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β-AGAROFURANS FROM SEEDS OF *MAYTENUS BOARIA*

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Key Word Index—*Maytenus boaria*, Celastraceae, sesquiterpenes, β-agarofurans.

Abstract—An extract of the seeds of *Maytenus boaria* contained four β-agarofuran polyesters. The full assignment of all ^{1}H and ^{13}C NMR signals for two of them was achieved using two-dimensional NMR techniques.

INTRODUCTION

Highly oxygenated sesquiterpenes with a dihydro-β-agarofuran skeleton are widespread within the family Celastraceae [1]. The genus *Maytenus*, characterized by the occurrence of different bioactive compounds like maytenosides (antitumour activity) or alkaloidal sesquiterpenes (insect antifeedant activity), is especially rich in these metabolites [2]. Continuing our study of Chilean *Maytenus* [3–5], we have now investigated the seeds of *Maytenus boaria*.

RESULTS AND DISCUSSION

The ^{1}H and ^{13}C NMR data for compound **1** (Tables 1 and 2) indicated the presence of an agarofuran with two acetates, a furanote and a hydroxyl group. All signals in the ^{1}H NMR spectrum were assigned by spin decoupling. The protonated sites in the ^{13}C NMR spectrum were assigned with the aid of an HMQC experiment, while quartenary carbons and the relative position of the ester groups followed from the results of an HMBC experiment. Selected results are summarized in Table 3 along with the results of the NOE experiments, which were helpful for the assignment of stereochemistry.

The structure of compound **2** followed immediately from comparison of the spectral data (Table 1) with those of compound **1**. Accordingly, an acetate signal was missing and H-6 was shifted upfield.

Table 1. ^{1}H NMR data for compounds **1** and **2** (CDCl$_3$, 400 MHz, int. standard solvent peak = 7.26 ppm)

Proton	**1**	**2**
1	5.35 *dd* (4, 12)	5.35 *dd* (4, 11)
2α	1.60 *dddd* (3.5, 11, 12, 13)	1.60 *m*
2β	1.83 *dddd* (4, 4, 4, 13)	1.83 *m*
3α	1.43 *m*	1.43 *m*
3β	2.14 *m*	2.15 *m*
4	2.25 *m*	2.25*m*
6	5.87 *br s*	4.90 *br s*
7	2.40 *br s* (3.5)	2.45 (*br d* (3)
8	4.27 *br d* (3.5)	4.25 *br d* (3)
9	4.77 *br s*	4.75 *br s*
12	1.34 *s*	1.35 *s*
13	1.41 *s*	1.40 *s*
14	1.45 *s*	1.55 *s*
15	1.01 *d* (7)	1.15 *d* (7)
6-OH	—	3.05 *br s*
8-OH	2.74 *br s*	4.05 *br s*
1-OAc	1.71 *s*	1.70 *s*
6-OAc	2.11 *s*	—
OFur	8.03 *dd* (1.5, 1) 6.74 (*dd* (1, 2) 7.41 (*dd*, 1.5, 2)	8.10 *dd* (1.5, 1) 6.75 *dd* (1, 2) 7.45 *dd* (1.5, 2)

The ^{13}C NMR spectrum of compound **3** (Table 2) displayed, in addition to 15 signals for the sesquiterpene part (including a keto group), those for five acetates and a benzoate. In the ^{1}H NMR spectrum (Table 4) all signals for the A-ring were assigned by spin decoupling. Thus, the keto group had to be placed in the B ring. The placement at C-8, already indicated by the downfield shift of H-7 (if compared with the spectral data for **1** and **2**), was confirmed by the results of an HMBC experiment. The signal at $\delta 5.68$ must be assigned to H-9 as it shows three bonds correlation with C-1, C-14 and the acetate carbonyl at C-9 and two bonds correlations with C-8 and C-10. Coming from the other side, H-7 correlates with C-5 and C-9 (^3J) and C-6 and C-8 (^2J). All long range correlations are listed in Table 5. From these results the relative position of the ester groups was deduced as well as the assignment of all quartenary carbons. In particular, the correlation between H-1 and H-2/H-6 of the

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Table 2. ^{13}C NMR data for compounds **1**–**3** ($CDCl_3$, 100 MHz, int. standard $CDCl_3$ = 77.0 ppm)

