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First Examples of Dammarane Triterpenes Isolated from Celastraceae

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ABSTRACT: Eight new dammarane triterpenes were isolated from *Maytenus Macrocarpa*. Their structures were determined by means of ^{1}H and ^{13}C NMR spectroscopic studies, including ^{1}H-^{13}C heteronuclear correlation (HETCOR), long range correlation with inverse detection (HMBC), and chemical evidence. This is the first time that dammarane triterpenes have been isolated from Celastraceae. © 1997 Elsevier Science Ltd.

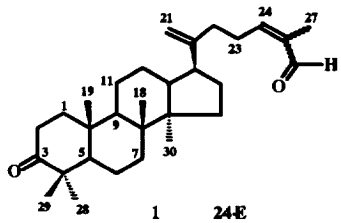
As part of an intensive study on the biologically active metabolites from Celastraceae species used in folk medicine[1,2], *Maytenus Macrocarpa* has been studied. This species[3,4] is distributed in the amazonian region of Peru and the inhabitants of this region use it for the treatment of rheumatism, flu, gastrointestinal diseases and as an antitumoral agent for skin cancer.

Nine dammarane triterpenes were isolated from the stem bark exudate of *M. macrocarpa*, eight of which (2-9) were new to the literature. *M. macrocarpa* also yielded 3-oxo-29-hydroxy-friedo-olean, friedelin, daturaolone, 3β-29-dihydroxy-glutin-5-eno and the nor quinone methide triterpenes : pristimerin, tingenone, celastrol, netzahualcoyene and scutione. This last compound has been recently isolated in our laboratories[5] from *Maytenus scutioides* and presents a strong antibiotic activity against Gram positive bacteria. Their structures were determined by means of ^{1}H and ^{13}C NMR spectroscopic studies, including ^{1}H-^{13}C heteronuclear correlation (HETCOR), long range correlation with inverse detection (HMBC), and chemical evidence. Although the biological activity of these dammaranes has yet to be evaluated, other similar triterpenes show phytohormonal[6] and cytotoxic[7,8] activities.

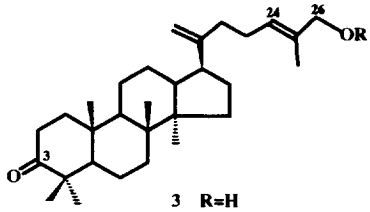
This is the first record of dammaranes in the Celastraceae and the first time that nor quinone methide triterpenes, typical components of the roots in *Maytenus* genus, are isolated from aerial parts. Taxonomically *M. macrocarpa* is characterized by the production of large amounts of exudate in its aerial parts, which is unusual in other *Maytenus* species.

Compound **1** was isolated as an amorphous solid and presented identical physical and spectroscopic data to 24(E)-3-oxodammara-20,24-dien-26-al, which has been previously isolate from *Rapanea umbellata*[9] (umbelliferae).

Compound **2** showed a positive optical activity, a [M^+] at *m/z* 438 and a molecular formula $C_{30}H_{46}O_2$. Its IR spectrum showed the presence of a terminal methylene (900 cm^{-1}), a carbonyl (1700 cm^{-1}), and an α,β-unsaturated carbonyl (1630 cm^{-1}) as functional groups. The ^1H NMR spectrum (Table 1) showed signals for a -CHO group, a vinylic methyl, five angular methyls and three olefinic protons, one of which was deshielded, typical of the β position on α,β-unsaturated aldehyde. Its NMR spectral data were similar to those of **1**. The main difference was the signal at δ 10.15, attributable to the aldehyde proton, which is shifted 0.75 ppm downfield with respect to the same signal in **1**. In its ^{13}C NMR spectra (Table 2) the main difference were the signals for C-24, C-25, C-26 and C-27. All the data mentioned above suggest that **2** is the *Z*-isomer of **1**, which was confirmed by NOEDIF experiments.



