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SESQUITERPENE ESTERS FROM *MAYTENUS DISTICHA*

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Key word Index—*Maytenus disticha*; Celastraceae; dihydro-β-agarofuran sesquiterpenes.

Abstract—Four new sesquiterpenes, 9β-benzoyloxy-1α,6β-diacetoxy-15-hydroxy-dihydro-β-agarofuran, 9β-benzoyloxy-1α,6β, 15-triacetoxy-8α-hydroxydihydro-β-agarofuran, 9β-benzoyloxy-1α,6β,8α,15-tetracetoxydihydro-β-agarofuran and 1α, 9β-dibenzoyloxy-6β,8β-diacetoxy-4β-hydroxydihydro-β-agarofuran were isolated from *Maytenus disticha*. Their structures were determined by spectroscopic studies, chemical correlations and selective hydrolysis. The absolute configuration of the last compound mentioned above was determined by CD.

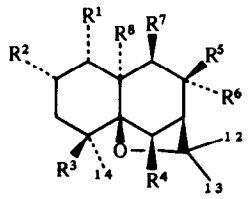
INTRODUCTION

Pursuing our study of Celastraceae used in folk medicine [1–6], we have examined an American species collected in Chile. *Maytenus disticha* Hook [7] was chosen because the *Artemia salina* test [8] for bioactivity showed an $LC_{50} > 650$. This paper deals with the isolation and structure elucidation of the secondary metabolites obtained from the methanol extract of the aerial part of the plant.

RESULTS

Repeated chromatography of the methanol extract of the aerial part of *M. disticha* on silica gel gave six compounds two of which, **5** and **6**, proved to be identical to substances with established absolute configurations previously isolated from *M chubutensis* Speg [9]. Compound **1** was isolated as a crystalline substance. mp 115–118°, $C_{26}H_{34}O_8$. Its IR spectrum had absorption bands for a hydroxy group, esters and an aromatic ring. The mass spectrum showed fragments suggestive of the presence of a benzoate at *m/z* 105 and acetates at $[M-42]^+$ and $[M-60]^+$. The ^1H NMR spectrum confirmed the presence of the benzoate and acetate groups as five aromatic protons were observed between δ7.30 and 8.10 and methyls for two acetates appeared at δ2.21 and 1.56 as singlets together with the geminal protons for these groups as a doublet centred at δ5.74 ($J=7.5$ Hz), and a broad singlet at δ5.87 and a double doublet at δ5.58 ($J_1=12.5$, $J_2=5.0$ Hz), respectively. Two protons of a hydroxymethylene group were seen as doublets of an AB system with signals centred at δ4.01 and 4.23 ($J=11.7$ Hz). From the above it can be assumed that **1** is a polyesterified sesquiterpene of the type usually found in the Celastraceae.

COSY experiments and the study of the coupling constants identified the ester-bearing positions as 1α,6β and 9β with a hydroxy group on C-15. The position of the benzoate group on C-9 was determined by studying the chemical shifts of its geminal proton (an acetate methyl shift to δ1.56 is only compatible with there being an acetate on C-1 and a benzoate on C-9 or *vice versa* in this sort of substance [10]). This was confirmed by selective hydrolysis [11] of **1** with 0.1 M $NaHCO_3$ which yielded the monobenzoate **8** as the major product. The ^1H NMR spectrum of **8** showed a geminal proton as a doublet centred at δ6.03 ($J=6.8$ Hz). When **1** was acetylated with acetic anhydride in pyridine at room temperature, **7** was



