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THE MANSUMBINANES: OCTANORDAMMARANES FROM THE RESIN OF *COMMIPHORA INCISA*

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Key Word Index—*Commiphora incisa*; Burseraceae; resin; dammaranes; 16(*S*),20(*R*)-dihydroxydammar-24-en-3-one; 17-octanordammaranes; mansumbinone; mansumbinol; 3,4-*seco*-mansumbinoic acid.

Abstract—The resin of *Commiphora incisa* (Burseraceae) has yielded three C_{22} compounds derived by loss of the C-17 side chain from a dammarane triterpene. They have been identified by spectral analysis and chemical modification as 4α,4β,8β,10β,14α-pentamethyl-5α-gon-16-en-3-one (mansumbinone), the corresponding 3-hydroxy compound (mansumbinol) and the derivative 3,4-*seco*-mansumbinoic acid in which the A-ring has opened between C-3 and C-4. A fourth compound was characterized as 16(*S*),20(*R*)-dihydroxydammar-24-en-3-one, a possible precursor of the mansumbinanes.

INTRODUCTION

Many species of the genus *Commiphora* produce oleo-gum-resins, several of which are items of commerce [1]. *Commiphora incisa* Choiv. (syn. *C. candidula* Sprague) [2], a species found in arid areas of central and northern Kenya, yields copious amounts of a yellow non-volatile gum-resin. Investigation of the diethyl ether extract of a sample of this resin, collected in the Kora National Reserve, Tana River District, Kenya, yielded two lignans [3] and four triterpene derivatives, all of which appear to be novel. Three of the isolated triterpenes represent a unique group of C_{22}-derivatives arising *via* the loss of the C-17 side chain from triterpenes of the dammarane type. They have been assigned trivial names based on mansumbinane as material was collected at the foot of Mansumbi Hill within the Kora Reserve. The fourth compound, a full dammarane triterpene, is a putative precursor of the mansumbinanes.

RESULTS AND DISCUSSION

A diethyl ether extract of the ground resin was subjected to column chromatography over silica gel and six compounds were either eluted singly or as mixtures that were subsequently purified by preparative circular TLC. Two of the isolated compounds were identified as lignans and their structures have already been reported [3].

Mansumbinone (**1**), $C_{22}H_{34}O$, was optically active and gave no UV spectrum. The IR spectrum showed a band at 1710 cm^{-1} and the mass spectrum significant ions at *m/z* 205 $[C_{14}H_{21}O]^+$, 108 $[C_8H_{12}]^{+\cdot}$, and 94 $[C_7H_{10}]^{+\cdot}$ (base peak) suggesting a tetracyclic 3-oxotriterpene fragmenting through ring-C, with a centre of unsaturation within the C/D-ring fragment, and lacking a C-17 side chain. The ^1H NMR spectrum (Table 1) revealed the H-2 protons as *ddd* at δ2.47 and 2.44 and the H-1 equatorial proton as a *ddd* at δ1.90, supporting the presence of the 3-oxotriterpene nucleus. Other features of the spectrum were five methyl resonances at δ0.94, 0.99 (*d*, $J = 0.9$ Hz), 1.03, 1.04, 1.07, two olefinic protons as multiplets at δ5.64 and 5.56, and complex signals (1H each) with several couplings, centred at δ2.74, 2.34 and 1.69. A series of decoupling experiments linked these signals as follows: –CH(δ2.74)–CH(5.56)=CH(5.64)–CH_2 (1.69 and 2.34), with the δ2.34 signal showing additional coupling to the δ0.99 methyl doublet. These signals strongly suggested the sequence H-13–H-17–H-16–2H-15, as in **1**, in which the β H-15 shows additional long range W-bond coupling to the C-14 methyl substituent [4]. The ^{13}C NMR spectrum (Table 2) revealed resonances for C-1 to C-11 in close agreement with those for 3-oxodammaranes [5–7] while two tertiary olefinic carbons at δ133.85 and 129.84 confirmed the presence of the double bond.