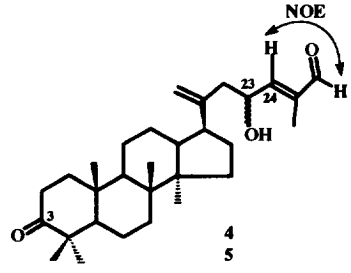
1 24-E
2 24-Z



3 R=H
3a R=Ac

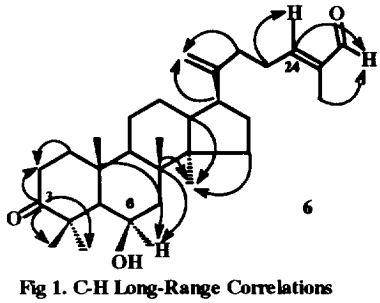
Compound **3** was an amorphous white solid. Its IR spectrum revealed the presence of hydroxy (3540 cm^{-1}) and carbonyl (1700 cm^{-1}) groups. Compound **3** showed a [M^+] at *m/z* 440, consistent with the molecular formula $C_{30}H_{48}O_2$. Its ^1H NMR spectrum showed a singlet at δ 4.14 for 2H characteristic of methylene groups joined to oxygenated functions. Compound **3** formed a monoacetate **3a** when it was treated with Ac_2O/Py and was transformed to **1** under oxidation conditions with PCC/CH_2Cl_2. The structure of **3** was established as 24-(*E*)-3-oxo-dammara-20,24-dien-26-ol.

Compounds **4** and **5** were separated by HPLC. They presented the same formula $C_{30}H_{46}O_3$. Their ^1H NMR spectra differ with respect to that of **1** by the presence of H-24 as a doublet instead of a triplet, (at δ 6.44 for **4** and δ 6.46 for **5**) and also a multiplet (1H) centred at δ 4.78 for **4** and at δ 4.74 for **5**. In their ^{13}C NMR and DEPT spectrum a signal appeared at δ 66.66 (d) for **4** and at δ 66.35 (d) for **5**, typical of a methine carbon with oxygenated function. The HMBC experiment showed three bond couplings between the multiplet at δ 4.70 and the signal corresponding to C-25, which established the position of the OH group on C-23. A ROESY experiment showing the NOE effect between H-26 and H-24 confirmed that the stereochemistry of the double bond (C-24-C-25) is *E*. All these data point out that **4** and **5** are epimeric compounds at C-23. The determination of the absolute configurations by Horeau, Mosher or CD methods



4
5

were not possible because of the small quantities of **4** and **5** available and because we could not obtain reliable conformational information of the lateral chain by MMC calculations. We tried to synthesize larger amounts of these compounds from the reaction of **1** with SeO_2, but this reaction was not successful as we obtained a complex mixture of products.



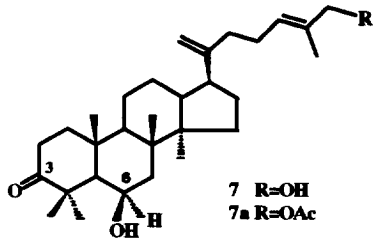
6

Fig 1. C-H Long-Range Correlations

The compound **6** was isolated as an amorphous white solid. Its ^1H NMR was similar to that of **1**. The main difference was the additional presence of a broad singlet at δ 4.49 (1H). Its IR spectrum showed bands for hydroxyl (3500 cm^{-1}) and carbonyl (1720 cm^{-1}) groups. The ^{13}C NMR spectrum showed a methine carbon at δ 69.60. The position of the OH group on C-6 was determined by the HMBC experiment (fig 1). The relative stereochemistry of the OH group was established as β on the basis of published data.[10,11] Compound **6** did not form the corresponding acetate derivative when it was treated under the usual conditions (Ac_2O/ Py). This was probably due to 1,3 steric interactions of the bulky Ac_2O with Me-18 and Me-19.

