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香港坚木中的达玛烷型三萜*

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摘要 从楝科植物香港坚木 (*Dysoxylum hongkongense* (Tufch.) Merr) 的树叶中分得了 4 个新的达玛烷型三萜, 基于详细的光谱分析及与同类化合物的光谱数据比较鉴定了其结构, 分别命名为: 20R, 24R - 表 - 25 - 达玛烷烯 - 3 - 酮 (3), 16 β - 羟基达玛烷 - 20 (22), 25 - 二烯 - 3 - 酮 (4), 26 - 羟基达玛烷 - 20, 24 - 二烯 - 3 - 酮 (5) 和 3 β - 乙酰基 - 7 α , 21S, 25 - 三羟基 - 21S, 23R - 表 - 9 (11) - 达玛烷烯 (8)。

关键词 20R, 24R - 表 - 25 - 达玛烷烯 - 3 - 酮, 16 β - 羟基达玛烷 - 20 (22), 25 - 二烯 - 3 - 酮, 26 - 羟基达玛烷 - 20, 24 - 二烯 - 3 - 酮, 3 β - 乙酰基 - 7 α , 21S, 25 - 三羟基 - 21S, 23R - 表 - 9 (11) - 达玛烷烯, 香港坚木, 楝科
分类号 Q 946

达玛烷型三萜

Dammarane Triterpenoids from *Dysoxylum hongkongense*ZHANG Qi - Feng LUO Shi - De⁺ WANG Hui - Ying

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Abstract Four new dammarane type triterpenoids, named (20R, 24R) - epoxy - 25 - dammarane - 3 - one; 16 β - hydroxy - dammarane - 20 (22), 25 - dien - 3 - one (4); 26 - hydroxy - dammarane - 20, 24 - dien - 3 - one (5); 7 α , 21S, 25 - trihydroxy - 3 β - acetoxy - 21S, 23R - epoxy - 9 (11) - en - dammarane (8) together with four known compounds, ergosterol peroxide, dammarane - 20, 24 - dien - 3 β - ol, 20 - R - form hydroxy - dammaranone and cycloart - 23 - ene - 3 β , 25 - diol were isolated from the leaves of *Dysoxylum hongkongense*. The proposed structures were established by spectral analysis and comparisons with closely related compounds.

Key words *Dysoxylum hongkongense*, Meliaceae, dammarane triterpenoids, (20R, 24R) - epoxy - 25 - dammarane - 3 - one, 16 β - hydroxy - dammarane - 20 (22), 25 - dien - 3 - one, 26 - hydroxy - dammarane - 20, 24 - dien - 3 - one, 7 α , 21S, 25 - trihydroxy - 3 β - acetoxy - 21S, 23R - epoxy - 9 (11) - en - dammarane.

INTRODUCTION

Dysoxylum is a large genus with about 140 species distributed in South East Asia and Australia (Govindachari *et al*, 1994). In Yunnan Province of China about 10 species occur of which *D. hongkongense* (Tufch.) Merr. is a high value

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leafy timber tree, endemic to Xishuangbanna, which grows in lowland forests (Yunnan Institute of Botany, 1984). The leaves and bark are used as a medicine by the indigenous people for treating malaria (Yunnan Institute of Tropical Botany, 1983). The chemistry of *D. hongkongense* has not been previously studied. We describe the isolation and structure elucidation of four novel dammarane triterpenoids and four known compounds from the leaves of *D. hongkongense*.

RESULTS AND DISCUSSION

The crude petrol-soluble fraction was fractionated and purified to yield eight compounds. Four of these were ultimately identified as the known compounds: 5 α , 8 α -epidioxyergosta-6, 22-dien-3 β -ol, dammara-20, 24-dien-3 β -ol, 20-R-form-hydroxydammaranone and cycloart-23-ene-3 β , 25-diol. Six of these compounds had very similar ^1H -NMR and ^{13}C -NMR (Table 1) spectra, showing the presence of a series of structurally similar compounds. Furthermore, these compounds all give a positive Liebermann-Burchard test indicating the presence of triterpenoids.