Treatment of **1** with *meta*-chloroperbenzoic acid gave the corresponding epoxide (**2**), in the ^1H NMR spectrum of which the olefinic resonances were replaced by oxymethine signals at δ3.16 and 3.52 ($J = 3.2$ Hz), assigned to H-17 and H-16 respectively. In addition H-16 showed a *J* of 3.8 Hz to the α H-15 proton at δ1.33 which was identified by the absence of W-bond coupling to the C-14 methyl. From a Dreiding model it is clear that this coupling requires H-16 and H-17 to be on the same face of the D-ring as the α H-15 proton, thus placing the epoxy group in the β-configuration. The presence of the 16,17-β-epoxy group was supported by (i) the absence of coupling between H-16 and the β H-15 proton and between H-17 and the β H-13 proton (dihedral angle approximately 110° in each case) and (b) by the much stronger shielding of the β H-13 (0.93 ppm) and H-15 (0.72 ppm) protons in **2** in comparison with the α H-15 proton (shielding 0.36 ppm). These observations are in agreement with the expected

*Part 3 in the series "Chemistry of the Burseraceae". For Part 2 see ref. [5]. Paper KRP-005 of The Royal Geographical Society—National Museums of Kenya, Kora Research Project 1983.

Table 1. ^{1}H NMR assignments for the mansumbinanes and related compounds

Proton	1	2	3	4	5	6
H-1_{eq}	1.90 *ddd* (12.7, 7.5, 4.6)	1.90 *ddd* (12.6, 7.5, 4.6)	—	—	1.61 *dd* (2H) (17.0, 8.5)	1.90 *ddd* (13.2, 7.5, 4.4)
H-2_{ax}	2.47 *ddd* (15.6, 9.5, 7.5)	2.46 *ddd* (15.6, 9.6, 7.6)	2.45 *m*	— —	2.39 *dt* (17.0, 8.3)	2.47 *ddd* (15.6, 9.7, 7.5)
H-2_{eq}	2.44 *ddd* (15.6, 7.9, 4.6)	2.42 *ddd* (15.6, 7.9, 4.6)	2.45 *m*	— —	2.19 *dt* (17.8, 7.6)	2.42 *ddd* (15.6, 7.7, 4.4)
H-3_{ax}	—	—	—	3.19 *dd* (11.1, 5.0)	—	—
H-5	—	—	—	0.75 *dd* (11.2, 2.8)	1.98 *dd* (12.6, 2.9)	—
H-6	—	—	—	—	1.86 *ddt* (12.8, 12.6, 3.2)	—
H-13	2.74 *d*	1.80 *ddd* (16.0, 3.6, 0.8)	2.80 *dd* (9.7, 7.2)	2.71 *ddd* (13.1, 3.5, 1.8)	2.73 *br d* (10.5)	—
H-15β	2.34 *d*	1.62 *br d* (13.4)	2.49* ABq (14.4)	2.34 *ddd* (14.0, 2.7, 1.2)	2.34 *d*	1.65 *dd* (12.9, 7.1)
H-15α	1.69 *m*	1.34 *dd* (13.4, 3.8)	2.27* ABq (14.4)	1.69 *ddd* (12.5, 3.9)	1.69 *dd* (15.5, 2.9)	1.51 *dd* (12.6, 5.2)
H-16	5.64 *m*	3.52 *ddd* (3.8, 3.2, 0.5)	—	5.64 *m*	5.64 *m*	4.50 *dt* (7.1, 5.2)
H-17	5.56 *m*	3.16 *dd* (3.2, 0.5)	—	5.55 *m*	5.56 *m*	1.80 *dd* (12.1, 7.2)
H-24	—	—	—	—	—	5.11 *br t* (6.5, 1.3)
C=CH_2	—	—	—	—	4.67 *br d*/4.84 *dd* (1.4) (1.4)	—
2 × OMe	—	—	3.62/3.59 2 × *s*	—	—	—
Me	0.93 *s*	0.90 *s*	0.91 *d* (0.6)	0.77 *s*	0.86 *s*	0.86 *s*
	0.99 *d* (0.9)	0.92 *s*	1.01 *s*	0.84 *d* (0.8)	1.01 *d* (0.7)	0.93 *s*
	1.03 *s*	1.01 *s*	1.03 *s*	0.97 *s*	1.06 *s*	1.02 *s*
	1.04 *s*	1.04 *d* (1.4)	1.07 *s*	0.99 *d* (1.0)	—	1.05 *s*
	1.07 *s*	1.05 *s*	1.27 *s*	1.00 *s*	—	1.06 *s*
=C–Me	—	—	—	—	1.74 *d* (0.7)	—
C_{20}Me	—	—	—	—	—	1.28 *s*
Me_2	—	—	—	—	—	1.61/1.67 2 × *s*

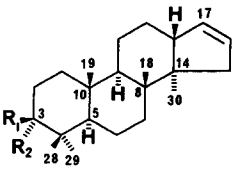
*Signals not assigned to α and β protons.

stereospecific introduction of the epoxide on the β-face of the D-ring due to the hindrance on the α-face caused by the C-14 methyl group.