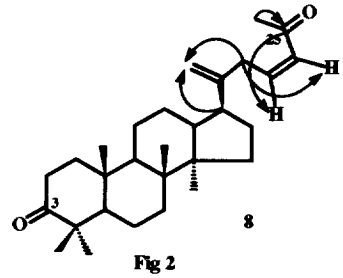
Table 1. ^1H NMR ($CDCl_3$) of 1-9

H	1	2	3	4	5	6	7	8	9
6	———	———	———	———	———	4.49 bs	4.50 bs	———	———
21	4.75 bs 4.83 bs	4.74 bs 4.83 bs	4.71 bs 4.77 bs	4.92 bs 5.03 bs	4.92 bs 4.99 bs	4.75 bs 4.84 bs	4.79 bs 4.73 bs	4.74 bs 4.88 bs	4.96 bs 4.88 bs
23	———	———	———	4.78 m	4.74 m	———	———	6.79 dt (7.7, 7.9)	———
24	6.50 t (6.7)	6.53 t (6.7)	5.31 t (6.8)	6.44 d (7.8)	6.46 d (8.0)	6.51 t (6.7)	5.32 t (6.7)	6.10 d (7.9)	7.10 bs
26	9.40 s	10.15 s	4.14 s	9.46 s	9.46 s	9.40 s	4.15 bs	2.26 s	———
Me-18	0.89 s	0.89 s	0.88 s	0.84 s	0.91 s	1.39 s	1.39 s	0.88 s	0.89 s
Me-19	0.95 s	0.95 s	0.95 s	0.90 s	0.96 s	1.17 s	1.17 s	0.95 s	0.95 s
Me-27	1.77 s	1.76 s	1.81 s	1.81 s	1.81 s	1.77 s	1.82 s	———	1.98 s
Me-28	1.02 s	1.02 s	1.02 s	0.95 s	1.04 s	1.43 s	1.44 s	1.01 s	1.01 s
Me-29	1.05 s	1.04 s	1.05 s	0.98 s	1.05 s	1.45 s	1.46 s	1.04 s	1.05 s
Me-30	1.09 s	1.09 s	1.10 s	1.02 s	1.10 s	0.85 s	0.84 s	1.09 s	1.09 s



7 R=OH
7a R=OAc

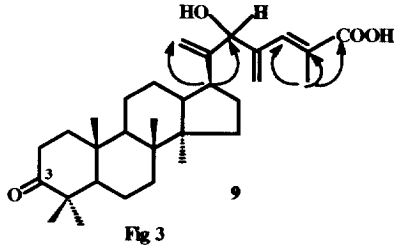
Compound **7** presented a M^+ at *m/z* 456 according to the molecular formula $C_{30}H_{48}O_3$. Its ^1H NMR spectrum showed two broad singlets at δ 4.60 (2H) and at δ 4.50 (1H), which are characteristic of methylene and methine protons joined to hydroxyl groups. The ^{13}C NMR data of **7** presented a signal at δ 69.68 (similar to C-6 in **6**) and another signal at δ 61.21 (similar to C-26 in **3**). Compound **7** formed a monoacetate **7a** when it was treated with Ac_2O/Py and it was transformed to **6** with PCC/CH_2Cl_2. All the data mentioned above suggest that compound **7** has the structure shown in the figure.



8

Fig 2

Compound **8** showed a M^+ at *m/z* 424, and the molecular formula $C_{29}H_{44}O_2$. The main signals of its ^1H NMR were the presence of a double of triplets at δ 6.79 (1H), a doublet at δ 6.14 (1H), a doublet at δ 2.20 (2H) and a singlet at δ 2.26 (3H), typical of methyl ketone. Its ^{13}C NMR spectrum showed the presence of 29 atoms of carbon and the dammarane nucleus, consequently, the main difference with respect to previous compounds has to be in the lateral chain. The following three bond coupling obtained from the HMBC spectrum (Fig 2) helped us to establish the structure of **8** as 23-(Z)-3,25-dioxo-25-nor-dammara-20,24-diene.



9

Fig 3

Compound **9** was also isolated as an amorphous white solid. It showed a M^+ at m/z 482, and the molecular formula $C_{31}H_{46}O_4$. Its ^{13}C NMR and DEPT spectrum showed the presence of a two carbonyl carbon (δ 218.03 and 174.05), six methyl groups (one of them on a conjugated double bond), one methine carbon joined to an oxygenated function (δ 79.98) and six vinyl carbons. Two among the vinyl carbons were methylene carbons (δ 111.11 and 111.31), one was a methine (δ 148.59) and the remaining three were quaternary carbons (130.10, 146.83, 146.88). When we compared the ^{13}C NMR data of **9** with those of **1** we found that the values for the carbons of A,B,C and D rings were very close, therefore, as it turned out to be the case with **8**, the difference must be in the lateral chain. HMBC showed the following three and two bond couplings (Fig 3) confirming the structure of **9** as a homo-dammarane.