Compound 3 was obtained as colourless needles. The molecular formula ($\text{C}_{30}\text{H}_{48}\text{O}_2$) can be deduced from its EIMS and ^{13}C -DEPT spectra. The ^{13}C -DEPT spectra of 3 exhibited the presence of 30 carbon atoms with two double bond carbons (δ 147.61, s; 110.42, t), a ketone carbonyl carbon (δ 217.78, s) and two oxygen bearing carbons (74.57, s; 76.08, d). From the molecular formula, 3 was considered to be a pentacyclic triterpenoid, with a cyclic ether moiety. The ^1H -NMR spectrum revealed the presence of a methylene group [δ 4.74 and 4.88 (each 1H, each s)], seven tertiary methyl groups [δ 0.80, 0.85, 0.91, 0.96, 1.00, 1.07, 1.66 (vinyl methyl)] and a ketonic group (δ 2.40, 2H, m). It also showed signals due to an oxygen bearing methine [δ 3.95 (1H, dd, $J_1 = 7.08$, $J_2 = 4.76$)]. The remaining 22 aliphatic hydrogen atoms resonated in complex, overlapping multiplet between δ 1.07 and 1.83 ppm. The IR spectrum of 3 showed the presence of a ketone carbonyl [1690 cm^{-1} (vs, C=O)] and olefinic groups [1640 cm^{-1} (w, C=C)]. The electron impact mass spectral fragmentation pattern of 3 was characteristic of a dammarane skeleton. Namely, 3 gave a significant fragment ion at m/z 205 ($\text{C}_{14}\text{H}_{21}\text{O}$) due to cleavage of the C-ring of the dammarane skeleton and showed a fragment at m/z 125 ($\text{C}_8\text{H}_{13}\text{O}$) ascribed to the side chain moiety as a result of C-17/20 bond fission. It also showed peaks at m/z 399 ($m - \text{C}_3\text{H}_5$, loss of an isopropenyl group) and m/z 315 ($m - \text{C}_8\text{H}_{13}\text{O}$, loss the side chain). The stereochemistry of Me-20 and H-24 was arranged by comparison of the ^{13}C -NMR spectrum of 3 with those of richenone and richenol, previously reported by Aalbersberg and Singh (1991). The configuration of C-17 can be determined as S by comparison of the ^{13}C -NMR data with those of salvilymitone and salvilymitol. The structures of salvilymitone and salvilymitol given by Pedreros and Rodriguez *et al* (1990) have been revised on the basis of X-ray crystallographic analysis. Thus, compound 3 is (20R, 24R)-epoxy-25-dammaren-3-one.

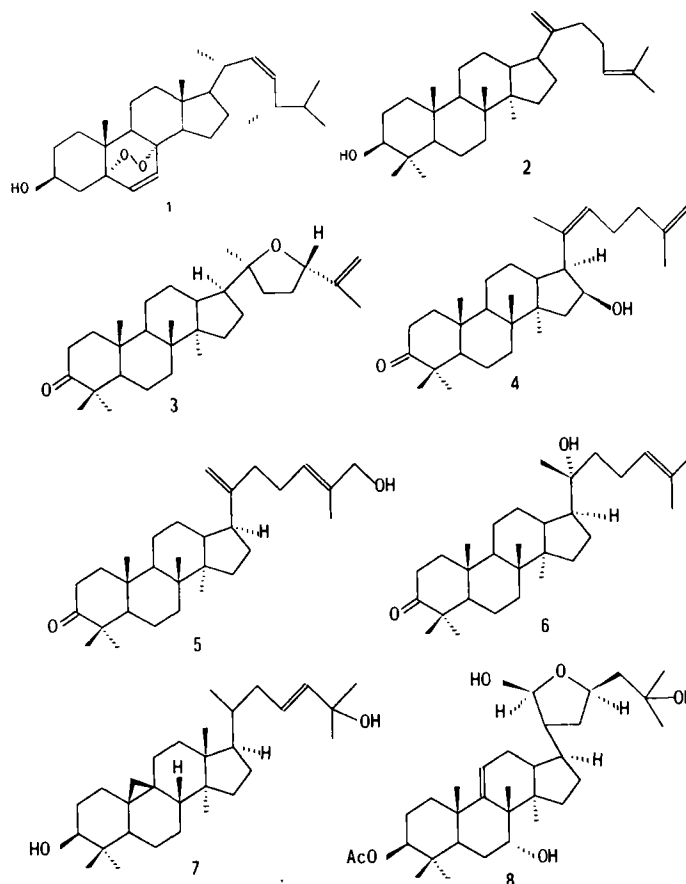
Compound 4 was obtained as colourless needles. The molecular formula ($\text{C}_{30}\text{H}_{48}\text{O}_2$) was determined by analysis of its EIMS and ^{13}C -DEPT spectra. The EIMS spectrum of 4 showed peaks at m/z 440 (m^+), 422 ($M - \text{H}_2\text{O}$), 407 ($M - \text{H}_2\text{O} - \text{CH}_3$), 366 ($M - \text{H}_2\text{O} - \text{C}_4\text{H}_8$). It also gave a significant fragment ion at m/z 205 ($\text{C}_{14}\text{H}_{21}\text{O}$) due to cleavage of the C-ring of the dammarane skeleton and showed a fragment ion at m/z 109 (C_8H_{13}) ascribed to the side chain moiety as a result of C-17/20 bond fission. The ^{13}C -DEPT spectra of 4 showed the presence of 30 carbon atoms with a ketone carbonyl carbon (δ 217.72, s), an isopropenyl group (δ 149.32, s, δ 110.97, t), and a trisubstituted double bond (δ 134.94, s, 127.77, d). Furthermore, down field signal at 66.89, d was observed. From the molecular formula, 4 could be deduced to be a tetracyclic dammarane triterpenoid. The ^1H NMR spectrum showed five shielded methyls (δ 0.85, 0.91, 0.98, 1.01, 1.05) and two vinyl methyls (δ 1.63, 1.70). In addition, a multiplet at 2.46 (2H), a multiplet at δ 4.45 (1H, ddd, $J = 13.52, 8.44, 5.04$), a doublet at δ 5.14 (1H, br, d, $J = 8.44$) and two singlets at δ 4.81,