The placement of the double bond between C-16 and C-17 was further confirmed by means of a ring-cleavage across the double bond using the Lemieux-Rudloff method [8] to give the dicarboxylic acid in high yield. Methylation of the product with diazomethane yielded **3**, the ^{1}H NMR of which (Table 1) revealed a double doublet at δ2.80 (J = 9.7, 7.2 Hz) for H-13 and an isolated AB quartet centred at δ2.49 and 2.27 (J = 14.4 Hz) for the H-15 protons. W-Bond coupling between β H-15 and the C-14 methyl was absent and the latter was deshielded to δ1.27. Structure **1** has recently been confirmed by X-ray diffraction studies [Schwalbe, C. H., unpublished].

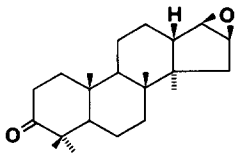
Mansumbinol (**4**) analysed for $C_{22}H_{36}O$ and differed from **1** only in the absence of the carbonyl substituent and its replacement by a secondary alcohol. Its identity as the 3-hydroxy derivative of **1** was confirmed by its oxidation with Jones' reagent to give **1** in quantitative yield. The oxymethine proton, H-3, was assigned to the axial (α) configuration by its large coupling constant (J = 11.1 Hz) thereby requiring that mansumbinol had the 3β-hydroxydammarane nucleus.

A third octanordammarane analysed fo $C_{22}H_{36}O_2$ and again revealed spectral characteristics for the 16,17-double bond. The IR spectrum showed an additional band at 1710 cm^{-1} and the ^{1}H NMR spectrum (Table 1) signals indicative of an isopropenyl moiety. The ^{13}C NMR spectrum (Table 2) gave signals comparable to rings C and D in **1** and **4** and also resonances at 180.1, 147.3 and 113.4 (triplet) ppm for a carboxylic acid carbonyl and a C=CH_2 moiety respectively. The above data are in agreement with structure **5** in which the A-ring of the dammarane has undergone fission between C-3 and C-4. This compound has been given the trivial name of



1 R_1,R_2 = O

4 R_1 = OH, R_2 = H



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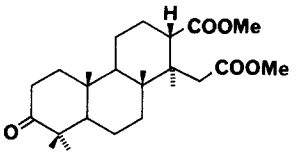

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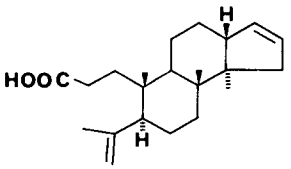


5

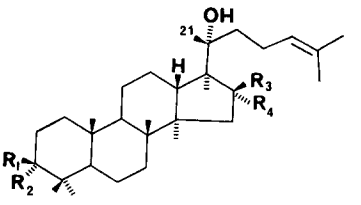
3,4-*seco*-mansumbinoic acid. Ring-A-*seco*-triterpenes are not uncommon in the Burseraceae [9].

The final compound did not give a molecular ion, the highest fragment being at *m/z* 442 $[C_{30}H_{50}O_2]^+$ due to loss of H_2O. The IR spectrum revealed bands for a carbonyl and for hydroxy function(s) while the ^{1}H NMR spectrum (Table 1) indicated a triterpene through the presence of eight methyl resonances. Two of there were deshielded to δ1.61 and 1.67 which together with an olefinic proton at δ5.11 required the presence of an unsubstituted CH=CMe$_2$ moiety in the C-17 side chain. Other major features of the ^{1}H NMR spectrum were: (a) the absence of a methyl doublet for C-21 and a relatively deshielded methyl resonance at δ1.28 suggesting that C-20 carried a tertiary hydroxy group as well as the 21-methyl, (b) signals for H-1$_{eq}$ and for H-2 protons typical of the 3-oxodammaranes (**1–3**), (c) an oxymethine proton at δ4.56 which showed coupling to three further discrete signals (all *dd*) at δ1.80, 1.65 and 1.51. As the δ1.65 resonance showed additional long-range coupling to the C-14 methyl it can be assigned to the β H-15 position thereby fixing the oxymethine proton at C-16. On this basis the triterpene can be assigned structure **6**. The ^{13}C NMR spectrum (Table 2) supports this assignment showing a carbonyl resonance at δ217.6, a tertiary carbinol at 74.2 and a quaternary carbinol at 75.5.