We still do not have any chemotaxonomic or phylogenetic evidence to account for the occurrence of these type of compounds. However, the interesting biological properties showed by similar products encouraged us to pursue the study of this singular species.

Table 2. ^{13}C NMR ($CDCl_3$) of 1-9

C	1	2	3	4	5	6	7	8	9
1	39.81 t	39.92 t	39.90 t	39.89 t	39.89 t	43.00 t	43.06 t	39.91 t	39.91 t
2	32.57 t	34.10 t	34.06 t	34.06 t	34.06 t	34.40 t	34.42 t	34.07 t	34.08 t
3	217.86 s	218.08 s	223.80 s	218.08 s	218.12 s	216.55 s	216.59 s	218.03 s	218.08 s
4	47.32 s	47.40 s	47.36 s	47.83 s	47.39 s	49.06 s	49.08 s	47.39 s	47.39 s
5	55.18 d	55.31 d	55.30 d	55.28 d	55.28 d	56.98 d	57.01 d	55.30 d	55.30 d
6	19.52 t	19.62 t	19.61 t	19.58 t	19.63 t	69.60 d	69.68 d	19.61 t	19.61 t
7	34.58 t	34.68 t	34.68 t	34.63 t	34.63 t	42.45 t	42.45 t	34.66 t	34.66 t
8	40.22 s	40.33 s	40.31 s	40.31 s	40.33 s	39.61 s	39.61 s	40.34 s	40.34 s
9	50.09 d	50.20 d	50.21 d	50.10 d	50.16 d	51.05 d	51.11 d	50.18 d	50.18 d
10	36.77 s	36.88 s	36.86 s	36.85 s	36.86 s	36.84 s	36.84 s	36.88 s	36.88 s
11	21.73 t	21.83 t	21.83 t	21.77 t	21.80 t	21.61 t	23.69 t	21.78 t	21.78 t
12	24.84 t	24.93 t	24.93 t	24.98 t	24.99 t	24.96 t	24.96 t	24.87 t	24.84 t
13	45.37 d	45.49 d	45.37 d	45.20 d	45.21 d	44.34 d	44.24 d	45.42 d	45.48 d
14	49.29 s	49.40 s	49.36 s	49.43 s	49.49 s	49.43 s	49.43 s	49.40 s	49.38 s
15	31.17 t	31.26 t	31.28 t	31.32 t	31.11 t	31.33 t	31.37 t	31.26 t	31.28 t
16	27.44 t	25.40 t	26.45 t	29.05 t	29.27 t	27.55 t	26.48 t	28.65 t	28.93 t
17	47.27 d	47.40 d	47.63 d	47.38 d	46.49 d	47.37 d	47.60 d	47.61 d	47.83 d
18	15.95 q	16.04 q	16.02 q	16.02 q	16.04 q	16.91 q	16.93 q	16.04 q	16.04 q
19	15.22 q	15.32 q	15.30 q	15.31 q	15.31 q	16.52 q	16.58 q	15.30 q	15.30 q
20	150.94 s	150.90 s	152.16 s	147.91 s	147.92 s	151.03 s	152.16 s	149.04 s	146.88 s
21	108.29 t	108.61 t	107.78 t	112.34 t	111.71 t	108.43 t	107.89 t	110.94 t	111.11 t
22	33.96 t	34.10 t	34.28 t	41.72 t	42.15 t	32.69 t	34.27 t	37.40 t	79.98 d
23	28.88 t	28.96 t	28.81 t	66.66 d	66.35 d	28.95 t	28.77 t	146.49 d	146.83 s
24	154.24 d	149.04 d	128.14 d	153.94 d	154.01 d	154.39 d	128.23 d	132.30 d	148.59 d
25	139.24 s	136.07 s	134.80 s	138.64 s	138.65 s	139.37 s	134.44 s	198.54 s	130.10 s
26	195.07 d	191.12 d	61.54 t	194.93 d	194.93 d	195.28 d	61.61 t	26.91 q	174.00 s
27	9.18 q	16.43 q	21.25 q	9.72 q	9.66 q	9.28 q	21.28 q	_____	10.67 q
28	26.62 q	26.70 q	26.70 q	26.68 q	26.69 q	23.67 q	23.69 q	26.71 q	26.70 q
29	20.90 q	21.00 q	20.97 q	20.99 q	21.01 q	24.87 q	24.88 q	20.99 q	21.00 q
30	15.71 q	15.81 q	15.79 q	15.78 q	15.90 q	15.99 q	16.00 q	15.81 q	15.86 q