	R¹	R²	R³	R⁴	R⁵	R⁶	R⁷	R⁸
1	OAc	H	H	OAc	H	H	OBz	CH_2OH
2	OAc	H	H	OAc	H	OH	OBz	CH_2OAc
3	OAc	H	H	OAc	H	OAc	OBz	CH_2OAc
4	OBz	H	OH	OAc	OAc	H	OBz	Me
5	OAc	OAc	H	OAc	H	OAc	OBz	CH_2OH
6	OAc	OAc	H	OAc	H	OAc	OBz	CH_2OAc
7	OAc	H	H	OAc	H	H	OBz	CH_2OAc
8	OH	H	H	OH	H	H	OBz	CH_2OH
9	OAc	H	H	OAc	H	OAc	OBz	CH_2OH
10	OAc	H	H	OH	H	OAc	OBz	CH_2OAc
11	OH	H	H	OAc	H	OH	OBz	CH_2OH
12	OH	H	H	OH	H	OH	OBz	CH_2OAc
13	OBz	H	OH	OH	OAc	H	OBz	Me
14	OBz	H	OH	OH	OH	H	OBz	Me
15	OH	H	OH	OH	H	OH	OH	CH_2OH
16	OH	H	OH	OH	OH	H	OH	Me

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Table 1 ^{1}H NMR data of compounds **1–4** and **7–14**

	H-1	H-6	H-7	H-8	H-9	H-15	OAc-1	OAc-6	OAc-8	OAc-15
1	5 58 *dd* (12.5, 5.9)	5.87 *br s*			5.74 *d* (7 5)	4 01–4.23 d_{AB} (11 7)	1 56 *s*	2 21 *s*		
2	5.59 *dd* (11.8, 4.2)	6.40 *br s*	2.32 *d* (2.2)	4.25 *d* (2.2)	5.30 *s*	4.54–4.72 d_{AB} (12 3)	1.49 *s*	2.25 *s*		2.10 *s*
3	5 51 dd (11.8, 4 2)	6.28 br s	2.31 *d* (3 0)	5.21 *d* (3 0)	5.45 *s*	4.56 *br s*	1.47 *s*	2.19 *s*	2 09 *s*	2.25 *s*
4	5.56 *dd* (12, 4.0)	5.57 *br s*	2 43 *d* (3 3)	5.67 *dd* (6 3, 3.3)	5.40 *d* (6.3)			2.15 *s*	1.85 *s*	
7	5 60 *dd* (12.5, 5 0)	5 93 *br s*			5.38 *d* (7.5)	4.43–4.67 d_{AB} (11 7)				
8	4 76 *dd* (12.5, 5.0)	5 33 *br s*			6.03 *d* (6 8)	4.47 *d* (11.6)	1.49 *s*	2.25 *s*		2 10 *s*
9	5 65 *dd* (12 0, 5.0)	6.06 *s*	2.48 *d* (3.3)	5.31 *d* (13.3)	5.83 *s*	3.85–4.48 d_{AB} (12.0)	1.56 *s*	2.19 *s*	2.08 *s*	
10	5.53 *dd* (12.0, 5.0)	4.97 *d* (2.5)	2.30 *d* (3.3)	5.32 *d* (3.3)	5.51 *s*	4.50–4 78 d_{AB} (12 0)	1 56 *s*		2.15 *s*	2.18 *s*
11	4 68 *dd* (11.0, 4 5)	5 86 *br s*	2.41 *d* (3.3)	4 43 *d* (3.3)	5.80 *s*	3.96–4.51 d_{AB} (11 6)		2 08 *s*		
12	4 62 *m**	4 46 *d* (2 5)	2.40 *d* (3.0)	4 10 *d* (3.3)	5 96 *s*	4 59–5 06 d_{AB} (11 6)				2.09 *s*
13	5 65 *dd* (12.0, 4.0)	5.52 *d* (5 0)	2 47 *d* (3.0)	5 51 *dd* (6 3, 3 0)	5.36 *d* (6 3)				1 86 *s*	
14	5.60 *dd* (12 5, 4 8)	4.40 *d* (5 0)	2 52 *d* (3.0)	4 42 *m**	5 29 *d* (6 4)					

*Overlapping signals

obtained and its ^{1}H NMR spectrum showed the protons on C-15 at δ4.43 and 4.67 while in **1** they appeared at δ4.01 and 4.23 (Table 1). The basic polyhydroxy skeleton of **1** corresponds to 15-hydroxycelorbicol [10].