Reduction of **6** with sodium borohydride gave the corresponding 3β-hydroxy compound (**7**) and oxidation of **6** with Jones' reagent yielded the 3,16-dione (**8**). On acetylation **6** gave a monoacetate, the H-16 oxymethine proton undergoing deshielding to δ5.30.

Whilst **6** appears to be novel, the corresponding 3β-acetoxy derivative (**9**) has recently been reported from another species of Burseraceae, *Boswellia frereana* [10]. Using the GC modification of the Horeau method [11] the stereochemistry of **6** at C-16 was established as *S*, the same as reported for **9** [10]. The stereochemistry of **6** as *R* at C-20 follows from the close similarity of OR and ^{1}H NMR data for **7** prepared from **6** with literature data reported for **7** prepared by deacetylation of **9** [10].

The mansumbinanes represent a novel group of triterpenes in which the entire C-17 side chain has been lost. The precursor of this nucleus can be envisaged as a triterpene like **6** in which fission of the C-17/C-20 bond is achieved *via* loss of the C-20 hydroxy group or perhaps of the C-16 hydroxy group with concomitant formation of the 16,17-double bond. Direct treatment of **6** with base under reflux for several hours showed it to be relatively stable, yielding only trace amounts of mansumbinone and 3,4-*seco*-mansumbinoic acid. By contrast preparation of the 16-tosylate of **6** and refluxing with sodium ethoxide showed significant degradation with the major product having identical chromatographic properties to those of mansumbinone. The closest analogues of the mansumbinanes would appear to be the guggulsterols and guggulsterones isolated from the Indian species *Commiphora mukul* [9, 12]. In this species also there are compounds with a full C-17 side-chain, oxygenated at C-20 (e.g. **10**) but here fission of the side chain has occurred between C-20 and C-22 to give steroidal compounds such as guggulsterone I (**11**).



6 R_1,R_2 = O, R_3 = OH, R_4 = H

7 R_1 = R_3 = OH, R_2 = R_4 = H

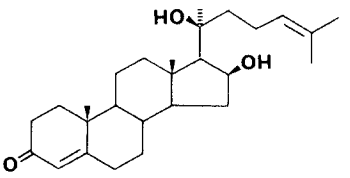
8 R_1,R_2 = R_3,R_4 = O

9 R_1 = OAc, R_3 = OH, R_2 = R_4 = H

Table 2. ^{13}C NMR assignments for the mansumbinanes and related compounds

Carbon No.	1	2	3	4	5	6
1	39.8	39.7	39.6	39.0	34.3*	39.7
2	34.0	33.9	33.8	27.4	28.3†	34.0
3	217.6	217.3	217.3	78.8	180.1	217.6
4	47.3	47.3	47.0	39.0	147.3	47.3
5	55.4	55.4	54.4	56.0	41.4	55.3
6	19.6	19.4	19.5	18.3	24.7†	19.6
7	34.7	34.5	33.3	35.4	34.0*	34.5
8	39.8	39.3	42.0	39.9	39.6	40.0
9	50.2	49.5	49.9	50.9	51.0	49.6
10	37.0	36.9	37.0	37.4	39.2	36.8
11	22.3	21.8	20.6	21.8	22.3	21.8
12	23.8	23.0	25.9	23.9	23.7	26.7
13	47.7	45.7	47.9	47.6	47.7	51.4*
14	52.9	59.1	43.5	52.9	53.3	47.6
15	39.8	36.2	40.3	39.9	39.9	43.5†
16	129.8*	60.4*	173.0*	129.9*	129.8§	74.2
17	133.9*	61.4*	175.0*	134.0*	133.9§	40.8*
18	17.8†	19.4†	16.2†	18.2†	17.9	17.9
19	15.8	15.8	15.7	16.0	19.9‡	15.6‡
20	—	—	—	—	—	75.5
21	—	—	—	—	—	25.9
22	—	—	—	—	—	43.2†
23	—	—	—	—	—	22.4
24	—	—	—	—	—	124.5
25	—	—	—	—	—	131.6
26	—	—	—	—	—	25.6
27	—	—	—	—	—	17.6
28	26.6	26.6	26.8	28.0	113.4	26.6
29	20.9	20.9	20.8	15.2	23.1‡	20.9
30	16.9†	15.7†	14.6	17.0†	17.0	15.7‡
2 × OMe	—	—	51.2	—	—	—

