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CARBON-13 NMR APPLICATION TO LAURENCIA POLYHALOGENATED SESQUITERPENES [1]

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SUMMARY By examining the chemical shifts of the carbons involved in vicinal *trans*-bromo-chloro systems, which are frequently isolated from Laurencia sesquiterpenes, it is possible to establish the position of the Br and Cl atoms beyond a doubt. This method was used in the structure determination of the new terpenoids, obtusane (3) and *iso*furocaespitane (17).

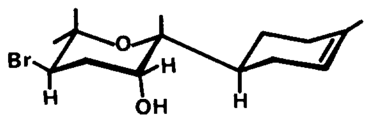
C-13 NMR has been applied to compounds of marine origin both to clear up stereochemical questions [2] and to pinpoint the whereabouts of the Br and Cl atoms in polyhalogenated molecules [3]. This paper deals with the chemical shifts in some terpenoid substances from the algae *L obtusa* [1] and *L caespitosa* [4] and the C-13 NMR data of the new polyhalogenated compounds, obtusane (3) and *iso*furocaespitane (17).

The spectra were taken in a $CDCl_3$ soln. using a pulsed Fourier transform system with proton noise-decoupling. The chemical shifts assigned to the various carbons were based on off-resonance-decoupled spectra, direct analysis of non-protonated carbon centres, comparison of pairs of compounds and consideration of the β, γ and δ substituents effects, the acetylation of OH functions and the general chemical shift arguments from literature on related structures [5].

Table 1 shows the chemical shifts seen in metabolites, their derivatives and exocyclic double bond isomerization products from the alga *L obtusa*. Ketones 7 (and 11) were obtained by oxidizing obtusol (1) {and *iso*-obtusol (5)} and treating it with HCl in C_6H_6. A mixture of the alcohols 8 and 9, formed when 7 was reduced with $NaBH_4$, was separated by chromatography on silica gel. Obtusol (1) {and *iso*-obtusol (5)} were stirred with neutral aluminium in an ether soln. at r.t. giving a copious yield of ketones 10 (and 12).

Repeated silica gel chromatography of the ether extracts of the alga *L obtusa* led to the isolation of the new hydrocarbon, obtusane (3) [6]: mp 174-175°, $\{\alpha\}_D$+38°, $C_{15}H_{23}Br_2Cl$, m/e M^+ 402, 400, 398; IR (KBr) cm^{-1} 3080, 1640, 1220, 1080, 910, 870 and 770; PMR δ 0·95, 1·13, 1·85 (s, 3H each), 4·45 (dd, 1H, J=12 and 5Hz), 4·70 (dd, 1H, J=13 and 7Hz), 4·87 and 5·22 (s, 1H each). The Br and Cl atoms in 3 were placed in accordance with similar chemical shifts observed for the Ring B carbons in obtusol and derivatives (Table 1). Zn/AcOH reduction of 3 gave 10-bromo-α-chamigrene [7].

Caespitol (14) [4a], *iso*caespitol (16) [4b] and furocaespitane (18) [4c] were isolated from the alga *L caespitosa*. Table 2 lists the chemical shifts seen in these compounds and derivatives. A recent chromatography of the ether extracts of the alga revealed a new furanic compound, *iso*furocaespitane (17) as an oil: $\{\alpha\}_D$-39°, $C_{12}H_{16}OBrCl$, m/e M^+ 292, 290; IR (film) cm^{-1} 1510, 1370, 950, 880 and 720; PMR δ 1·98, 2·24 (s, 3H each), 4·43 (t, 1H, J=3Hz), 6·26 and 7·23 (d, 1H each, J=2·5Hz). The relationship between the carbon chemical shifts of this compound and those of Ring A of furocaespitane (18), Ring B of *iso*caespitol (16) (Table 2) and *iso*-obtusol (5) and its derivatives (6, 11 and 12) {Table 1} definitely settled the position of the Br and Cl atoms in the cyclohexane ring and confirmed the provisionally-assigned structure 17.



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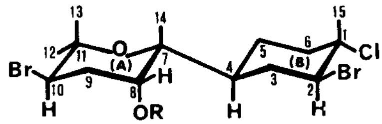
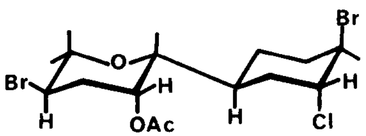


14, R=H
15, R=Ac



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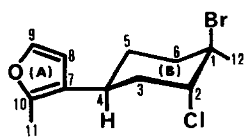

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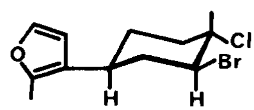

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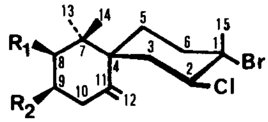
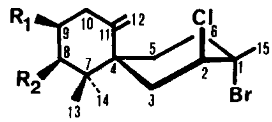
TABLE 2 *L caespitosa* Terpenoids Carbon-13 Chemical Shift Assignments