*** Data based on HMBC, HMQC and DEPT experiments**

EXPERIMENTAL

IR spectra were taken on a PE 681 spectrophotometer and ^{1}H and ^{13}C NMR on a Bruker W-200SY at 200 and 50 MHz, respectively, with TMS as internal reference. The HMBC , HMQC and ROESY were run on a Bruker at 400 MHz. Optical rotations were measured on a Perkin-Elmer 241 automatic polarimeter and $[\alpha]_D^{20}$ are given in 10^{-1} deg cm^2g^{-1}. UV spectra were collected on a Perkin-Elmer model 550-SE. MS were recorded on a VG Micromass ZAB-2F and a Hewlett Packard 5995. HRMS were recorded on a VG Autospec spectrometer. Schleicher-Schüll F-100/LS 254 and prep. TLC 1510/LS 254 foils were used for TLC, while silica gel (0.2-0.63 mm) and Sephadex LH-20 were used for CC.

Plant Material

The plant was gathered in Perú, in November 1995, and a voucher specimen is on file with the Herbarium of the Departamento de Botánica, Universidad Nacional de la Amazonía, Iquitos, Perú.

Extraction and Isolation

The stem bark exudates of *M. macrocarpa* (0.18 Kg) was extracted with n-hexane-Et_2O (1:1) (2 liters) in a Soxhlet apparatus. The extract (40 g) was repeatedly chromatographed on Sephadex LH-20 and Si gel using as solvent mixtures of n-hexanes-$CHCl_3$-MeOH (2:1:1) and of n-hexane-AcOEt, respectively, to afford **1** (500 mg), **2** (20 mg), **3** (50 mg), **4** (3 mg), **5** (4 mg), **6** (40 mg), **7** (10 mg) **8** (12 mg) and **9** (6 mg).

24-(Z)-3-oxo-dammara-20,24-dien-26-al (2). Amorphous white solid.$[\alpha]_D^{20}$ +39.1 (c 0.9, $CHCl_3$); IR ν_{max} ($CHCl_3$) cm^{-1} : 2960, 2800, 1700, 1630, 1460, 1380, 1260, 1100, 900; ^{1}H NMR ($CDCl_3$): see Table 1; ^{13} CNMR ($CDCl_3$): see Table 2;EIMS m/z (%) 438 (M^+) (6), 423 (3), 316 (3), 205 (22), 187 (7), 163 (12), 159 (14), 149 (25), 147 (11); HREIMS: calculated for $C_{30}H_{46}O_2$ 438.349781; found 438.350354.

24-(E)-3-oxo-dammara-20,24-dien-26-ol (3). Amorphous white solid.$[\alpha]_D^{20}$ +50.3 (c 0.4, $CHCl_3$); IR ν_{max} ($CHCl_3$) cm^{-1} : 3540, 2960, 2890, 1700, 1460, 1360, 1260, 1100, 900; ^{1}H NMR ($CDCl_3$): see Table 1; ^{13} CNMR ($CDCl_3$): see Table 2;EIMS m/z (%) 440 (M^+) (6), 422 (10), 316 (3), 234 (21), 205 (26), 191 (47), 163 (16), 159 (13), 149 (25), 147 (20); HREIMS: calculated for $C_{30}H_{48}O_2$ 440.365431; found 440.366832.