4.86, each integrating for one proton, were observed. The multiplet centred to δ 4.45 indicates the presence of a proton on a carbon bearing an oxygen function and the 1H - singlets at δ 4.81 and 4.86 suggest the presence of a exomethylene group. The IR spectrum of 4 showed the presence of hydroxyl, ketonic and vinyl [3480 cm^{-1} , (vs, O - H); 1035 cm^{-1} (s, C - O), 1695 cm^{-1} (s, C = O), 1950 cm^{-1} (m, C = C), $890, 840\text{ cm}^{-1}$ (m)] groups. The location and stereochemistry of the hydroxyl group could be determined as 16 - β by comparison the ^{13}C NMR data of 4 with those reported for elabunin, whose structure was determined by 2D - NMR experiments (Kubo *et al*, 1990). The C - 16 bearing an α - OH resonated at δ 77.64 ppm and the H - 16 resonated at δ 4.05 ppm in elabunine, while in compound 4 the C - 16 bearing an β - OH resonated at δ 66.89 ppm and the H - 16 resonated at δ 4.45 ppm (Kubo *et al*, 1990). The presence of isopropyl group and the fragment peaks at 366 ($\text{M} - \text{H}_2\text{O} - \text{C}_4\text{H}_8$) and 55 (C_4H_7) indicated a 20(22), 25 - diene system in the side chain of 4. From all these evidence, compound 4 was identified as 16 β - hydroxy - dammara - 20(22), 25 - diene - 3 - one.

The EIMS and ^{13}C - DEPT spectra showed compound 5 to possess the molecular formula ($\text{C}_{30}\text{H}_{48}\text{O}_2$) and showed the characteristics of a dammarane skeleton. A resonance at δ 217.81 (s) could be assigned to a ketone carbonyl carbon and resonances at δ 134.54, s, 107.88, t, 128.23, d, 152.24, s could be assigned to olefinic carbons. A de - fielded resonance at δ 61.68 (t) could be assigned to a oxygen bearing carbon. An OH stretching band at 3380 cm^{-1} in the IR spectrum of 5 indicated that there was a hydroxyl group. The ^1H NMR spectrum revealed six C - methyl groups (δ 0.86, 0.93, 0.99, 1.02, 1.06, 1.78), One of them (δ 1.78) was a vinyl methyl. Other resolved features in the ^1H - NMR spectrum included a triplet at δ 2.17 (2H, t, $J = 7.40$), a multiplet at δ 2.43 (4H, m), a singlet at δ 4.11 (2H, s), at δ 4.68 and 4.74 (each 1H), and a triplet at δ 5.29 (1H, t, $J = 7.42$). The EIMS spectrum of 5 showed peaks at m/z 440 (M^+), 422 ($\text{M} - \text{H}_2\text{O}$), 409 ($\text{M} - \text{H}_2\text{O} - \text{CH}_3$), 357 ($\text{M} - \text{C}_5\text{H}_7\text{O}$), 343 ($\text{M} - \text{C}_6\text{H}_9\text{O}$), 315 ($\text{M} - \text{side chain, M} - \text{C}_8\text{H}_{13}\text{O}$), 205 ($\text{C}_{14}\text{H}_{21}\text{O}$, cleavage of C - ring). Analysis of these fragment ion peaks allowed the location of the double bonds and the hydroxyl group to be arranged as $\text{C}_{20} - \text{C}_{21}$, $\text{C}_{24} - \text{C}_{25}$ and C_{26} , respectively. By comparison of the ^{13}C - NMR spectrum of 5 with that of cucurbit - 5, 24 - diene - 3 - β , 11 α , 26 - triol, previously reported (Kasai *et al*, 1987), the double bond of $\text{C}_{24} - \text{C}_{25}$ was determined as the E form. Thus, compound 5 is 26 - hydroxy - dammara - 20, 24 - diene - 3 - one.