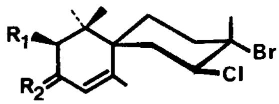
Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15
13	140·1	120·0	26·1	41·5	22·6	31·0	78·0	71·4	36·0	54·0	75·4	31·1	24·0	19·9	33·4
14	71·8	63·6	36·3	46·0	22·8	43·0	77·2	71·0	36·4	53·0	75·5	31·1	24·2	20·0	24·1
15	71·5	62·8	36·3	46·2	22·9	43·0	76·1	73·0	32·9	52·5	75·6	31·0	24·0	20·1	24·1
16	70·6	66·6	36·3	31·3	22·0	37·5	77·0	72·6	33·1	53·1	75·4	31·1	24·0	19·9	33·4
17	69·5	66·5	37·7	26·9	29·6	36·1	121·0	108·8	140·1	146·6	11·6	33·5			
18	71·2	62·3	42·3	35·4	30·3	43·0	121·0	108·8	140·1	147·2	11·6	24·0			



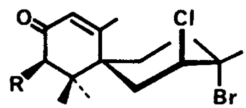
1 R1,-Br, R2,-OH
2 R1,-Br, R2,-OAc
3 R1,-Br, R2,-H
4 R1,-H, R2,-OAc



5 R1,-Br; R2,-OH
6 R1,-Br, R2,-OAc



7 R1,-Br, R2=O
8 R1,-Br, R2 OH, H
9 R1,-Br, R2 OH, H
10 R1,-H, R2=O



11 R,-Br
12 R,-H

TABLE 1 L obtusa Sesquiterpenes Carbon-13 Chemical Shift Assignments[1]

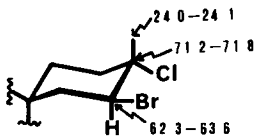
COMPOUND	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	other
A RING EXOCYCLIC CHAMIGRENES																
1	68·0	67·6	40·6	50·3	25·6	37·2	44·3	70·4	71·8	38·6	141·4	117·7	24·2	20·8	23·9	
2	67·9	67·5	40·6	50·2	25·7	37·2	44·5	62·5	73·3	37·2	141·3	117·8	24·2	20·2	23·9	20·9
3	68·2	67·9	40·5	50·4	25·5	37·2	53·9	63·4	35·9	33·5	145·8	114·7	23·6	17·5	23·9	
4	68·7	67·9	40·7	48·3	25·8	37·9	38·3	41·4	70·6	36·0	144·5	116·3	24·5	23·7	23·9	21·2
5	71·0	65·2	34·0[2]	44·0[3]	33·1[2]	33·4[2]	43·7[3]	76·2	69·7	39·2	147·5	113·8	25·3[4]	24·3[4]	25·7[4]	
6	71·0	65·2	34·0[2]	44·3[3]	33·1[2]	33·4[2]	43·8[3]	66·4	71·6	35·3	146·9	114·6	25·1[4]	24·6[4]	25·6[4]	21·1
A RING ENDOCYCLIC CHAMIGRENES																
7	66·0	68·4	41·5	49·2	30·9	37·5	42·3	65·7	199·3	126·5	166·5	26·5	24·6	19·0	23·7	
8	67·2	69·2	42·0	47·9	31·0	38·3	42·8	66·2	68·4	124·0	143·2	26·2	24·8	19·5	23·9	
9	67·1	69·2	42·1	47·6	31·7	37·8	45·8	71·0	73·2	127·6	143·1	25·8	25·2	17·9	24·0	
10	66·8	68·6	41·9	42·0[2]	n/o	36·1	42·2[2]	48·8	n/o	128·2	166·2	26·5	n/o	n/o	23·7	
11	68·0	65·7	40·1	49·6	25·5	35·4	44·8	64·2	n/o	126·8	156·1	24·8	32·3	19·1	24·2	
12	68·3	65·4	39·6	43·1[2]	29·7	36·3	42·4[2]	49·1	n/o	127·4	167·0	25·7	31·5	24·1	24·3	

1 Chemical shifts in ppm downfield from TMS. The solvent is $CDCl_3$.

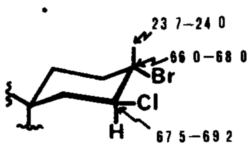
2, 3, 4 Any assignment is interchangeable with any other identified with the same number in the same line.

n/o Not observed.

The three vicinal *trans*-bromo-chloro systems found to date in Laurencia sesquiterpenes (I, II and III) are set out below with the chemical shifts of the carbons involved.



I



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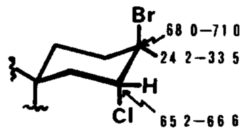

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R E F E R E N C E S

1 Part 22 in the series 'Marine Natural Products from the Atlantic Zone'. For Part 21 see: A G González J D Martín V S Martín M Martínez-Ripoll and J Fayos *Tetrahedron Letters* (submitted for publication)

2 P Crews and E Kho-Wiseman *Tetrahedron Letters* 2483 (1978)

3 R S Norton R G Warren and R J Wells *Tetrahedron Letters* 3905 (1977)

4 a) A G González J Darias J D Martín and C Pérez *Tetrahedron Letters* 1249 (1974); b) A G González J Darias J D Martín C Pérez J J Sims G H Y Lin and R M Wing *Tetrahedron* 31 2449 (1975); c) A G González J Darias and J D Martín *Tetrahedron Letters* 3625 (1973)

5 A F Rose R P Izac and J J Sims "Marine Natural Products: Chemical and Biological Perspectives" Vol 2 ed P J Scheuer Academic Press Inc (in press)

6 A product with identical structure according to x ray analysis has been isolated from a green variety of *L obtusa* by J J Sims (private communication)

7 Identical with an authentic sample isolated as a minor constituent of *L obtusa* in this laboratory

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