The natural products **2** and **3** were shown to be related, as the acetylation of **2** with acetic anhydride in pyridine gave a product identical to **3** with one more acetate group than **7**. This acetate group was sited at 8α by means of double resonance experiments showing the coupling of the geminal proton with H-7 and α stereochemistry determined from the 3 Hz coupling constants H-7/H-8 and non-coupling of H-8/H-9 [12]. These data were confirmed by the hydrolysis of **3** with 0.1 M $NaHCO_3$ which afforded five products: **2**, **9**–**12**. The free hydroxyl was observed at C-8 in **2**, the acetate on C-15 disappeared in **9**, that on C-6 disappeared in **10**, those at C-1, C-8 and C-15 were not seen in **11** and those at C-1, C-6 and C-8 were missing in **12** (Table 1). All the spectral data of **2**, **3** and **9**–**12** agree with the structures proposed as shown in the Experimental. The basic polyhydroxy skeleton of **2** and **3** is that of 15-hydroxycelapanol (**15**) [13].

The natural product **4** is a crystalline solid, mp 205–210°, $C_{33}H_{38}O_{10}$, with a mass fragmentation pattern indicative of the presence of acetate and benzoate groups. The IR spectrum showed signals for a hydroxy group and given that compound **4** does not acetylate under usual conditions, the molecule possesses a tertiary hydroxyl. Double resonance experiments and analysis of the coupling constant values showed substitutions at C-1α, C-4β, C-6β, C-8β and C-9β [14] but did not place the esters. Hydrolysis of **4** with 0.1 M $NaHCO_2$ gave **13** and **14**, the latter being a fundamental dibenzoate for the determination of the positions of the substituents which were located at C-1α and C-9β (Table 1). All the spectral data are in agreement with the structures proposed (Experimental). The determination of the absolute stereochemistry of **4** by applying the dibenzoate chirality rule [15], an extension of the exciton chirality method [16] confirmed these assignments The CD spectrum of the dibenzoate **4** showed intense split Cotton effects of the exciton coupling type, a positive first Cotton effect at 237 nm (ε + 21.1) and a negative second Cotton effect at 222 nm (ε − 10.9). The basic polyhydroxy skeleton of **4** is that of 4β-hydroxycelapanol (**16**) [13].

EXPERIMENTAL

Voucher specimens of the plant, gathered in January 1987 in the IX Region in Bio-Bio province (Chile), are lodged with the department of Botany, Facultad de Ciencias, Universidad de Chile.

Fresh aerial part and pulverized leaves of *M disticha* (3 kg) were extracted with cold MeOH Filtration and solvent evapn *in vacuo* gave a reddish-brown extract (320 g). The residue was partitioned between H_2O–EtOH–hexane–EtOAc (5 2:5 2). The upper phase (10.5 g) was subjected to flash CC and the residue of the lower phase was extracted with EtOAc and then subjected to flash CC (47 g) on silica gel. The fraction obtained from the two columns was subjected to repeated chromatography on silica gel using mixtures of *n*-hexane–EtOAc as solvent

9β-Benzoyloxy-1α,6β-diacetoxy-15-hydroxydihydro-β-agarofuran (**1**). Crystalline solid; mp 119–122°; molecular formula, $C_{26}H_{34}O_8$ (found, $[M]^+$, 474 2209; requires, 474.2165); $[\alpha]_D^{20}$ −4.0° (EtOH, *c* 0 20), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3660 w, 3560 w, 2980 m, 2900 s, 2820 w, 1720 vs, 1590 w, 1350 s, 1260 s; UV λ_{max}^{EtOH} nm: 229, 273, 280; ^{1}H NMR: δ1.02 (3H, *d*, *J* = 7.0 Hz, Me-14), 1.39 (3H, *s*, Me-12), 1.44 (3H, *s*, Me-13), 1.56 (3H, *s*, OAc-1), 2.21 (3H, *s*, OAc-6), 4.01–4.23 (2H, d_{AB}, *J* = 11 7 Hz, H-15), 5.58 (1H, *dd*, *J* = 12.5, 5.9 Hz, H-1), 5.74 (1H, *d*, *J* = 7.5 Hz, H-9), 5.87 (1H, *br s*, H-6), 7.50 (3H, *m*, OBz), 8.00 (2H, *m*, OBz); EIMS *m/z* (rel. int.): 474 $[M]^+$ (2), 456 (4), 432 (10), 414 (2), 410 (2), 368 (2), 352 (5), 310 (3), 264 (4), 249 (12), 248 (58), 233 (7), 204 (22), 203 (44), 189 (13), 174 (14), 105 (100), 83 (20).