Compound 8 was crystallized from CHCl_3 as colourless needles that gave a parent ion in the HREIMS at m/z 532.3735 Daltons, appropriate for a molecular formula of $\text{C}_{32}\text{H}_{52}\text{O}_6$ (calcd. 532.376490). The ^{13}C - DEPT spectra of 8 exhibited an ester carbonyl carbon (170.65, s), two olefinic carbons (145.86, s, 118.15, d), and five down - field oxygen bearing carbons (97.29, d, 78.68, d, 78.42, d, 75.47, d, 73.25, s). From the molecular formula, compound 8 could be deduced to be a pentacyclic triterpenoids. The EIMS spectrum of 8 showed peaks at m/z 532 (M^+), 514 ($\text{M} - \text{H}_2\text{O}$), 499 ($\text{M} - \text{H}_2\text{O} - \text{CH}_3$), 456 ($\text{M} - \text{H}_2\text{O} - \text{CH}_3 - \text{COCH}_3$), 439 ($\text{M} - \text{H}_2\text{O} - \text{CH}_3 - \text{CH}_3\text{COOH}$), 356 ($\text{M} - \text{side chain, M} - \text{C}_8\text{H}_{15}\text{O}_3$), 341 ($\text{M} - \text{OH} - \text{CH}_3 - \text{side chain}$), 297 ($\text{M} - \text{OH} - \text{CH}_3\text{COOH} - \text{side chain}$), 293, 281 ($\text{M} - \text{OH} - \text{CH}_3 - \text{CH}_3\text{COOH} - \text{side chain}$), 239, 159 (side chain, $\text{C}_8\text{H}_{15}\text{O}_3$), 59 ($\text{C}_3\text{H}_7\text{O}$). The fragment ion peaks at m/z 293 and 239 (as a result of a cleavage of the C - ring) showed the double bond location at $\text{C}_9 - \text{C}_{11}$. By analysis the EIMS fragment pattern and the ^{13}C - DEPT data, 8 must be a dammarane triterpenoid with a cycle in the side chain, an acetate at the C_3 , and with a hydroxy at C_7 . The chemical shift value of C - 6 (δ 17.5) and C - 8 (δ 43.6) also indicated a hydroxyl group might be presented at the 7 α position. The ^1H - NMR spectrum of 8 showed signals at δ 5.30 (1H, br), 5.27 (1H, d, $J = 3.56$), 4.65 (1H, br), 4.24 (1H, m), 3.20 (1H, br) as well as eight methyls (δ 0.73, 0.81, 0.86, 0.90, 0.94, 1.23, 2.02). The structure and the stereochemistry of side - chain of 8 was determined by comparison of the ^{13}C - NMR data of 8 with those of 21 - O - acetyl - toosendantriol and 21 - O - methyl - toosendanpentol previously reported. The structures of 21 - O - acetyl - toosendantriol and 21 - O - methyl - toosendanpentol have been revised on the basis of

X-ray crystallographic analysis (Inada *et al*, 1989, Nakanishi *et al*, 1986). Thus, the structure of compound 8 could be elucidated as 7 α , 21S, 25-trihydroxy-3 β -acetoxy-21S, 23R-epoxy-9(11)-en-dammarane.



EXPERIMENTAL

General. all mps; uncorr. TLC: silica gel precoated glass plates with petroleum ether: EtOAc(4:1, 1:1). Spots were detected by spraying with 15% H_2SO_4 (in EtOH), followed by heating at 110°C. CC: silica gel (220~300 mesh), 1H -NMR and ^{13}C -NMR spectra were recorded at 400 MHz in $CDCl_3$ using TMS as int. standard.

