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Carexanes: prenyl stilbenoid derivatives from *Carex distachya*

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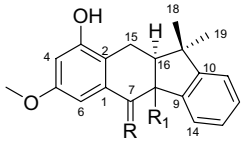
Abstract—Metabolites with a new molecular skeleton, named carexane, have been isolated from the leaves of *Carex distachya*. The structures have been determined on the basis of the spectroscopic characteristics of the compounds. Bidimensional NMR has furnished important data useful for the characterization and the stereochemistry of the molecules. The compounds have a tetracyclic skeleton derived from the coupling of the prenyl moiety on a stilbenoid structure.

Carex species produce oligostilbenes,[1,2] constituted by two to four monomers of resveratrol (3,5,4′-trihydroxystilbene), most of them showing antimicrobial activity.

In studying the allelopathic effects of natural products, isolated from Mediterranean plants, on aquatic[3] and agronomic[4] ecosystems, we investigated *Carex distachya*,[5] a herbaceous plant, growing in the Mediterranean bush.

The hexane extract of the plant was chromatographed successively on silica gel, Sephadex LH-20 and RP-8 HPLC to give three new compounds (**1**–**3**, 0.03% w/w) originating from 2-prenylstilbene precursors and named carexanes A–C, respectively (Fig. 1).



1 R = βOH,αH R_1 = βH
2 R = O R_1 = αOH
3 R = O R_1 = βOH

Figure 1. Structures of carexanes A–C.

The elemental analysis of carexane A[6] and the presence of 20 carbon signals in the ^{13}C NMR spectrum (Table 1) justified the molecular formula $C_{20}H_{22}O_3$. The EIMS spectrum showed the molecular peak at *m/z* 310 (42) confirming the presence of 10 unsaturations in the molecule. In the aromatic region, the ^1H NMR spectrum showed two meta coupled doublets at δ 6.28 and 6.69, a proton at δ 7.61 and a signal, integrated for three protons, centred at δ 7.18. In the aliphatic region of the spectrum were evident a doublet at δ 4.49, a methine proton as a double doublet at δ 3.35, a diastereotopic methylene as two double doublets at δ 3.09 and 1.86, a methine double double doublet at δ 2.16 and two methyl singlets at δ 1.34 and 1.21. The ^{13}C NMR spectrum and the DEPT experiment indicated the presence of a carbinol carbon, seven quaternary carbons, eight methines, a methylene and three methyls.

The value and the multiplicity of the protons at δ 6.28 and 6.69 suggested the presence of two *meta* orientated oxygenated functional groups on an aromatic ring. This hypothesis was supported by an HMBC experiment (Table 1) showing correlations between both the protons and the mutual methine carbon. The upfield resonating proton showed heterocorrelations with the carbon at δ 117.6 and with two tetrasubstituted oxygenated carbons at δ 155.1 and 160.0. This latter signal was also correlated with the proton at δ 6.69 and with the methoxyl at δ 3.75.

The DQ-COSY experiment showed cross peaks between the proton at δ 4.49, bonded to the carbon at δ 74.6 and the proton at δ 3.35 and between this latter and

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Table 1. NMR data of carexanes A (**1**)

Position	δ ^{1}H	DQ-COSY	δ ^{13}C	DEPT	HMBC	NOESY
1	—	—	144.9	C	—	—
2	—	—	117.6	C	—	—
3	—	—	155.1	C	—	—
4	6.28 d (2.9)	H-6	100.5	CH	C-2, C-3, C-5, C-6	OMe
5	—	—	160.0	C	—	—
6	6.69 d (2.9)	H-4	101.7	CH	C-2, C-4, C-5, C-7	OMe
7	4.49 d (8.1)	H-8	74.6	CH	C-1, C-2, C-5, C-6, C-8, C-16	
8	3.35 dd (8.1, 7.8)	H-7, H-16	51.8	CH	C-7, C-9, C-10, C-14, C-15, C-16, C-17	
9	—	—	145.0	C	—	—
10	—	—	153.3	C	—	—
11	7.18 m	H-12	123.0	CH	C-9, C-10, C-13, C-17	
12	7.20 m	H-11	128.2	CH	C-11, C-14	
13	7.20 m	H-14	127.9	CH	C-11, C-14	
14	7.61 m	H-13	125.8	CH	C-10, C-12	
15α	3.09 dd (14.4, 5.4)	H-15β, H-16	21.7	CH_2	C-1, C-2, C-3, C-8, C-16, C-17	H-18
15β	1.86 dd (14.4, 11.4)	H-15α, H-16			C-1, C-2, C-3, C-8, C-16, C-17	H-18
16	2.16 ddd (11.4, 7.8, 5.4)	H-8, H-15α, H-15β	51.3	CH	C-2, C-8, C-9, C-10, C-15, C-17, C-18, C-19	H-19
17	—	—	46.4	C	—	—
18	1.34 s	—	24.5	CH_3	C-10, C-16, C-17, C-19	15α, 15β
19	1.21 s	—	32.7	CH_3	C-10, C-16, C-17, C-18	15α, H-16
OMe	3.75	—	55.6	CH_3	C-5	H-4, H-6