Hydrolysis of **1**. Compound **1** (9 mg), dissolved in MeOH (2 ml), was treated with a soln of 0.1 M $NaHCO_3$ (3 ml) heated to 50° and stirred for 4 hr. The reaction mixture was extracted with EtOAc and then chromatographed to give compound **8**. Oily product: ^{1}H NMR: δ0.95 (3H, *d*, *J* = 6 0 Hz, Me-14), 1.41 (3H, *s*, Me-12), 1.47 (3H, *s*, Me-13), 4.47 (2H, *d*, *J* = 11 6 Hz, H-15), 4.76 (1H, *dd*, *J* = 12 5, 5.0 Hz, H-1), 5.33 (1H, *br s*, H-6), 6.03 (1H, *d*, *J* = 6.8 Hz, H-9), 7.52 (3H, *m*, OBz), 8.12 (2H, *m*, OBz); EIMS *m/z* (rel. int.): 390 $[M]^+$ (3), 372 (3), 310 (3), 265 (4), 250 (4), 232 (5), 222 (7), 217 (5), 204 (14), 192 (11), 189 (7), 174 (22), 161 (21), 145 (13), 123 (11), 109 (11), 105 (100).

Acetylation of **1**. Treatment of **1** (3 mg) with Ac_2O in pyridine followed by work-up and purification by prep. TLC gave **7** (1.5 mg). ^{1}H NMR: δ0 95 (3H, *d*, *J* = 8.0 Hz, Me-14), 1.40 (3H, *s*, Me-12), 1.44 (3H, *s*, Me-13), 1.55 (3H, *s*, OAc-1), 2 09 (3H, *s*, OAc-15), 2 25 (3H, *s*, OAc-6), 4.43–4.67 (2H, d_{AB}, *J* = 11 7 Hz, H-15), 5.38 (1H, *d*, *J* = 5 Hz, H-9), 5.60 (1H, *dd*, *J* = 12 5, 5 0 Hz, H-1), 5.93 (1H, *br s*, H-6), 7 50 (3H, *m*, OBz), 8 10 (2H, *m*, OBz).

9β-Benzoyloxy-1α,6β,15-triacetoxy-8-hydroxydihydro-β-agarofuran (**2**). This compound was obtained as an amorphous solid, mp 186–190°, molecular formula $C_{28}H_{36}O_{10}$ (found, $[M]^+$, 532 2267, requires, 532 2226); $[\alpha]_D^{20}$ +25° (EtOH· *c* 0.1); IR $\nu_{max}^{CHCl_3}$ cm^{-1}· 3630 w, 3540 w, 2980 m, 2900 m, 1720 s, 1710 s, 1435m, 1350 s, 1260 s, 1220 s; UV λ_{max}^{EtOH} nm: 228, 274, 282, ^{1}H NMR: 0.92 (3H, *d*, *J* = 7.5 Hz, Me-14), 1 41 (3H, *s*, Me-12), 1.43 (3H, *s*, Me-13), 1.49 (3H, *s*, OAc-1), 2.10 (3H, *s*, OAc-15), 2.25 (3H, *s*, OAc-6), 2.32 (1H, *d*, *J* = 2.2 Hz, H-7), 4.25 (1H, *d*, *J* = 2 2 Hz, H-8), 4.54–4.72 (2H, d_{AB}, *J* = 12.3 Hz, H-15), 5.59 (1H, *dd*, *J* = 11.8, 4.2 Hz, H-1), 6.40 (1H, *br s*, H-6), 7.45 (3H, *m*, OBz), 8.00 (2H, *m*, OBz); EIMS *m/z* (rel. int.): 532 $[M]^+$ (1), 490 (5), 430 (2), 410 (14), 368 (5), 353 (5), 308 (3), 293 (4), 280 (3), 265 (3), 248 (4), 123 (5), 107 (6), 105 (100), 85 (10), 83 (30)