Plant materials *Dysoxylum hongkongense* leaves were collected in June 1995 from Xishuangbanna and identified by Prof. Wang Hong (Kunming Institute of Botany, The Academy of Sciences of China, Kunming, Yunnan, China).

Extraction and isolation of the triterpenoids Dried and powdered *D. hongkongense* leaves (6.0 kg) was extracted with MeOH for 15 days at room temperature. Conc. of the MeOH extract under red. pres. below 40°C gave a syrup which was suspended in water and the suspension was extracted successively with petrol., CH_2Cl_2 and n-BuOH. The petrol. soluble material (170g) was chromatographed on silica gel using a petrol. (60~90°)-EtOAc gradient to give 8 Frs. Fr.2 was rechromatographed on silica gel, eluted with petrol-EtOAc (4:1) to give 5 α , 8 α -epidioxyergosta-3 β -6, 22-diene (1) (21mg) and dammara-20, 24-dien-3 β -ol (2) (324mg). Fr.3 was rechromatographed on silica gel, eluted with petrol.- Me_2CO (4:1) to give (20R, 24R)-epoxy-25-dammaren-3-one (3) (38mg). Fr.4

was rechromatographed on silica gel, eluted with petrol. - Me₂CO(4:1) to give 16 β -hydroxy - dammara - 20(22), 25 - dien - 3 - one (4) (17mg) and 26 - hydroxy - dammara - 20, 24 - dien - 30 - one (5) (16mg). Fr.6 was rechromatographed on silica gel, eluted with petrol. - EtOAc (3:1) to give 20 - R - form - hydroxydammaranone (6) (1137mg) and cycloart - 23 - ene - 3 β , 25 - diol (7) (19mg). Fr.7 was rechromatographed on silica gel, eluted with petrol. - EtOAc(2:1) to give 7 α , 21S, 25 - trihydroxy - 3 β - acetoxy - 21S, 23R - epoxy - 9(11) - en - dammarane(8) (124mg).

Table 1 ¹³C - NMR chemical shifts of compounds 1 ~ 8 (CDCl₃ solution. TMS as int. standard)

Carbon	1	2	3	4	5	6	7	8*
1	34.67, t	35.50, t	39.77, t	39.88, t	39.99, t	39.89, t	32.00, t	34.26, t
2	29.83, t	34.28, t	33.97, t	34.09, t	34.11, t	34.06, t	30.44, t	32.02, t
3	66.00, d	78.99, d	217.78, s	217.72, s	217.81, s	217.71, s	78.86, d	78.68, d
4	36.93, t	40.54, s	47.30, s	47.41, s	47.42, s	47.31, s	40.52, s	34.88, s
5	82.19, s	55.98, d	55.31, d	55.48, d	55.48, d	55.43, d	47.16, d	46.64, d
6	135.13, d	18.33, t	19.56, t	19.17, t	19.72, t	19.67, t	21.12, t	17.47, t
7	130.60, d	29.67, t	34.47, t	34.81, t	34.51, t	34.59, t	28.09, t	75.47, d
8	79.43, s	39.18, s	40.21, s	40.46, s	40.46, s	40.33, s	47.93, d	43.61, s
9	51.14, d	51.04, d	50.16, s	50.31, d	50.35, d	50.04, d	20.06, s	145.86, s
10	36.77, s	37.29, s	36.74, s	36.97, s	36.99, s	36.85, s	26.01, s	36.66, s
11	23.32, t	21.42, t	21.94, t	21.93, t	21.94, t	22.04, t	26.20, t	118.15, d
12	39.31, t	25.00, t	24.75, t	25.02, t	25.03, t	24.78, t	35.61, t	30.42, t
13	44.52, s	45.43, d	42.37, d	46.09, d	45.61, d	42.42, d	45.38, s	45.74, d
14	51.64, d	49.47, s	50.16, s	49.46, s	49.47, s	50.26, s	48.88, s	50.89, s
15	20.53, t	31.41, t	31.03, t	31.43, t	31.37, t	31.14, t	32.87, t	31.65, t
16	28.49, t	27.47, t	27.39, t	66.89, d	26.59, t	27.53, t	26.51, t	27.36, t
17	56.21, d	47.85, d	49.93, d	48.13, d	47.71, d	49.90, d	52.07, d	48.63, d
18	12.78, q	15.68, q	15.84, q	15.88, q	15.88, q	15.95, q	18.07, q	27.36, q
19	18.06, q	15.37, q	15.07, q	15.39, q	15.38, q	15.21, q	29.94, t	23.25, q
20	39.53, d	131.33, s	74.57, s	134.94, s	152.24, s	75.26, s	36.43, d	45.38, d
21	20.78, q	107.51, t	17.58, q	18.32, q	107.88, t	25.48, q	18.32, q	97.26, d
22	135.43, d	39.01, t	36.58, t	127.77, d	34.82, t	40.52, t	39.07, t	23.85, t
23	132.28, d	29.17, t	29.22, t	28.99, t	28.96, t	22.56, t	139.45, d	78.42, d
24	42.72, d	124.51, d	76.08, d	42.94, t	128.23, d	124.73, d	125.63, d	22.57, t
25	32.99, d	152.73, s	147.61, s	149.32, s	134.54, s	131.48, s	70.71, s	73.25, s
26	19.81, q	28.04, q	25.16, q	25.73, q	61.68, t	25.64, q	29.94, q	26.73, q
27	19.52, q	17.68, q	110.42, t	110.97, t	21.33, q	17.65, q	29.94, q	26.73, q
28	17.45, q	16.21, q	20.87, q	21.04, q	21.04, q	20.97, q	14.01, q	21.24, q
29		25.64, q	26.60, q	26.80, q	26.81, q	26.72, q	19.32, q	27.36, q
30		15.97, q	16.21, q	16.02, q	16.04, q	16.33, q	25.47, q	12.97, q