Carbon	**1**	**2**	**3**
1	73.5 *d*	73.2 *d*	72.4 *d*
2	21.3 *t*	21.5 *t*	80.2 *d*
3	26.7 *t*	26.8 *t*	73.3 *d*
4	33.8 *d*	33.5 *d*	37.2 *d*
5	90.6 *s*	91.8 *s*	90.7 *s*
6	75.4 *d*	73.2 *d*	75.4 *d*
7	55.4 *d*	57.1 *d*	64.0 *d*
8	74.5 *d*	74.7 *d*	197.7 *s*
9	80.0 *d*	81.1 *d*	79.2 *d*
10	49.3 *s*	48.9 *s*	51.6 *s*
11	81.5 *s*	81.6 *s*	83.6 *s*
12	25.5 *q*	25.7 *q*	25.0 *q*
13	31.0 *q*	31.6 *q*	30.5 *q*
14	19.0 *q*	19.3 *q*	59.8 *t*
15	17.3 *q*	17.8 *q*	15.3 *q*
1-OR	170.3 *s*	170.3 *s*	129.0 *s*
	20.9 *q*	20.9 *q*	129.7 *d*
			128.7 *d*
			133.7 *d*
			164.7 *s*
2-OR			168.7 *s*
			21.2 *q*
3-OR			170.0 *s*
			20.9 *q*
6-OR	170.0 *s*		169.0 *s*
	21.4 *q*		21.1 *q*
9-OR	148.8 *d*	149.1 *d*	169.1 *s*
	118.4 *s*	118.4 *s*	19.6 *q*
	109.7 *d*	109.7 *d*	
	143.8 *d*	143.9 *d*	
	162.3 *s*	163.9 *s*	
14-OR			169.9 *s*
			20.5 *q*

benzoate, both with the benzoate carbonyl, placed the only differing ester group at the correct position. The NOE results, which require the stereochemistry as depicted in the formulae, are also summarized in Table 5. The 'W' long range coupling between H-2 and H-4 due to their zig-zag orientation in worthy of note and confirmed the axial orientation of substituents at these centres.

The structure of compound **4** was deduced from the ^{1}H NMR data (Table 4), which were similar to those of **3**, but showing signals for a furanoate instead of a benzoate.

Table 4. ^{1}H NMR data for compounds **3** and **4** ($CDCl_3$, 400 MHz, int. standard solvent peak = 7.26 ppm)

Proton	**3**	**4**
1	6.23 *d* (3.5)	6.13 *d* (3.5)
2	5.46 *ddd* (3.5, 3, 1.5)	5.41 *ddd* (3.5, 3, 1.5)
3	4.90 *dd* (3, 1.5)	4.87 *dd* (3, 1.5)
4	2.72 *ddq* (1.5, 1.5, 8)	2.71 *ddq* (1.5, 1.5, 8)
6	6.33 *d* (1)	6.30 *d* (1)
7	3.03 *d* (1)	3.03 *d* (1)
9	5.68 *s*	5.66 *s*
12	1.46 *s*	1.44 *s*
13	1.46 *s*	1.45 *s*
14	5.11 *d* (13)	5.04 *d* (13)
14'	4.53 *d* (13)	4.44 *d* (13)
15	1.30 *d* (8)	1.28 *d* (8)
2-OAc	2.15 *s*	2.13 *s*
3-OAc	2.15 *s*	2.14 *s*
6-OAc	2.15 *s*	2.15 *s*
9-OAc	1.54 *s*	1.74 *s*
14-OAc	2.01 *s*	2.00 *s*
OBz(OFur)	7.96 *AA'*	8.00 *dd* (1.5, 1)
	7.46 *BB'*	6.69 *dd* (2, 1)
	7.59 *C*	7.43 *dd* (2, 1.5)

Table 3. Selected NOE's and hetero long range correlations for compound **1**

NOEs		Long range correlations	
Saturated H*	Observed NOEs†	Proton	Carbon
1	2_{Fur}(4); 4_{Fur}(2); 3(3)	1	C=O 170.3
6	7(5); 14(5); 15(3); 9(1)	6	C=O 170.0
7	6(5); 8(7); 12(1); 13(3)	9	C=O 162.3
8	9(4); 7(7); 12(5)	OAc(1.71)	C=O 170.3
9	6(1); 8(5); 1-OAc(1); 14(5)	OAc(2.11)	C=O 170.0
12	2_{Fur}(5); 4_{Fur}(3); 8(10); 7(3)		
13(3α)	7(3)		
14(3α)	6(12); 9(10); 15(10)		
15	6(4); 14(10)		
1-OAc(2)	9(3)		
6-OAc(3β)	14		
OH	8(5); 9(4)		
2_{Fur}	1(2); 12(2)		
4_{Fur}	1(1); 12(1)		

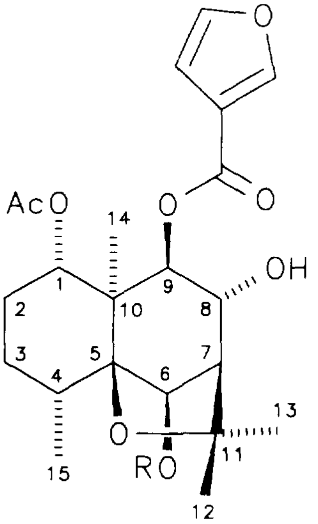
*Signals overlapping with saturated one in parentheses.

†Percentage intensity increase in parentheses.