Acetylation of **2**. Treatment of **2** (2 mg) with Ac_2O in pyridine followed by work-up and purification by prep TLC gave **3** (1 4 mg). identical to the natural product

9β-Benzoyloxy-1α,6β,8α,15-tetracetoxydihydro-β-agarofuran (**3**). This compound was isolated as a crystalline solid, mp 115–118°; molecular formula $C_{30}H_{38}O_{11}$ (found, $[M]^+$, 574 2397; requires, 574.2413); $[\alpha]_D^{20}$ −5° (*c* 0 08, EtOH), IR $\nu_{max}^{CHCl_3}$ cm^{-1}· 2990 s, 2940 m, 1730 s, 1720 s, 1710 s, 1585m, 1435m, 1350 s, 1260 s, UV λ_{max}^{EtOH} nm. 230, 273, 280; ^{1}H NMR· δ0 97 (3H, *d*, *J* = 7.0 Hz, Me-14), 1.41 (3H, *s*, Me-13), 1.47 (3H, *s*, OAc-1), 1.55 (3H, *s*, Me-12), 2.04 (3H, *s*, OAc-8), 2 19 (3H, *s*, OAc-6), 2 25 (3H, *s*, OAc-15), 2.31 (1H, *d*, *J* = 3 0 Hz, H-7), 4 56 (2H, *br s*, H-15), 5.21 (1H, *d*, *J* = 3.0 Hz, H-8), 5.45 (1H, *s*, H-9), 5.51 (1H, *dd*, *J* = 11.8, 4.2 Hz, H-1), 6 28 (1H, *br s*, H-6), 7.48 (3H, *m*, OBz), 8.00 (2H, *m*, OBz), EIMS *m/z* (rel. int): 574 $[M]^+$ (1), 532 (21), 472 (2), 453 (2), 410 (2), 350 (2), 309 (4), 290 (10), 249 (5), 248 (4), 232 (5), 220 (5), 203 (5), 190 (5), 184 (5), 161 (7), 106 (20), 105 (100).

Hydrolysis of **3**. Compound **3** (57 mg) was dissolved in MeOH (8 ml) and treated with a soln of 0.1M $NaHCO_3$ (7 ml) while stirring at 50° for 4 5 hr The reaction mixture was then extracted with EtOAc and purified by prep. TLC. Compounds **9**–**12** were isolated.

Compound **9** ^{1}H NMR· δ0.88 (3H, *s*, Me-14), 1.40 (3H, *s*, Me-13), 1.54 (3H, *s*, Me-12), 1 56 (3H, *s*, OAc-1), 2.08 (3H, *s*, OAc-8), 2.19 (3H, *s*, OAc-6), 2.48 (1H, *d*, *J* = 3.3 Hz, H-7), 3 85–4.48 (2H, d_{AB}, *J* = 12.0 Hz, H-15), 5 31 (1H, *d*, *J* = 13.3 Hz, H-8), 5 65 (1H,

dd, $J = 12.0$, 5 0 Hz, H-1), 5 83 (1H, *s*, H-9), 6 06 (1H, *s*, H-6), 7 05 (3H, *m*, OBz), 8.00 (2H, *m*, OBz); EIMS *m/z* (rel. int.) 532 $[M]^+$ (1), 413 (6), 412 (16), 369 (5), 355 (22), 351 (6), 341 (7), 328 (6), 327 (18), 314 (5), 309 (6), 300 (10), 270 (10), 256 (10), 255 (25), 243 (12), 242 (12), 227 (11), 213 (13), 201 (20), 199 (17), 185 (15), 155 (33), 105 (80), 57 (100)