* The ¹³C - NMR chemical shifts of the acetyl group are 21.43 and 170.65 ppm.

5 α , 8 α - epidioxysterosta - 6, 22 - dien - 3 β - ol(1). colourless needles; mp 176 ~ 178°C, $[\alpha]_D^{25}$ - 32.9° (CHCl₃, c 1.0). IR_{max}^{KBr} cm⁻¹: 3400 (s, O - H), 2960, 2880, 1450, 1360, 1270, 1160, 1040, 970. EIMS: *m/z* (%): 428(M⁺, 8), 410(M - H₂O, 12), 396(M - O₂, 31), 377(6), 363(9), 337(4), 303(3), 285(3), 267(4), 251(5), 119(10), 107(19), 91(33), 81(50), 69(97), 55(100). ¹H - NMR: H - 3, 3.95, *m*; H - 6, 6.23, *d* (*J* = 8.32); H - 7, 6.49, *d*, (*J* = 8.32); H - 18, 0.83, *s*; H - 19, 0.88, *s*; H - 21, 1.00, *d* (*J* = 6.64), H - 22, 5.15, *dd* (*J*₁ = 15.32, *J*₂ = 7.24); H - 23, 5.23, *dd* (*J*₁ = 15.32, *J*₂ = 7.24); H - 26, 0.84, *d* (*J* = 6.42); H - 27, 0.82, *d* (*J* =

6.42); $H-28$, 0.91, $d(J=6.64)$. ^{13}C -NMR data; see Table 1.

Dammara-20, 24-dien-3 β -ol(2). colourless needles; mp 136°C, crystallized from CHCl_3 . $[\alpha]_D^{21.5} + 49^\circ$ (CHCl_3 , c 1.0). $\text{IR}_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3380 (vs, O-H), 2920, 2830, 1640 (w, C=C), 1450, 1440, 1390, 1365, 1030 (s, C-O), 970, 890 (s). EIMS; m/z (%): 426 (M^+ , 99), 408 ($M-\text{H}_2\text{O}$, 10), 393 ($M-\text{H}_2\text{O}-\text{CH}_3$, 7), 383 ($M-\text{C}_3\text{H}_7$, 17), 365 (6), 316 (15), 299 (14), 257 (6), 247 (8), 229 (11), 218 (35), 207 (75), 189 (55), 175 (25), 161 (31), 147 (26), 135 (46), 121 (36), 109 (73), 93 (58), 81 (49), 69 (100), 55 (52). ^1H -NMR: 0.75 (3H, s), 0.82 (3H, s), 0.84 (3H, s), 0.95 (6H, s), 1.58 (3H, br, s), 1.66 (3H, br, s), 3.18 (1H, dd, $J_1 = 11.04$, $J_2 = 5.16$), 4.67, 4.68 (each 1H, each, s, $H-21$), 5.16 (1H, s, $H-24$). ^{13}C -NMR data; see Table 1.