24-(E)-3-oxo-dammara-20,24-dien-26-acetate (3a). Compound 3 (5 mg) was treated with Ac_2O in pyridine at room temperature for 24 h to give **3a** (5.1 mg) as an amorphous white solid; $[\alpha]_D^{20}$ +55.0 (c 0.6, $CHCl_3$); IR ν_{max} ($CHCl_3$) cm^{-1} : 2900, 2890, 1730, 1690, 1380, 1280, 1100, 1125, 900; ^{1}H NMR ($CDCl_3$): 5.45 (t, J=6.7, H-24), 4.77 (bs, 1H, H-21a), 4.71 (bs, 1H, H-21b), 4.60 (s, 2H, H-26), 2.08 (s, 3H, CH_3COO-), 1.76 (s, 3H, H-27); 1.09 (s, 3H, Me-30), 1.05 (s, 3H, Me-29), 1.02 (s, 3H, Me-28), 0.95 (s, 3H, Me-19), 0.88 (s, 3H, Me-18); ^{13} CNMR ($CDCl_3$): 218.19 (s), 171.50 (s), 151.86 (s), 130.55 (d), 129.85 (s), 107.89 (t), 63.21 (t), 55.32

(d), 50.24 (d), 49.38 (s), 47.61 (d), 47.40 (s), 45.39 (d), 40.34 (s), 39.93 (t), 36.90 (s), 34.70 (t), 34.09 (t), 31.30 (t), 28.85 (t), 26.72 (q), 26.56 (t), 24.94 (t), 21.86 (t), 21.43 (q), 21.00 (q), 19.64 (t), 16.04 (q), 15.80 (q), 15.32 (q);EIMS m/z (%) 482 (M^+) (4), 422 (39), 245 (13), 205 (35), 189 (13), 163 (13), 159 (12), 149 (21), 147 (20); HREIMS: calculated for $C_{32}H_{50}O_3$ 482.375996; found 482.374838.

Oxidation of (3). Pyridinium chlorochromate (13.45 mg) was suspended in methylene chloride (10 mL), and **3** (10 mg) dissolved in dry CH_2Cl_2 was rapidly added at room temperature. After 24h, the black reaction mixture was diluted with anhydrous ether and the black solid was washed twice with ether. Product was isolated by filtration of the organic extracts and evaporation of the solvent at reduced pressure. Purification of the crude product by TLC preparative nhex:AcOEt (4:1) afforded a product (8 mg) with identical spectroscopic and physical data to **1**.

24-(E)-3-oxo-dammara-23-α-hydroxy-20,24-dien-26-al (4). Amorphous white solid.$[\alpha]_D^{20}$ +54.5 (c 0.2, $CHCl_3$); IR ν_{max} ($CHCl_3$) cm^{-1} : 3550, 2960, 2890, 1690, 1460, 1380, 1250, 900; ^1H NMR ($CDCl_3$): see Table 1; ^{13} CNMR ($CDCl_3$): see Table 2;EIMS m/z (%) 454 (M^+) (1), 245 (3), 205 (10), 149 (8), 135 (11), 133 (13), 123 (18), 121 (22); HREIMS: calculated for $C_{30}H_{46}O_3$ 454.344696; found 454.347361.

24-(E)-3-oxo-dammara-23-β-hydroxy-20,24-dien-26-al (5). Amorphous white solid.$[\alpha]_D^{20}$ +31.7 (c 0.3, $CHCl_3$); IR ν_{max} ($CHCl_3$) cm^{-1} : 3550, 2960, 2870, 1690, 1460, 1380, 1250, 900; ^1H NMR ($CDCl_3$): see Table 1; ^{13} CNMR ($CDCl_3$): see Table 2;EIMS m/z (%) 454 (M^+) (1), 205 (8), 149 (12), 135 (14), 133 (14), 123 (24), 121 (35); HREIMS: calculated for $C_{30}H_{46}O_3$ 454.344696; found 454.346894.