Compound **10**. ^{1}H NMR δ1.15 (3H, *d*, $J = 8$ 0 Hz, Me-14), 1.46 (3H, *s*, Me-13), 1 52 (3H, *s*, Me-12), 1.56 (3H, *s*, OAc-1), 2.15 (3H, *s*, OAc-8), 2.18 (3H, *s*, OAc-15), 2.30 (1H, *d*, $J = 3.3$ Hz, H-7), 4.50–4.78 (2H, d_{AB}, $J = 12$ 0 Hz, H-15), 4.97 (1H, *d*, $J = 2.5$ Hz, H-6), 5 32 (1H, *d*, $J = 3$ 3 Hz, H-8), 5.53 (1H, *dd*, $J = 12.0$, 5.0 Hz, H-1), 5 51 (1H, *s*, H-9), 7 50 (3H, *m*, OBz), 8.00 (2H, *m*, OBz); EIMS *m/z* (rel int.) 532 $[M]^+$ (1), 490 (16), 430 (4), 410 (28), 368 (10), 353 (10), 308 (6), 293 (9), 280 (5), 265 (6), 248 (6), 195 (5), 185 (5), 165 (6), 153 (6), 105 (100).

Compound **11** ^{1}H NMR δ0 96 (3H, *d*, $J = 8.0$ Hz, Me-14), 1.34 (3H, *S*, Me-13), 1.40 (3H, *s*, Me-12), 2 08 (3H, *s*, OAc-6), 2.41 (1H, *d*, $J = 3.3$ Hz, H-7), 3.96–4.51 (2H, d_{AB}, $J = 11$ 6 Hz, H-15), 4 43 (1H, *d*, $J = 3$ 3 Hz, H-8), 4.68 (1H, *dd*, $J = 11$ 0, 4.5 Hz, H-1), 5.80 (1H, *s*, H-9), 5 86 (1H, *br s*, H-6), 7.40 (3H, *m*, OBz), 7.88 (2H, *m*, OBz); EIMS *m/z* (rel. int.): 369 $[M - MeCO_2H - H_2O - H^+]^+$ (8), 368 (14), 286 (14), 271 (17), 270 (41), 257 (12), 256 (13), 255 (31), 241 (11), 236 (14), 227 (13), 190 (38), 185 (24), 173 (13), 147 (17), 135 (22), 129 (24), 123 (24)m 105 (34), 55 (100)

Compound **12** ^{1}H NMR δ0 85 (3H, *d*, $J = 6$ 0 Hz, Me-14), 1.47 (3H, *s*, Me-13), 1 52 (3H, *s*, Me-12), 2.09 (3H, *s*, OAc-15), 2 40 (1H, *d*, $J = 3$ 0 Hz, H-7), 4 10 (1H, *d*, $J = 3$ 3 Hz, H-8), 4 46 (1H, *d*, $J = 2$ 5 Hz, H-6), 4 59–5 06 (2H, d_{AB}, $J = 11$ 6 Hz, H-15), 4.62 (1H, *m*, H-1), 5 96 (1H, *s*, H-9), 7 50 (3H, *m*, OBz), 8 20 (2H, *m*, OBz)

