Tetrahedron Letters,Vol.23,No.32,pp 3271-3272,1982 0040-4039/82/323271-02$03.00/0
Printed in Great Britain

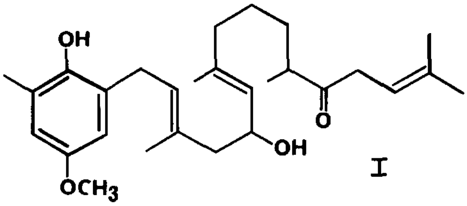
HYDROXYLATED DITERPENOID-HYDROQUINONES FROM *CYSTOSEIRA ELEGANS* : SIGNIFICANT PRODUCTS OR ARTIFACTS ?

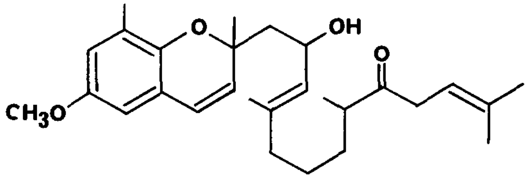
B. BANAIGS[*+], C. FRANCISCO[*], E. GONZALEZ[*], L. CODOMIER[*] and William FENICAL[+]

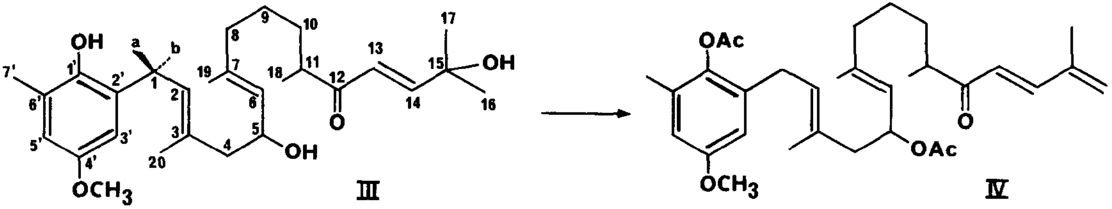
[*] Groupe de recherches en biologie et chimie des végétaux marins
Université de Perpignan 66025 (France)
[+] Scripps Institution of Oceanography, La Jolla, CA 92093 (USA)

Summary : New diterpenoid-hydroquinones were isolated and identified from the brown alga *Cystoseira elegans*. We have shown that these metabolites can also be obtained by a natural degradation of another diterpene.

Recently we described the structures of several new diterpenoid-hydroquinones from the seaweed *Cystoseira elegans* (Cystoseiraceae)[1]. We noted then that compound I (recently also described from *Halidrys siliquosa*[2]) was found in association with its corresponding chromenol derivative II. We wish to report here the structure determination of a new metabolite (III) from *Cystoseira elegans* and also the presence of other compounds which may be artifacts produced from I.


I


II


III IV

An HPLC-purified fraction from the MeOH extract of *Cystoseira elegans* yielded III, $[\alpha]_D$ + 5.7° (c 9.5, MeOH), as a light yellow oil which analysed for $C_{28}H_{42}O_5$ by HRMS (M^+-H_2O, $C_{28}H_{40}O_4$, m/z obs. 440.2932, calc. 440.2916). The infrared spectrum of III showed absorptions for hydroxyl (ν_{OH} = 3400 cm^{-1}), α,β-unsaturated ketone ($\nu_{C=O}$ = 1680 cm^{-1}, $\nu_{C=C}$ = 1620 cm^{-1} through 1680 cm^{-1} for S-cis conformation[3]), and benzenoid functionalities (ν = 1600 cm^{-1}). UV absorptions at 214 and 289 nm (ε = 10,500 and 2,200) indicated a phenol moiety, and an absorption at 224 nm (ε = 11,800) characterized the α,β-unsaturated ketone. The ^1H and ^{13}C NMR features (Tables I and II) including decoupling experiments, permitted the structure III to be formulated for this metabolite. The presence of the tertiary alcohol in III was confirmed by IR absorptions for hydroxyl (ν_{OH} = 3600 cm^{-1}) which remained after acetylation (Ac_2O, py, RT) of III. Oxidation with pyridinium chlorochromate[4] (CH_2Cl_2/0°) gave a complex mixture which appeared to be composed of cyclization products (chromenols) by NMR analysis. The final assignment for III was provided by a thorough analysis of compound IV, produced from III by acetylation and $POCl_3$- induced dehydration[5]. After HPLC purification, the dienylketone IV showed UV absorptions at 272 nm (ε = 11,500). Lastly, structure III was consistent, in the following ways, with the high-resolution mass fragmentations recorded :

m/z 149.9904 [$C_9H_{10}O_2$]; m/z 191.1072 [$C_{12}H_{15}O_2$]; m/z 204.1138 [$C_{13}H_{16}O_2$]; m/z 271.1679 [$C_{18}H_{23}O_2$]
m/z 151.0755 [$C_9H_{11}O_2$]; m/z 189.0917 [$C_{12}H_{13}O_2$]; m/z 217.1205 [$C_{14}H_{16}O_2$]; m/z 298.1932 [$C_{20}H_{26}O_2$].

