 resulted in a sharpening of the complex multiplet at δ2.22. Irradiation at the centre of the doublet of doublets at δ6.70 (H -11) caused both the doublets at δ5.05 and 5.16 (H_2 -12) to become singlets. Irradiation at either δ5.05 or δ5.16 resulted in collapse of the doublet of doublets at δ6.70 to a doublet in each case. Irradiation at δ1.94 (H_3 -14) caused collapse of the allylic couplings in the quartet at δ6.01 (H -5) giving a sharp singlet. The low field position of the internal proton of the diene system (δ6.70, H -11) was similar to the value reported for the α-ocimenes 2 and 3 (*cis*- δ6.6; *trans* δ6.3)[7] and by comparison, it appeared likely that 1 was *cis*

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† Tentative classification; Registered sample number G 10655.
Queensland Museum, Brisbane, Q'land, Australia.

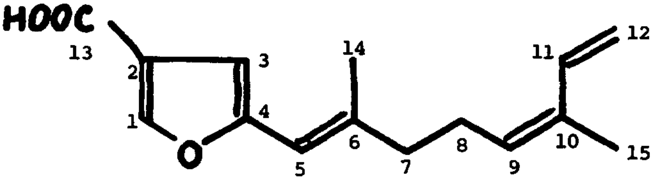

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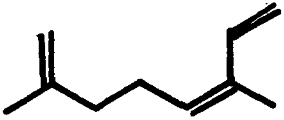
Table 1: ^{1}H-and ^{13}C-n.m.r. assignments for 1.

	^{13}C - n.m.r.$^{+}$		^{1}H - n.m.r.#		
arbon	ppm	Multiplicity	δ, integral	multiplicity	J(Hz)
1	129.6, 133.43	d	7.92, 1H	s	
2	119.92	s	- -	-	
3	106.67	d	6.45, 1H	s	
4	154.99	s	- -	-	
5	129,6, 133.43	d	6.01,,1H	q	∿1.5
6	132.91	s	- -	-	
7	40.71	t	2.22, 2H	m	
8	25.84	t	2.22, 2H	m	
9	113.5	d	5.30, 1H	t	6
10	140.9	s	- -	-	
11	146.94	d	6.70, 1H	dd	10.5, 16.5
12	113.76	t	5.16,1H; 5.05,1H.	pr. ds.	*trans* 16.5, *cis* 10.5
13	168.95	s	9.85, 1H	s	
14	18.7, 19.74	q	1.94, 3H	s	
15	18.7, 19.74	q	1.78, 3H	s	

$^{+}$Data obtained at 15 MHz on a 20% w/v solution in $CDCl_3$ with TMS as reference

#Data obtained at 100 MHz on a 10% w/v solution in $CDCl_3$ with TMS as reference.



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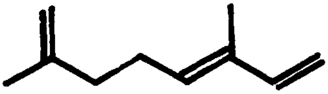

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about the Δ^9 - bond with respect to the continuous carbon chain. Further, the u.v. data reported for *cis*-α-ocimene 2 (λmax 237 nm) more closely resembled the value for 1 (λmax 236 nm) than did *trans*-α-ocimene 3 (λmax 232 nm).

Further evidence for structure 1 came from the preparation of a hexahydroderivative 4[8] by hydrogenation of 1 over Adams' catalyst in ethanol. Methylation of 1 with etherial diazomethane afforded the methyl ester 5[9] confirming the presence of a carboxylic acid group, and the presence of the terminal diene entity capable of existing in an S-*cis* conformation was demonstrated by the obtention of the Diels Alder adduct 6.[10]

Micro-ozonolysis of 1[11] afforded one equivalent of laevulinaldehyde [identified by gc-ms and by quantitative comparison with the major product from the ozonolysis of squalene] confirming the relationship between the diene system and the double bond conjugated with the furan ring. The fact that the signal for the methyl group (C -13) in the ^{13}C- n.m.r. spectrum appeared near 19 ppm was consistent with the transoid nature of this double bond (*trans ca* 17 ppm; *cis ca* 25 ppm).[6]

The structure of the sesquiterpene was thus represented by 1. This compound bears some structural similarity to the prenylated quinol recently reported from this laboratory.[12] Both compounds were extracted from *Sinularian* soft corals.

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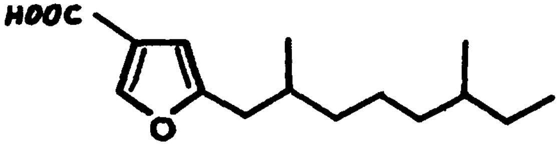

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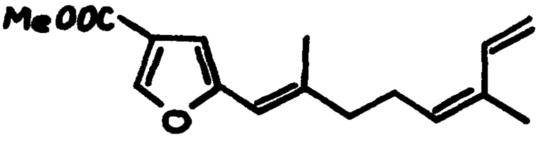

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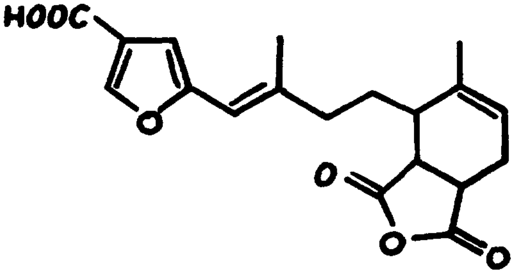

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9. $M^{\bullet}$ (mass spectrometry) 260.13, $C_{16}H_{20}O_3$ requires 260.14; u.v. λ_{max}^{EtOH} 207, 237, 255 nm. i.r. ν_{max}^{film} 2940, 1720 cm^{-1} ^{1}H- n.m.r. δ^{CDCl_3} 1.79 (s, 3H), 1.95 (s, 3H), 2.25 (m, 4H), 3.78 (s, 3H), 5.05 (d, 1H), 5.17 (d, 1H), 5.32 (t, 1H), 6.01 (s, 1H), 6.46 (s, 1H), 6.72 (dd, 1H), 7.85 (s, 1H).
10. $M^{\bullet}$ (mass spectrometry) 344.121, $C_{19}H_{20}O_6$ requires 344.126; u.v. λ_{max}^{EtOH} 207, 263 nm. i.r. ν_{max}^{film} 3020-2500, 1835, 1760, 1675 cm^{-1}; ^{1}H- n.m.r. δ^{CDCl_3} 1.75(s, 3H), 1.97 (s, 3H), 3.32 (m, 2H), 5.56 (m, 1H), 6.05 (s, 1H), 6.50 (s, 1H), 7.95 (s. 1H), 9.01 (variable, bs., 1H).
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