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SESQUITERPENES FROM SEEDS OF *MAYTENUS BOARIA*

JOSE BECERRA, LEONARDO GAETE, MARIO SILVA, FERDINAND BOHLMANN and JASMIN JAKUPOVIC

Departamento de Botanica, Facultad de Ciencias Biologicas y de Recursos Naturales, Universidad de Concepcion, Casilla 2407 Apartado 10 Concepcion, Chile; Institute of Organic Chemistry, Technical University of Berlin, Berlin, F.R.G.

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Key Word Index—*Maytenus boaria*; Celastraceae; sesquiterpenes; eudesmane esters.

Abstract—The examination of seeds of *Maytenus boaria* led to the isolation of three new sesquiterpenes of the eudesmane type. The structures of these compounds were elucidated by spectroscopic methods, especially high field NMR and mass spectra.

INTRODUCTION

Several species of the genus *Maytenus* have been studied in different parts of the world, due to the anticancer activity of the sesquiterpenes [1, 2] and ansamacrolides [3, 4] isolated from them. These types of compounds have also been found in seeds [5].

Triterpenes and hydrocarbons have been isolated previously from aerial parts of *M. boaria* [6]. Continuing with our study of biologically active compounds from seeds of *M. boaria*, we have isolated three new sesquiterpenes of the eudesmane type named eumaitenin (**1**), eumaitenol (**2**) and acetyleumaitenol (**3**).

RESULTS AND DISCUSSION

The sesquiterpene (**1**) was isolated by conventional chromatographic methods from the chloroform extract. Its molecular formula was determined to be $C_{26}H_{34}O_{10}$ ($[M]^+$ *m/z* 506.217) and the ^{13}C NMR spectra (Table 1) exhibited 26 carbon signals.

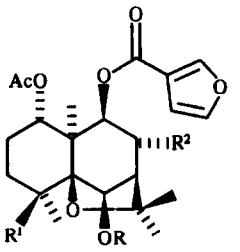
Its ^1H NMR spectrum (Table 2) showed the typical signals of a β-substituted furan ring (δ6.72, H-3′; 7.40 H-4′; 8.01 H-5′ [7]. Furthermore, typical signals were present for an eudesmane with an angular methyl group (H-14) at 1.43 (*s*), a secondary methyl group (H-15) at 1.00 (*d*) and singlets at 1.38 (H-12) and 1.45 (H-13). Three signals at 2.18 (*s*), 2.08 (*s*), and 1.71 (*s*) corresponded to the protons of acetate groups.

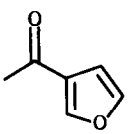
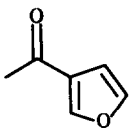
Spin decoupling allowed the assignment of all signals. Together with the ^{13}C NMR spectrum (Table 1) therefore, the presence of an eudesmane could be established with oxygen functions at C-1, C-5, C-6, C-9 and C-11. The stereochemistry and also the relative position of the ester groups were determined by NOE difference spectroscopy (Table 3). Furthermore inspection of a model indicated

Table 1. ^{13}C NMR spectrum of compound **1** (67.9 MHz, $CDCl_3$)

Carbon	S	Carbon	S
1	73.3 *d*	11	81.7 *s*
2	21.3 *t*	12	30.8 *q*
3	26.6 t	13	25.4 *q*
4	33.7 d	14	18.6 *q*
5	90.3 s	15	17.3 *q*
6	76.4 *d*	1′	161.3 *s*
7	52.9 d	2′	118.4
8	76.0 d	3′	109.7 *d*
9	75.7 d	4′	143.8 *d*
10	49.7 s	5′	148.7 *d*

Acetate (CO) 170.1; 169.9; 169.4 *s* and (Me) 20.9; 21.1; 21.0 *q*.



	1	2	3
R	Ac		
R¹	H	OH	OH
R²	OAc	H	OAc

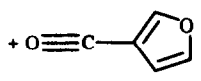


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Table 2. ^{1}H NMR data of compounds **1**, **2** and **3** ($CDCl_3$)