*†‡§Figures, in any column, with the same symbol are interchangeable.



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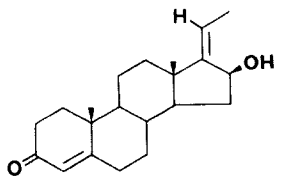

11

EXPERIMENTAL

Mps uncorrected. IR: KCl discs. NMR: $CDCl_3$ with TMS as internal standard, field strengths given in text. EIMS: 70 eV, direct probe insert between 120 and 150°. Petrol refers to the bp 60–80° fraction.

Plant material. Resin was collected in the Kora National Reserve, Kenya, in August 1983. A voucher specimen, P. G. Waterman 1073, is deposited at the East African Herbarium, Nairobi.

Extraction and isolation of the mansumbinanes. Ground resin (20 g) was extracted with Et_2O, the extract concd and chromatographed over a column of silica gel. The column was eluted with petrol containing increasing amounts of EtOAc. Fractions eluted with 0–5% EtOAc afforded compounds **1** (500 mg) and **5** (180 mg). Elution with 10% EtOAc gave a gum which was recrystallized from aq. Me_2CO to give **4** (110 mg). Compound **6** (180 mg) crystallized from eluant containing 30% EtOAc.

Mansumbinone (1). Crystallized from petrol (bp 40–60°)–EtOAc as needles, mp 122–123°, $[\alpha]_D^{25}$ +17° (*c* 0.60; $CHCl_3$). IR ν_{max} cm^{-1}: 3050, 1710. ^1H and ^{13}C NMR: see Tables 1 and 2 respectively. Found: $[M]^+$ 314.2607; $C_{22}H_{34}O$ requires 314.2609. EIMS *m/z* (rel. int.): 314 (30), 205 (33), 108 (69), 107 (27), 95 (67), 94 (100), 93 (35), 81 (40), 79 (34).

Mansumbinone epoxide (**2**). Compound **1** (100 mg) in 5 ml CH_2Cl_2 was treated with 10 ml *m*-chloroperbenzoic acid in CH_2Cl_2 (120 mg/5 ml). Excess peracid was removed using 10% Na_2SO_3 soln and the reaction mixture washed with 5% $NaHCO_3$ soln and then H_2O. The organic layer was separated and the product recrystallized from aq. Me_2CO to give **2** (70 mg) as needles, mp 140–141°, $[\alpha]_D^{25}$ +45° (*c* 0.55; $CHCl_3$). IR ν_{max} cm^{-1}: 1710. ^1H NMR and ^{13}C NMR: see Tables 1 and 2 respectively. Found: $[M]^+$ 330.2563; $C_{22}H_{34}O_2$ requires 330.2559. EIMS *m/z* (rel. int.): 330 (17), 312 (3), 219 (23), 205 (37), 135 (14), 124 (19), 106 (34), 97 (10), 93 (46), 55 (68), 41 (100).