Curiously, compound III was very similar to an obvious artifact obtained from compound I. Exposure of I to oxygen in the presence of acidic NMR solvents resulted first in a very facile epimerization of the methyl group at C-11. Further exposure converted the C-11 epimer of I to III', the C-11 epimer of III. It would appear that this latter reaction would involve an autoxidation of the homoconjugated ketone (C-12 to C-15). The propensity of this autoxidation should be considered in future studies where molecules of this type are involved.

Table I : 360 MHz ^1H NMR data for compounds III and III'
(δ ppm values relative to internal TMS)

Common part										Difference between structure III and III'				
n°C	$CDCl_3$	C_6D_6	J(Hz)		n°C	$CDCl_3$	C_6D_6	J(Hz)		n°C	$CDCl_3$	C_6D_6	J(Hz)	
CH_3-O	3.73	3.43	s		C_5	4.50	4.43	ddd	8.3,8.3,8.4	Structure III				
CH_3-Ø	2.21	2.21	s		C_6	5.13	5.17	bd	8.3	C_{11}	2.68	2.53	m	
C_3'	6.52	6.63	d	2.9	C_{16}	1.36	1.08	bs		C_{13}	6.39	6.48	d	15.6
C_5'	6.57	6.68	d	2.9	C_{17}	1.36	1.09	bs		C_{14}	6.91	6.97	d	15.6
										Structure III'				
C_{1a}	3.40	3.42	dd	16,7.5	C_{18}	1.09	1.05	d	6.9	C_{11}	2.76	2.61	m	
C_{1b}	3.27	3.22	dd	16,6.5	C_{19}	1.65	1.50	bs		C_{13}	6.29	6.39	d	16.3
C_2	5.38	5.44	bt	7	C_{20}	1.80	1.65	bs		C_{14}	6.88	6.95	d	16.2

Table II : ^{13}C NMR data for compound III in $CDCl_3$. Assignments are based upon off-resonance multiplicities and comparisons with suitable model compounds[6].

	C_1'	C_2'	C_3'	C_4'	C_5'	C_6'	O-CH_3	C_7'	C_1	C_2	C_3	C_4	C_5	C_6
^{13}C	146.7	127.6^a	113.3^b	152.7	114.2^b	125.6^a	55.7	16.3^c	30.6	125.9	138.4	48.0	66.1	127.7
mult.	s	s	d	s	d	s	q	q	t	d	s	t	d	d
	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}
^{13}C	134.3	39.2	24.9	32.3	44.9	206.3	153.4	124.1	71.0	29.5	29.5	16.5^c	16.4^c	16.3^c
mult.	s	t	t	t	d	s	d	d	s	q	q	q	q	q

a, b, c : assignments may be reversed.

Acknowledgements : We wish to thank M.M. Bandurraga, S.A. Look and V.J. Paul (SIO) for measurements of ^1H NMR spectra. Research at SIO was supported by NOAA-Office of Sea Grant under grant ≠≠ NA80AA-0-00120, project R/WP-22.

References

1. B. BANAIGS, C. FRANCISCO, E. GONZALEZ and W. FENICAL, *Tetrahedron*, submitted, 1982.
2. M.D. HIGGS and L.J. MULHEIRN, *Tetrahedron*, 3209 (1981).
3. T. PURDIE and J.C. IRVINE, *J. Chem. Soc.*, 1021 (1903).
4. W.H. GERWICK, W. FENICAL and M.U.S. SULTANBAWA, *J. Org. Chem.*, 2233 (1981).
5. A similar dehydration was employed in the structure elucidation of bifurcarenone, see: H.H. SUN, N.M. FERRARA, O.J. McCONNELL and W. FENICAL, *Tetrahedron Letters*, 3123 (1980).
6. *a)* J.B. STOTHERS, Carbon^{13} NMR spectroscopy, *Academic Press New York* (1972). *b)* F.W. WEHRLI and T. WIRTHLIN, Interpretation of Carbon^{13} NMR spectra, HEYDEN, London (1976).
c) P.J. SCHEUER, Marine Natural Products (vol. II), *Academic Press New York* (1978).

(Received in France 11 May 1982)