1α,9β-Dibenzoyloxy-6β,8β-diacetoxy-4β-hydroxydihydro-β-agarofuran (**4**) Isolated as a crystalline solid, mp 205–210°, molecular formula, $C_{33}H_{38}O_{10}$ (found, $[M]^+$, 594 2441; requires 594 2418), $[\alpha]_D^{20}$ +74° (*c* 0 19, EtOH), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3640 w, 3520 m, 3000 m, 2900 m, 1730 s, 1705 s, 1580 s, 1440 s, 1350 s, 1270 s, UV λ_{max}^{EtOH} nm 226, 270, 278, ^{1}H NMR δ1 36 (3H, *s*, Me-13), 1 57 (6H, *s*, Me-12, 15), 1.66 (3H, *s*, Me-14), 1 85 (3H, *s*, OAc-8), 2 15 (3H, *s*, OAc-6), 2 43 (1H, *d*, $J = 3$ 3 Hz, H-7), 5 40 (1H, *d*, $J = 6$ 3 Hz, H-9), 5 56 (1H, *dd*, $J = 12$ 0, 4 0 Hz, H-1), 5 57 (1H, *br s*, H-6), 5 67 (1H, *dd*, $J = 6$ 3, 3 3 Hz, H-8), 7 39 (6H, *m*, OBz), 7 80 (4H, *m*, OBz), EIMS *m/z* (rel int) 594 $[M]^+$ (1), 579 (2), 552 (1), 534 (10), 475 (6), 457 (18), 335 (5), 248 (8), 215 (6), 202 (12), 148 (11), 105 (100) Prior to measurement of the CD spectra, compound **4** was purified by HPLC (μPorasil, 10μ, 0 8 × 30 cm, C_6H_{14}–EOAc, 3 2, 1 5 ml m^{-1}, 254 nm, room temp, 31 m); UV λ_{max}^{MeCN} nm 230, CD λ_{max}^{MeCN} nm 237 ($\Delta\varepsilon = +21$ 1) and 222 ($\Delta\varepsilon = -10$ 9)

Hydrolysis of **4** Compound **4** (10 mg) dissolved in MeOH (4 ml) and treated with a soln of 0 1 M $NaHCO_3$ (3 5 ml) while stirring and heated at 50° for 5 hr The reaction mixture was then extracted with EtOAc and purified by prep. TLC, giving **13** and **14**.

Compound **13** ^{1}H NMR δ1.53 (6H, *s*, Me-13, 15), 1.63 (3H, *s*, Me-12), 1 68 (3H, *s*, Me-14), 1 86 (3H, *s*, OAc-8), 2 47 (1H, *d*, $J = 3$ 0 Hz, H-7), 3 20 (1H, *s*, OH-4), 4 52 (1H, *d*, $J = 5$ 0 Hz, H-6), 5 36 (1H, *d*, $J = 6.3$ Hz, H-9), 5 51 (1H, *dd*, $J = 6.3$, 3.0 Hz, H-8), 5 65 (1H, *dd*, $J = 12$ 0, 4 0 Hz, H-1), 7 40 (6H, *m*, OBz), 7 80 (4H, *m*, OBz), (200 MHz, D_2O, TMS); δ4 50 (1H, *s*, OH), EIMS *m/z* (rel int.): 537 $[M - Me]^+$ (3) 519 (4), 415 (16), 370 (3), 293 (6), 248 (6), 205 (11), 202 (12), 105 (100)

Compound **14** ^{1}H NMR: δ1.59 (6H, *s*, Me-13, 15), 1.62 (3H, *s*, Me-12), 1 67 (3H, *s*, Me-14), 2.52 (1H, *d*, $J = 3$ 0 Hz, H-7) 4 40 (1H, *d*, $J = 5$ 0 Hz, H-6), 4.42 (1H, *m*, H-8), 5.29 (1H, *d*, $J = 6.4$ Hz, H-9), 5.60 (1H, *dd*, $J = 12$ 5, 4 8 Hz, H-1), 7 35 (6H, *m*, OBz), 7 75 (4H, *m*, OBz); EIMS *m/z* (rel int) 239 $[M - 271]^+$ (4) 199 (10), 185 (6), 171 (6), 165 (4), 155 (6), 152 (10), 149 (7), 138 (13), 135 (17), 129 (23), 123 (15), 121 (27), 109 (22), 98 (33), 55 (100).

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