H	1	2	3
1	5.33 *dd*	5.27 *dd*	5.23 *dd*
2α	1.84 *dddd*	1.20 *m*	1.90 *m*
2β	1.58 *dddd*	1.50 *m*	1.50 *m*
3α	2.15 *m*	1.90 *m*	1.90 *m*
3β	1.44 *m*	1.70 *m*	1.75 *m*
4	2.24 *dq br*	—	—
6	5.68 *s*	5.53 *s*	5.92 *s*
7	2.46 *br*	2.32 *dd*	2.59 *d*
8	5.21 *d*	2.51 *ddd*	5.27 *d*
8	—	2.21 *dd*	—
9	4.91 *s*	4.98 *d*	4.99 *s*
12	1.38 *s*	1.51 *s*	1.57 *s*
13	1.45 *s*	1.53 *s*	1.54 *s*
14	1.48 *s*	1.40 *s*	1.53 *s*
15	1.00 *d*	1.34 *s*	1.37 *s*
OAc	2.18 *s*	—	2.25 *s*
OAc	2.08 *s*	—	—
OAc	1.71 *s*	1.76 *s*	1.74 *s*
3′	6.72 *d*	6.75 *d*	6.74 *d*
4′	7.40 *t*	7.43 *t*	7.43 *t*
5′	8.01 *d*	8.03 *d*	8.03 *d*
8′	—	6.83 *d*	6.81 *d*
9′	—	7.44 *t*	7.43 *t*
10′	—	8.18 *d*	8.15 *d*

J (Hz): Compound **1**: 3′,4′ = 4′,5′ = 1.5; 1,2α = 4; 1,2β = 11.5; 2α,3α = 2α,3β = 2β, 3β = 3; 2α,2β = 2β,3α = 3α,3β = 12; 3α,4α = 4α,15 = 7; 7,8 = 3; Compound **2**: 1,2α = 4, 1,2β = 12; 7,8α = 7,8β = 3; 8α,8β = 16; 8β,9β = 7; Compound **3**: 1,2α = 4; 1,2β = 12.

that the furane moiety was responsible for the observed shielding of the 1-acetoxy methyl.

The structures of **2** and **3** followed from the ^{1}H NMR spectra (Table 2) which were close to that of **1**. In the spectrum of **3** a second furane ester group was visible while the methyl doublet (H-15) was replaced by a down field shifted methyl singlet. Accordingly, in agreement with the mass spectrum an additional hydroxy group was at C-4. The down field shift of H-6 indicated the relative position of the furane ester group. Comparison of the spectrum of **2** with that of **3** clearly showed that the 8-acetoxy group was missing. The absolute configuration of **1**, **2** and **3** is most likely identical with that of similar compounds from this family [8].

EXPERIMENTAL

Seeds (5 kg) were collected in Paredones, VI region of Chile and extracted with MeOH. This extract was further fractionated with $CHCl_3$, EtOAc and H_2O. The compounds in the $CHCl_3$ extract were sepd by CC (silica gel) using increasing proportions of EtOAc in petrol as solvent. Eumaitenin was isolated (115 mg) by elution with 20% EtOAc and crystallized in this mixture.

The crystals have mp 183–185°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3140, 1505, 872 (furan ring) and 1735 (OAc) UV λ_{max}^{MeOH} nm: 210 and 237. MS *m/z* (rel. int.): 506.217 (7) (calculated for $C_{26}H_{34}O_{10}$ 506.215), 491 [M − Me]$^+$ (18), 464 [M − ketene]$^+$ (100), 446 [M − HOAc]$^+$ (3), 404 [M − RCOOH]$^+$ (4), 353 [464 − RCOO]$^+$ (3), 95 [A]$^+$ (100).

Eumaitenol was isolated (45 mg) by elution with petrol–EtOAc (80:20) and crystallized in this solvent. The crystals have mp 208–212°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3480 (OH), 3140, 1505, 872 (furan ring) and 1735 (OAc). MS *m/z* (rel. int.): 516.199 (calculated for $C_{27}H_{32}O_{10}$ 516, 199), 501 [M − Me]$^+$ (2), 404 [M − RCOOH]$^+$ (4), 95 [A]$^+$ (100). Acetyl eumaitenol was isolated (61 mg) by elution with a mixture of petrol–EtOAc (75:25) and crystallized in this solvent. The crystals have mp 95–97°; IR $\nu_{max}^{CCl_4}$ cm^{-1} 3140, 1505, 872 (furan ring) and 1735 (OAc). UV λ_{max}^{MeOH} nm: 210 and 237. MS *m/z* (rel. int.): 574.205 (calculated for $C_{29}H_{34}O_{12}$ 574.205), 509 [M − Me]$^+$ (2), 514 [M − HOAc]$^+$ (2), 462 [M − RCOOH]$^+$ (2), 95 [A]$^+$ (70).

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Table 3. NOE's of compound **1** (% in parenthesis)

irrad.	NOE	irrad.	NOE
H-15	14 (7), 2β (4), 6β (3)	1-OAc	14 (2), 3′ (2), 5′ (2)
H-14	15 (8), 2β (10), 6β (12), 9β (11)	H-7	8 (19), 6 (6), 12 (6)
H-13	8α (10), 3 (4), 5 (6)	H-9	8 (8), 14 (10)
H-12	7 (8), 6-OAc (2)	H-1	5 (3)
H-2β	14, (3), 15 (2)	H-5′	1 (3), 1-OAc (2)