(20R, 24R)-Epoxy-25-dammaren-3-one (3). colourless needles; mp 225°C, crystallized from CHCl_3 , $[\alpha]_D^{21.5} + 57^\circ$ (CHCl_3 , c 1.0). $\text{IR}_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 2920, 2870, 1690 (vs, C=O), 1640 (w, C=C), 1440, 1380. EIMS; m/z (%): 440 (M^+ , 7), 425 ($M-\text{CH}_3$, 7), 399 ($M-\text{C}_3\text{H}_5$, 2), 359 (16), 341 (6), 316 (22), 315 (19, M -side chain), 301 (12), 300 (8), 285 (10), 245 (9), 229 (4), 221 (8), 219 (8), 205 (27), 189 (21), 177 (13), 163 (23), 143 (61), 135 (29), 125 (100, side chain), 107 (52), 95 (61), 81 (55), 67 (49), 55 (63). ^1H -NMR: 0.80 (3H, s), 0.85 (3H, s), 0.91 (3H, s), 0.96 (3H, s), 1.00 (3H, s), 1.07 (3H, s), 1.66 (3H, s), 2.40 (2H, m, $H-2$), 3.95 (1H, dd, $J_1 = 7.08$, $J_3 = 4.76$), 4.74, 4.88 (each 1H, each s, $H-27$). ^{13}C -NMR data; see Table 1.

16 β -Hydroxy-dammare-20(22), 25-dien-3-one (4). colourless needles. mp 182°C crystallized from MeOH, $[\alpha]_D^{21.5} + 58^\circ$ (CHCl_3 , c 1.0). $\text{IR}_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3480 (vs, O-H), 3110 (w), 2920, 2870, 1695 (vs, C=O), 1650 (w, C=C), 1450, 1385, 1375, 1035 (s, C-O), 890, 840 (s). EIMS; m/z (%): 440 (M^+ , 16), 422 ($M-\text{H}_2\text{O}$, 57), 407 ($M-\text{H}_2\text{O}-\text{CH}_3$, 14), 366 (13), 356 (38), 338 (11), 313 (17), 300 (11), 288 (9), 245 (35), 229 (14), 215 (15), 205 (37), 189 (19), 175 (17), 159 (21), 147 (26), 134 (45), 119 (34), 109 (side chain, 41), 95 (42), 85 (100), 67 (35), 55 (44). ^1H -NMR: 0.85 (3H, s), 0.91 (3H, s), 0.98 (3H, s), 1.01 (3H, s), 1.05 (3H, s), 1.68 (3H, s), 1.70 (3H, s), 4.45 (1H, ddd, $J_1 = 13.52$, $J_2 = 8.44$, $J_3 = 5.04$, $H-16$), 4.81, 4.86 (each 1H, each, s, $H-27$), 5.14 (1H, br, d, $J = 8.44$). ^{13}C -NMR data see Table 1.

26-Hydroxy-dammara-20, 24-dien-3-one (5). mp 69°C, $[\alpha]_D^{21.5} + 58^\circ$ (CHCl_3 , c 1.0). $\text{IR}_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3380 (vs, O-H), 2920, 2840, 1690 (vs, C=O), 1630 (m, C=C), 1440, 1370, 1000, 830 (s). EIMS; m/z (%): 440 (M^+ , 41), 422 ($M-\text{H}_2\text{O}$, 65), 409 ($M-\text{H}_2\text{O}-\text{CH}_3$, 14), 381 (10), 357 ($M-\text{C}_3\text{H}_7\text{O}$, 18), 343 ($M-\text{C}_6\text{H}_9\text{O}$, 18), 327 (M -side chain, 4), 316 (36), 300 (13), 285 (9), 273 (11), 257 (8), 245 (46), 232 (19), 221 (30), 205 (82), 189 (42), 175 (35), 163 (41), 147 (43), 134 (63), 121 (55), 109 (75), 95 (100), 81 (76), 69 (66), 55 (71). ^1H -NMR: 0.86 (3H, s), 0.93 (3H, s), 0.99 (3H, s), 1.02 (3H, s), 1.06 (3H, s), 1.78 (3H, s, $H-27$), 2.17 (2H, t, $J = 7.40$, $H-2$), 2.43 (m, 4H, $H-22$, $H-23$), 4.11 (2H, s, $H-26$), 4.68, 4.74 (each 1H, each s, $H-21$), 5.29 (1H, t, $J = 7.42$, $H-24$). ^{13}C -NMR data see Table 1.