s = singlet, d = doublet, dd = double doublet, ddd = double double doublet, m = multiplet; the couplings (Hz) are reported in brackets.

the proton at δ 2.16 which was correlated with the methylene protons at δ 1.86 and 3.09. Both protons were heterocorrelated with the carbons at δ 117.6, 144.9, 51.3, 51.8, 46.4. This last carbon showed interactions with the methyls at δ 1.21, 1.34 and with an aromatic proton at δ 7.18. The carbinolic carbon at δ 74.6 was also correlated with the methine at δ 3.35 which in turn was correlated with the carbons at δ 153.3, 145.0, 51.3, 21.7. These correlations were in accordance with a pentahydrobenzo[*b*]fluorene ring system with a methoxyl group at the carbon C-5 and two hydroxyl groups at the carbons C-3 and C-7. The complete interpretation of the NMR data was based on the results of DQ-COSY, HSQC and HMBC experiments (Table 1). The coupling constants of the H-7 (d, 8.1 Hz), H-8 (dd, 8.1 and 7.8 Hz) and H-16 (ddd, 11.4, 7.8 and 5.4 Hz), suggested a trans orientation between the H-7/H-8 and H-8/H-16 protons. Furthermore the coupling constants of the diastereotopic protons H-15α (dd, 14.4 and 5.4 Hz) and 15β (dd, 14.4 and 11.4 Hz) indicated

Table 2. NMR data of carexanes B (**2**) and C (**3**)

Position	Carexane B				Carexane C			
	δ ^{1}H	δ ^{13}C	DEPT	HMBC	δ ^{1}H	δ ^{13}C	DEPT	HMBC
1	—	134.2	C	—	—	135.5	C	—
2	—	125.8	C	—	—	125.8	C	—
3	—	157.1	C	—	—	157.4	C	—
4	6.63 d (2.4)	108.7	C	C-2, C-3, C-5	6.62 d (2.4)	107.3	C	C-2, C-3, C-5, C-6
5	—	160.3	C	—	—	160.3	C	—
6	6.93 d (2.4)	102.0	CH	C-2, C-4, C-7	7.11 d (2.4)	103.6	CH	C-2, C-4
7	—	198.6	C	—	—	196.7	C	—
8	—	82.2	C	—	—	80.3	C	—
9	—	143.1	C	—	—	141.7	C	—
10	—	153.2	C	—	—	155.5	C	—
11	7.18 m	123.1	CH	C-9, C-13	7.31 m	123.6	CH	C-9, C-13
12	7.28 m	129.9	CH	C-14	7.35 m	130.1	CH	C-14
13	7.23 m	127.9	CH	C-9, C-11, C-14	7.26 m	127.5	CH	C-9, C-11
14	7.65 m	127.0	CH	C-8, C-10, C-12	7.90 m	127.4	CH	C-10, C-12
15	3.04 d (4.8)	18.9	CH_2	C-1, C-2, C-3, C-4, C-6, C-8, C-16, C-17	3.09 dd (16.5, 10.8)	20.7	CH_2	C-1, C-2, C-3, C-8, C-16
					2.94 dd (16.5, 5.4)			C-1, C-2, C-3, C-8, C-16
16	2.72 t (4.8)	57.1	CH	C-2, C-7, C-8, C-15, C-17, C-18, C-19	2.22 dd (10.8, 5.4)	58.6	CH	C-7, C-17, C-18, C-19
17	—	46.1	C	—	—	44.9	C	—
18	0.75 s	26.5	CH_3	C-10, C-16, C-17, C-19	1.39 s	27.7	CH_3	C-10, C-16, C-17, C-19
19	1.43 s	29.4	CH_3	C-10, C-16, C-17, C-18	1.42 s	27.0	CH_3	C-10, C-16, C-17, C-18
OMe	3.74	55.7	CH_3	C-5	3.74	58.6	CH_3	C-5

s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet; the couplings (Hz) are reported in brackets.