Table 5. Hetero long range correlations and NOE effects with compound **3**

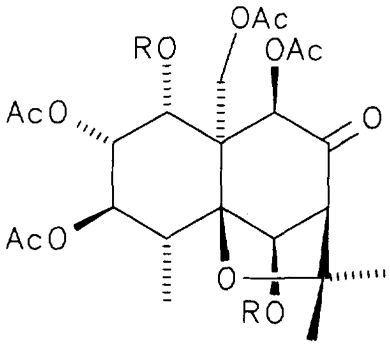
Long range correlations		NOE effects	
Proton	Carbon	Saturated H	Observed NOEs*
1	10; C=O (164.7)	1	9(12); 2(6)
2	1, 3, 10	2	1(6); 3(5)
3	1, 2, 5, 15, C=O (170.0)	3	2(7); 4(6); 15(5)
4	2, 3, 5, 10, 14	4	3(4); OAc 2.15
6	11, C=O (169.0)	6	14′(3); 7(7); 15(3); OAc 2.01
7	5, 6, 8, 9	7	6(6); 12/13
9	1, 8, 10, 14, C=O (169.1)	9	1(15); 12/13; OAc 1.54
12	7, 11	12\13	9(15); 7(12); 4(4); OAc 2.15
13	7, 11	14	$2/6_{Bz}$(1)
14	5, 10, C=O (169.9)	14′	15(2)
14′	5, 9	15	6(3); 3(3); 14′(4); OAc 2.15
15	3, 4, 5	$2/6_{Bz}$	14(2); OAc 1.54
$2/6_{Bz}$	4_{Bz}, C=O (164.7)	OAc 1.54	$2/6_{Bz}$(3); 9(1); OAc 2..01
OAc 1.54	C=O (169.1)	OAc 2.01	6(3); OAc 1.54
OAc 2.01	C=O (169.9)	OAc 2.15 (9H)	$2/6_{Bz}$; 6(1); 1(1); 2(1); 4(2); 12/13; 15
OAc 2.15 (9H)	C=O (168.7, 169.0, 170.0)		

*Percentage intensity increase in paraentheses.



1 2

R Ac H



3 4

R Bz Fur

The relative positions of the ester groups were deduced by analogy to **3**.

EXPERIMENTAL

Seeds (5 kg) were collected in Paredonas, VI Region of Chile, and extracted with MeOH. The extract was solvent partitioned using $CHCl_3$, EtOAc and H_2O. The $CHCl_3$ extract was chromatographed on a silica gel column using petrol–EtOAc mixts. Polar frs were combined and sepd by TLC (petrol–EtOAc, 1:1) to give three bands, which were further sepd by HPLC (RP 18, 250 × 8 mm, MeOH–H_2O, 7:3). Band 1 gave 36 mg **3** (R_t 12.4 min) and 3 mg **4** (R_t 11.6 min), band 2 20 mg **1** (R_t 8.9 min) and band 3 16 mg **2** (R_t 7.7 min).

1α,6β-Diacetoxy-8α-hydroxy-9β-furoyloxy-β-agarofuran (**1**). Amorphous solid; MS m/z (rel. int.): 464.205$[M]^+$ (16) (calc. for $C_{24}H_{32}O_9$ 464.205), 449 $[M - Me]^+$ (32), 422 $[M - \text{ketene}]^+$ (64), 352 $[M - \text{FurCOOH}]^+$ (100), 95 $[\text{FurCO}]^+$ (98).

1α-Acetoxy-6β,8α-dihydroxy-9β-furoyloxy-β-agarofuran (**2**) Amorphous solid; MS m/z (rel. int.): 422 $[M]^+$

(28), 407 $[M - Me]^+$ (45), 404 $[M - H_2O]^+$ (25), 362 $[M - AcOH]^+$ (18), 310 $[M - FurCOOH]^+$ (86), 95 $[FurCO]^+$ (100).

1α-*Benzoyloxy*-2α,3β,6β,9β,14-*pentaacetoxy*-8-*oxo*-β-*agarofuran* (**3**). Oil; MS *m/z* (rel. int.): 631.203 $[M - Me]^+$ (4) (calc for $C_{31}H_{35}O_{14}$ 631.203) 618 $[M - CO]^+$ (8), 604 $[M - ketene]^+$ (40), 558 $[618 - AcOH]^+$ (8), 554 $[604 - AcOH]^+$ (4), 422 $[544 - PhCOOH]^+$ (32), 353 [57], 253 [100].

1α-*Furoyloxy*-2α,3β,6β,9β,14-*pentaacetoxy*-8-*oxo*-β-*agarofuran* (**4**). Oil MS *m/z* (rel. int.): 636 $[M]^+$ (0.5), 621 $[M - Me)^+$ (2) 594 $[M - ketene]^+$ (37), 534 $[594 - AcOH]^+$ (20), 524 $[M - FurCOOH]^+$ (44), 464 $[524 - AcOH]^+$ (32), 422 ($[464 - ketene]^+$ (67), 95 $FurCO]^+$ (100).

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