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TWO CHROMONE DERIVATIVES FROM THE BROWN ALGA ZONARIA TOURNEFORTII

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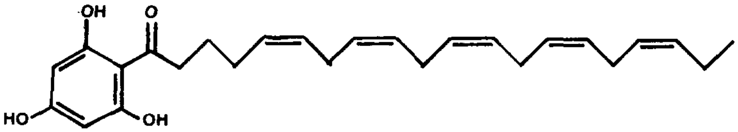
Two minor lipid components of the brown seaweed Zonaria tournefortii were characterized as (all Z) - 5',7'-dihydroxy-2'-nonadeca-4,7,10,13,16-pentenylchromone (3) and 5',7'-dihydroxy-2'-pentadecylchromone (4).

In previous work[1,2] we reported the isolation of the acylphloroglucinols 1 and 2 from the brown alga Zonaria tournefortii (Lamour.) Mont. Further investigation of the minor lipids of this species has now led to the isolation of the biogenetically related chromones 3 and 4.

Chromatography on a silica gel column (increasing concentrations of ether in hexane as the eluent) of the alkali-soluble fraction from the chloroform exctract of the alga afforded a mixture of 3 and 4 which was further submitted to rechromatography on Lichroprep Si 60 (eluent acetone-hexane 1:9).

Compound 3 (0.03% dry weight alga), m. p. 53-54° C , had molecular formula $C_{28}H_{34}O_4$ (high resolution mass spectrometry M^+ m/z obs. 434.2449; calc. 434.2457). Upon mild catalytic hydrogenation it gave the decahydro-derivative 5, $C_{28}H_{44}O_4$, m/z 444, 429, 415, 401, 387, 373, 359, 345, 331, 317, 303, 289, 275 , 261, 247, 233, 219, 205 (base), 192, 179, 163, 153, which indicated the presence of five olefinic groups. The spectral properties of 3 $\left[\nu_{max}^{CHCl_3}\right.$ 1659, 1625, 1586 cm^{-1} (γ-pyrone);[3] λ_{max}^{EtOH} (log ε) 228 (4.35), 250 (4.41), 258 (4.40), 292 (4.11) and 325 nm (sh, 3.95); 268 and 335 in base $\left.\right]$ were strongly indicative of a 5,7 - dihydroxychromone chromophore.[4] Indeed, the cmr spectrum (Table 1) contained all the appropriate resonances for this ring system[5,6] , and in addition displayed signals for ten olefinic carbons, eight methylenes and a methyl group. Formulation of structure 3 could be made by analysis of its 270 MHz pmr features, including the results of extensive double resonance experiments (Table 1). In the aromatic region of the spectrum two meta-coupled (J = 2 Hz) protons appeared at δ 6.68 and 6.74, while the proton at C-3' was seen as a singlet at δ 6.21, thus fixing the side chain at C-2'. A ten-proton multiplet at δ 5.45 and an eight-proton multiplet at δ 2.94 indicated the presence of five non-conjugated double bonds and four doubly allylic methylenes, respectively. Double resonance experiments evidenced the spin systems C-17 through C-19 and C-1 through C-4, thus establishing the structure of the side chain. The Z nature of the olefinic double bonds was indicated by the chemical shifts observed in the cmr spectrum for the signals of the allylic methylenes.[7] The mass spectrum of **3** (*m/z* 434, 419, 405, 379, 365, 339, 325, 299, 285, 271, 257, 245, 231, 218, 205 (base), 192, 179, 175, 163, 153



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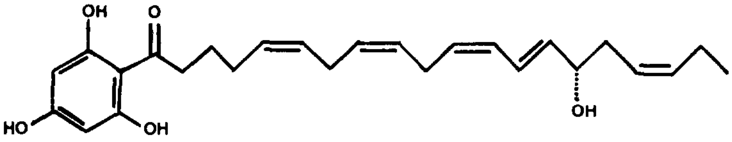

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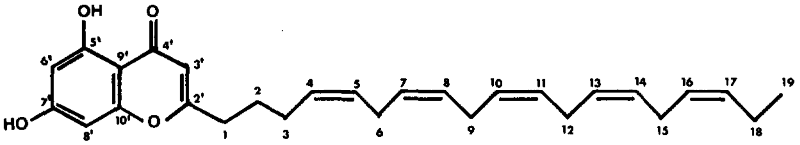