Mansumbinone 16,17-dicarboxylic acid methyl ester (**3**). Compound **1** (100 mg) in 10 ml *t*-BuOH was slowly added to a soln containing 20 ml oxidant (sodium metaperiodate 20.86 g per litre 0.0025 M $KMnO_4$), 25 mg K_2CO_3, 20 ml *t*-BuOH and H_2O to 100 ml, and shaken for 8 hr at 25° [8]. The reaction was halted by addition of sodium metabisulphite, 2 g KOH added and the solvent removed (50°, 90 min). The soln remaining was acidified (10% H_2SO_4), extracted continuously with Et_2O for 8 hr, dried over anhydrous Na_2SO_4 and the solvent removed. Treatment with CH_2N_2 gave **3** (60 mg) as needles, mp 142–144°, $[\alpha]_D^{25}$ +55° (*c* 0.13; $CHCl_3$). IR ν_{max} cm^{-1}: 1735, 1700. ^1H NMR and ^{13}C NMR: see Tables 1 and 2 respectively. Found: $[M]^+$ 406.2717; $C_{24}H_{38}O_5$ requires 406.2719. EIMS *m/z* (rel. int.): 406 (86), 375 (30), 374 (23), 346 (27), 320 (18), 205 (100), 125 (31), 121 (21), 113 (13), 107 (26), 95 (30), 93 (26), 81 (43), 69 (32), 67 (40), 55 (47).

Mansumbinol (**4**). Recrystallized from aq. Me_2CO as needles, mp 110–112°, $[\alpha]_D^{25}$ −23° (*c* 0.18; $CHCl_3$). IR ν_{max} cm^{-1}: 3400 (broad), 3050. ^1H NMR and ^{13}C NMR: see Tables 1 and 2 respectively. Found: $[M]^+$ 316.2766; $C_{22}H_{36}O$ requires 316.2776. EIMS *m/z* (rel. int.): 316 (56), 208 (33), 207 (100), 191 (23), 135 (22), 108 (44), 107 (26), 95 (42), 94 (89), 93 (40), 81 (36), 79 (24), 69 (22), 55 (40). Oxidation of **4** (25 mg) in Me_2CO by titration with Jones' reagent followed by normal work-up gave a product (18 mg) identical in all respects to **1**.

3,4-seco-*Mansumbinoic acid* (**5**). Crystallized from petrol (bp 40–60°)–EtOAc as needles, mp 155–157°, $[\alpha]_D^{25}$ −18° (*c* 0.72; $CHCl_3$). IR ν_{max} cm^{-1}: 2700 (broad), 1710. ^1H NMR and ^{13}C NMR: see Tables 1 and 2 respectively. Found: $[M]^+$ 330.2539; $C_{22}H_{34}O_2$ requires 330.2559. EIMS *m/z* (rel. int.): 330 (41), 315 (8), 287 (10), 262 (7), 257 (27), 249 (33), 161 (23), 147 (42), 135 (37), 119 (44), 108 (100), 94 (89), 79 (72), 67 (39), 55 (42).

16(S),20(R)-*Dihydroxydammar-24-en-3-one* (**6**). Crystallized from petrol (bp 40–60°)–EtOAc as needles, mp 181–183°, $[\alpha]_D^{25}$ +55° (*c* 0.85; $CHCl_3$). IR ν_{max} cm^{-1}: 3300 (broad), 1710. ^1H NMR and ^{13}C NMR: see Tables 1 and 2, respectively. EIMS *m/z* (rel. int.): 440 $[M-H_2O]^+$ (18), 422 (50), 313 (11), 205 (17), 161 (20), 149 (23), 147 (32), 135 (59), 133 (24), 121 (37), 119 (30), 109 (100), 108 (98), 107 (64), 106 (24), 105 (31), 95 (68), 94 (76), 93 (74), 91 (29), 81 (67), 79 (41), 69 (71), 67 (39), 55 (53). *Acetylation of* **6**. Compound **6** (35 mg) dissolved in 4 ml pyridine was treated with 1 ml Ac_2O at room temp. for 24 hr. Dilution with H_2O and extraction with Et_2O gave the acetate (30 mg) as a gum. $[\alpha]_D^{25}$ +59° (*c* 0.21; $CHCl_3$). IR ν_{max} cm^{-1}: 3500, 1745, 1715. ^1H NMR (250 MHz): δ5.30 (1H, *dt*, *J* = 6.8, 3.9 Hz, H-16), 5.10 (1H, *t*, *J* = 5.8 Hz, H-24), 2.47 (1H, *ddd*, *J* = 15.6, 9.7, 7.5 Hz, H-2_{ax}), 2.42 (1H, *ddd*, *J* = 15.6, 7.7, 4.4 Hz, H-2_{eq}), 2.06 (3H, *s*, COMe), 1.92 (1H, *dd*, *J* = 12.5, 6.4 Hz, H-17), 1.80 (1H, *dd*, *J* = 14.3, 7.1 Hz, H-15), 1.68 (3H, *d*, *J* = 0.7 Hz, =CMe), 1.61 (3H, *s*, =CMe), 1.23, 1.08, 1.03, 1.01, 0.95, 0.93 (6 × 3H, 6 × *s*). EIMS *m/z* (rel. int.): 482 $[M-H_2O]^+$ (2), 457 (3), 440 (3), 423 (32), 422 (61), 417 (4), 357 (31), 313 (24), 219 (11), 205 (33), 175 (12), 143 (22), 135 (74), 125 (23), 121 (34), 109 (69), 95 (63), 81 (55), 71 (29), 43 $[C_3H_7]^+$ (48), 43 $[C_2H_3O]^+$ (100). *Horeau method for assignment of C-16 stereochemistry*. Compound **6** in dry pyridine was treated with excess of (±)-α-phenylbutyric anhydride. After normal work-up [11] an excess of (*R*)-α-phenylbutyric acid was identified by GC analysis.