24-(E)-3-oxo-dammara-6-β-hydroxy-20,24-dien-26-al (6). Amorphous white solid.$[\alpha]_D^{20}$ +5.2 (c 2.0, $CHCl_3$); IR ν_{max} ($CHCl_3$) cm^{-1} : 3500, 1720, 1640, 1260, 900; ^1H NMR ($CDCl_3$): see Table 1; ^{13} CNMR ($CDCl_3$): see Table 2;EIMS m/z (%) 454 (M^+) (2), 205 (5), 135 (10), 133 (12), 123 (38), 121 (20), 119 (14); HREIMS: calculated for $C_{30}H_{46}O_3$ 454.344696; found 454.344027.

24-(E)-3-oxo-dammara-6-β-hydroxy-20,24-dien-26-ol (7). Amorphous white solid.$[\alpha]_D^{20}$ +6.8 (c 0.6, $CHCl_3$); IR ν_{max} ($CHCl_3$) cm^{-1} : 3550, 2960, 2890, 1700, 1640, 1460, 1380, 1240, 1100; ^1H NMR ($CDCl_3$): see Table 1; ^{13} CNMR ($CDCl_3$): see Table 2;EIMS m/z (%) 456 (M^+) (8), 438 (13), 203 (20), 121 (40), 107 (62); HREIMS: calculated for $C_{30}H_{48}O_3$ 456.360346 ; found 456.361584.

24-(E)-3-oxo-dammara-6-β-hydroxy-20,24-dien-26-acetate (7a). Compound **7** (4 mg) was treated with Ac_2O in pyridine at room temperature for 24 h to give **7 a** (4.2 mg) as an amorphous white solid; .$[\alpha]_D^{20}$ +3.3 (c 0.3, $CHCl_3$); IR ν_{max} ($CHCl_3$) cm^{-1} : 3400, 2890, 1730, 1690, 1380, 1280, 1100, 900. ^1H NMR ($CDCl_3$): 5.42 t (1H, J=6.5 Hz, H-24); 4.78 bs (1H, H-21 a); 4.72 bs (1H, H-21 b) ; 4.60 (2H, H-26); 4.50 bs (1H, H-6); 2.08 s (3H, CH_3COO); 1.16 (s, 3H, Me-18); 1.38 (s, 3H, Me-19); 1.45 (s, 3H, Me-29); 1.43 (s,3H, Me-28); 1.76 (s, 3H, Me-27); 0.83 (s, 3H, Me-30);EIMS m/z (%) 498 (M^+) (1); 438 (15), 261 (20), 203 (40), 121 (56), 107 (100); HREIMS: calculated for $C_{30}H_{50}O_4$ 498.370911; found 498.369607.

Oxidation of 7. Following the same procedure described for **3**. **7** (5 mg) was oxidised in similar fashion to give

after purification 3 mg of a compound which showed identical physical and spectroscopic data to compound **6**.

23-(Z)-3,25-dioxo-25-nor-dammara-20,24-diene (8). Amorphous white solid.$[\alpha]_D^{20}$ +42.7 (c 0.6, $CHCl_3$); IR ν_{max} ($CHCl_3$) cm^{-1} : 2960, 2860, 1700, 1460, 1380, 1100; ^1H NMR ($CDCl_3$): see Table 1; ^{13} CNMR ($CDCl_3$): see Table 2; EIMS m/z (%) 424 (M^+) (10), 315 (13), 246 (13), 245 (54), 206 (30), 187 (18); HREIMS: calculated for $C_{29}H_{44}O_2$ 424.334131; found 424.333226.

24-(E)-3-oxo-23-methylene-dammara-20,24-dien-26-oico (9). Amorphous white solid.$[\alpha]_D^{20}$ +64.2 (c 0.6, $CHCl_3$); IR ν_{max} ($CHCl_3$) cm^{-1} :3300, 2960, 2800, 1750, 1700, 1460, 1380, 1250, 1100 and 900;^1H NMR ($CDCl_3$): 4.88 bs (1H, H-31 a); 4.96 bs (1H, H-31 b); 5.05 bs (1H, H-22);for the rest of the signals see Table 1; ^{13} CNMR ($CDCl_3$):111.31 (t, C-31); for the rest of the signals see Table 2;EIMS m/z (%) 482 (M^+) (4), 452 (40), 245 (85), 205 (100), 121 (50), 97 (100); HREIMS: calculated for $C_{31}H_{46}O_4$ 482.339610 ; found 482.338758.

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