20-R-hydroxydammara-24-en-3-one (6). colourless crystal; mp 134~136°C, crystallized from MeOH, $[\alpha]_D^{21.5} + 66^\circ$ (CHCl_3 , c 1.2). $\text{IR}_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3510 (s, O-H), 2930, 2840, 1680 (s, C=O), 1440. EIMS; m/z (%): 442 (M^+ , 3), 424 ($M-\text{H}_2\text{O}$, 86), 409 ($M-\text{H}_2\text{O}-\text{CH}_3$, 9), 355 ($M-\text{H}_2\text{O}-\text{C}_3\text{H}_9$, 51), 342 (18), 327 (M -side chain, 10), 313 (28), 205 (68), 189 (27), 177 (11), 163 (18), 149 (43), 135 (41), 123 (44), 109 (100), 95 (87), 81 (67), 69 (98). ^1H -NMR: 0.84 (3H, s), 0.90 (3H, s), 0.96 (3H, s), 1.00 (3H, s), 1.04 (3H, s), 1.11 (3H, s), 1.59 (3H, s), 1.65 (3H, s), 5.08 (1H, br, s, $H-24$). ^{13}C -NMR data; see Table 1.

Cycloart-23-ene-3 β , 25-diol (7). colourless needles. mp 204°C, $[\alpha]_D^{21.5} + 38^\circ$ (CHCl_3 , c 0.85). $\text{IR}_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3300 (vs, O-H), 2960, 2920, 2870, 1460, 1370, 970, 910 (s). EIMS; m/z (%): 442 (M^+ , 8), 424 (M

- H₂O, 86), 409 (M - H₂O - CH₃, 13), 379 (7), 366 (16), 353 (19), 355 (18), 313 (M - side chain, 23), 298 (10, loss of ring A along with C₆ and C₁₉), 245 (38), 215 (16), 205 (51), 203 (53), 187 (24), 173 (16), 159 (24), 147 (37), 134 (73), 121 (62), 107 (63), 95 (72), 81 (79), 69 (68), 53 (100). ¹H - NMR: 0.31 (1H, d, J = 4.20, H - 19), 0.52 (1H, d, J = 4.20, H - 19), 0.75 (3H, s), 0.83 (3H, d, J = 10.42, H - 21), 0.94 (3H, s), 1.06 (6H, s), 1.31 (3H, s), 1.32 (3H, s), 3.26 (1H, dd, J₁ = 11.14, J₂ = 4.40, H - 3), 5.57 (2H, dd, J₁ = 4.80, J₂ = 3.24, H - 23, H - 24). ¹³C - NMR data; see Table 1.

7a, 21S, 25 - Trihydroxy - 3β - acetoxy - 21S, 23R - epoxy - 9(11) - en - dammarane(8). mp 201 °C, crystallized from CHCl₃. [α]_D^{21.5} - 32° (CHCl₃, c, 1.0). IR_{max}^{KBr} cm⁻¹: 3400 (vs, O - H), 2970, 1720 (vs, C = O), 1450, 1380, 1270 (vs, C - O), 1090, 1040, 900, 810. EIMS: m/z(%): 532 (M⁺, 33), 514 (M - H₂O, 74), 499 (M - H₂O - CH₃, 56), 481 (M - 2H₂O - CH₃, 19), 456 (M - H₂O - CH₃ - COCH₃, 39), 439 (M - H₂O - CH₃ - CH₃COOH, 47), 421 (M - 2H₂O - CH₃ - CH₃COOH, 29), 409 (34), 393 (28), 381 (39), 367 (26), 356 (M - side chain, 21), 341 (M - OH - CH₃ - side chain, 27), 309 (11), 297 (M - OH - CH₃COOH - side chain, 16), 281 (M - OH - CH₃ - CH₃COOH - side chain, 48), 255 (32), 241 (25), 215 (29), 199 (27), 187 (43), 184 (50), 173 (37), 161 (45), 159 (side chain, 33), 145 (46), 133 (51), 119 (53), 107 (66), 91 (56), 79 (50), 69 (52), 59 (100). ¹H NMR: 0.73 (3H, s), 0.81 (3H, s), 0.86 (3H, s), 0.90 (3H, s), 0.94 (6H, s), 1.23 (3H, s), 2.02 (3H, s, OAc), 3.20 (1H, br, H - 7), 4.24 (1H, m, H - 23), 4.65 (1H, br, H - 3), 5.27 (1H, d, J = 3.56, H - 21), 5.30 (1H, br, H - 11). ¹³C NMR data see Table 1.

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