3β,16(S),20(R)-*Trihydroxydammar-24-ene* (**7**). Compound **6** (30 mg) in EtOH–$CHCl_3$ was treated with excess $NaBH_4$ for 1 hr at 60° under reflux. The reaction mixture was cooled, acidified using dil. HCl and diluted with H_2O. The organic layer was then removed, washed with H_2O, dried and recrystallized from MeOH to give **8** (10 mg) as needles, mp 206–208° (lit. [10] 212–214°), $[\alpha]_D^{25}$ +18° (*c* 0.04; $CHCl_3$) (lit. [10] +17.8°). IR ν_{max} cm^{-1}: 3440 (broad). ^1H NMR (250 MHz): δ5.14 (1H, *t*, *J* = 7 Hz, H-24), 4.52 (1H, *dt*, *J* = 7.1, 5.5 Hz, H-16), 3.19 (1H, *dd*, *J* = 10.4, 5.3 Hz, H-3_{ax}), 1.69, 1.63, 1.30, 1.03, 0.97, 0.87, 0.85, 0.78 (8 × 3H, 8 × Me). EIMS *m/z* (rel. int.): 442 $[M-H_2O]^+$ (30), 424 (80), 360 (11), 341 (14), 315 (12), 207 (33), 135 (65), 121 (28), 109 (57), 95 (39), 81 (42), 71 (20), 69 (100), 55 (42), 43 (52).

20(R)-*Hydroxydammar-24-en-3,16-dione* (**8**). Compound **6** (50 mg) in Me_2CO was titrated with Jones' reagent and after normal work-up gave **8** (40 mg) as a yellow gum, $[\alpha]_D^{25}$ −17° (*c* 0.20; $CHCl_3$). Found: $[M]^+$ 456.3605; $C_{30}H_{48}O_3$ requires 456.3603. IR ν_{max} cm^{-1}: 3500, 1730, 1710. ^1H NMR (250 MHz): δ5.06 (1H, H-24), 1.67, 1.61, 1.11, 1.09, 1.09, 1.05, 0.98, 0.98 (8 × 3H, 8 × Me). EIMS *m/z* (rel. int.): 456 $[M]^+$ (1), 438 (59), 413 (49), 371 (28), 330 (21), 205 (16), 143 (37), 129 (51), 123 (40), 109 (100), 85 (89), 69 (42).

Base treatment of **6**. (i) Compound **6** (8 mg) was dissolved in Et_2O and refluxed with 1 M NaOH in EtOH for 3 hr. The reaction mixture was acidified with HCl and after removal of EtOH extracted into Et_2O. TLC analysis (silica gel; solvent, toluene–EtOAc–AcOH, 80:18:2) revealed **6** together with traces of **1** and **5**. (ii) Compound **6** (16 mg) was treated with TsCl at 0° overnight. The reaction mixture was diluted with water and extracted into Et_2O. The resulting 16-tosyl derivative of 6 was refluxed with NaOEt in EtOH (100 mg/10 ml) for 2 hr, the mixture acidified, evaporated to dryness and extracted into Et_2O. TLC of the ethereal extract revealed a mixture the major product being identical to **1**.

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