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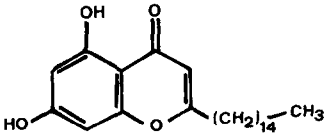

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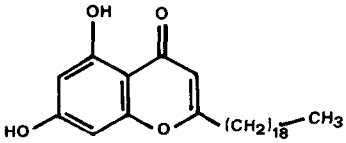

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Table 1. ^{13}C and ^{1}H chemical shifts and multiplicities for compounds 3, 4 and 5[a]

Position	^{13}C		^{1}H			
	3	4	3	DR[f]	4	5
2'	171.4 s	176.8 s				
3'	107.7 d	108.1 d	6.21 s		5.94 s	5.92 s
4'	183.2 s	181.6 s				
5'	158.9 s	157.6 s				
6'	100.0 d[b]	99.4 d[b]	6.68 d(2)[b]		6.27 bs	6.25 bs
7'	163.9 s	169.8 s				
8'	94.7 d[b]	94.2 d[b]	6.74 d(2)[b]		6.27 bs	6.25 bs
9'	105.1 s	96.4 s				
10'	162.5 s	161.8 s				
1	33.8 t	33.7 t	2.51 t(7)	s{1.73}	2.10 t(7)	2.08 t(7)
2	26.8 t[c]	26.8 t	1.73 p(7)	t{2.51}, t{2.17}	1.98 p(7)	1.98 p(7)
3	26.5 t[c]	24.8 t	2.17 q(7)	d{1.73}	1.32	1.31
4	129.7 d	29.8 t[c]	5.45		1.32	1.31
5	128.9 d	29.8 t[c]	5.45		1.32	1.31
6	25.6 t[d]	29.8 t[c]	2.94		1.32	1.31
7	128.7 d[e]	29.8 t[c]	5.45		1.32	1.31
8	128.3 d[e]	29.5 t[c]	5.45		1.32	1.31
9	25.7 t[d]	29.5 t[c]	2.94		1.32	1.31
10	128.6 d[e]	29.5 t[c]	5.45		1.32	1.31
11	128.3 d[e]	29.2 t[c]	5.45		1.32	1.31
12	25.7 t[d]	29.2 t[c]	2.94		1.32	1.31
13	128.6 d[e]	32.0 t	5.45		1.32	1.31
14	128.3 d[e]	22.8 t	5.45		1.32	1.31
15	25.7 d[d]	14.2 q	2.94		0.92 b	1.31
16	127.3 d		5.45			1.31
17	132.3 d		5.45			1.31
18	20.6 t		2.06 p(7)	d{0.94}		1.31
19	14.3 q		0.94 t(7)	s{2.06}		0.90 b
OH			6.00 b		5.50 b	5.50 b

a: ^{13}C NMR spectra were run at 20.1 MHz, $CDCl_3$, ppm from TMS: multiplicities were obtained by off-resonance decoupling; ^{1}H NMR spectra were run at 270 MHz in C_5D_5N (3) or C_6D_6 (4 and 5) with TMS as internal standard: chemical shifts are δ values, coupling constants (J in parentheses) are given in Hz. Signal multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet. Assignments are based on decoupling experiments and extrapolation from literature data.[5-8]

b – e: Assignments may be intermixed.

f: Signal multiplicities after irradiation at {δ}

g: Affected.

(the last two peaks arise from 192 fragment by loss of CO followed by a hydrogen atom and from the parent ion by a retro-Diels-Alder reaction involving the heterocyclic ring, respectively, according to the known fragmentation pattern of chromone derivatives[9]) agree with the assigned structure.

Compound 4 (0.01% dry weight alga), m.p. 79-80° C, according to high resolution mass spectrometry had the elemental composition $C_{24}H_{36}O_4$. Ultraviolet and infrared spectra contained absorptions [$\nu_{max}^{CHCl_3}$ 1660, 1625, 1590 cm^{-1} ; λ_{max}^{EtOH} (log ε) 228 (4.36), 250 (4.40), 258 (4.39), 295 (4.12) and 325 (sh, 4.01) nm] attributable to a 5,7-dihydroxychromone derivative. The cmr and pmr spectra (Table 1) led unambiguously to the conclusion that 4 was 5',7'-dihydroxy-2'-pentadecylchromone. This was confirmed by the mass spectrum which showed peaks at m/z 388, 373, 359, 345, 331, 317, 303, 289, 275, 261, 247, 233, 219, 205 (base), 192, 163 and 153.

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