



# Tirucallane triterpenoids from *Dysoxylum hainanense*

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Received 12 October 1999; received in revised form 3 February 2000

## Abstract

Four tirucallane derivatives, 3 $\beta$ ,22*S*-dihydroxy-tirucalla-7,24-dien-23-one, 22,23-epoxy-tirucalla-7-ene-3 $\beta$ ,24,25-triol, 3 $\beta$ ,25-dihydroxy-tirucalla-7,23-diene, 23,26-dihydroxy-tirucalla-7,24-dien-3-one, together with two known triterpenoids, 24,25-epoxy-3 $\beta$ ,23-dihydroxy-7-tirucallene, tirucalla-7,24-diene-3 $\beta$ ,23-diol, were isolated from *Dysoxylum hainanense*. Their structures were elucidated on the basis of spectroscopic evidence. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** *Dysoxylum hainanense*; Meliaceae; Tirucallanes; 3 $\beta$ ,22*S*-Dihydroxy-tirucalla-7,24-dien-23-one; 22,23-Epoxy-tirucalla-7-ene-3 $\beta$ ,24,25-triol; 3 $\beta$ ,25-Dihydroxy-tirucalla-7,23-diene; 23,26-Dihydroxy-tirucalla-7,24-dien-3-one

## 1. Introduction

The genus *Dysoxylum* Bl., found in India, Southeast Asia, Australia and New Zealand, comprises about 200 species, 14 of which are distributed in China. About 10 species of this genus have been found in Yunnan province. *D. hainanense* Merr. is distributed in Guangxi Zhuang Autonomous, Hainan province, and Xishuangbanna, Yunnan province (Yunnan Institute of Botany, 1977). In previous reports (Aalbersberg and Singh, 1991; Singh and Aalbersberg, 1992; Govindachari et al., 1994), many dammarane triterpenoids were isolated from plants of this genus. However, no chemical work has been done on *D. hainanense*. As part of a program seeking bioactive compounds from Meliaceae plants (Luo et al., 1999), we examined the extracts of the bark from *D. hainanense*, and isolated four new triterpenoids (**1**)–(**4**), together with two known triterpenoids (**5**) and (**6**). In this paper, we describe the isolation and structural elucidation of these compounds.

## 2. Results and discussion

The ethanolic extract of the bark from *D. hainanense* was partitioned between H<sub>2</sub>O and EtOAc, and the EtOAc-soluble fraction was subjected to repeated silica gel CC to yield six triterpenoids: 3 $\beta$ ,22*S*-dihydroxy-tirucalla-7,24-dien-23-one (**1**), 22,23-epoxy-tirucalla-7-ene-3 $\beta$ ,24,25-triol (**2**), 3 $\beta$ ,25-dihydroxy-tirucalla-7,23-diene (**3**), 23,26-dihydroxy-tirucalla-7,24-dien-3-one (**4**), 24,25-epoxy-3 $\beta$ ,23-dihydroxy-7-tirucallene (**5**), tirucalla-7,24-diene-3 $\beta$ ,23-diol (**6**). The known compounds, (**5**) and (**6**), were identified by comparison of their spectroscopic data with those reported previously (Kumar et al., 1991; Mulholland and Taylor, 1988). The structures of the new compounds **1**–**4** were established as follows.

The molecular formula of **1** was assigned as C<sub>30</sub>H<sub>48</sub>O<sub>3</sub> by negative ion HR-FABMS. The IR spectrum exhibited absorptions at 3341 cm<sup>-1</sup> (OH), 1711 cm<sup>-1</sup> (C=O) and 1622 cm<sup>-1</sup> (C=C). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1** showed signals for seven tertiary methyls, a secondary methyl, and resonances for four methine carbons [ $\delta_C$  50.7 (C-5), 49.1 (C-9), 49.0 (C-17), 39.6 (C-20)], four quaternary carbons [ $\delta_C$  51.4 (C-14), 43.4 (C-13), 39.0 (C-4), 35.0 (C-10)], two olefinic carbons [ $\delta_C$  118.0 (*d*), 145.7 (*s*)], and one oxymethine

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carbon ( $\delta_C$  79.2,  $\delta_H$  3.22, *dd*,  $J = 10.7$  and  $5.3$  Hz). These data are consistent with a tirucallane–euphane system having a double bond between C-7 and C-8, and a  $3\beta$ -hydroxy group (Sherman et al., 1980; Chan et al., 1970; Jolad et al., 1981). In addition, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **1** indicated the presence of  $\alpha,\beta$ -unsaturated ketone signals [ $\delta_C$  201.4 (*s*), 159.3 (*s*), 119.3 (*d*),  $\delta_H$  6.06 (*s*)], and two downfield methyl protons [ $\delta_H$  2.19 (*s*), 1.95 (*s*)] attributed to a side chain, suggesting that a double bond was formed between C-24 and C-25, and a ketonic carbonyl group was present at C-23. These structural features were confirmed by cross signals from  $\delta_H$  6.06 (H-24) to  $\delta_C$  201.4 (C-23), H-24 to  $\delta_C$  26.7 (*q*, C-26), and H-24 to  $\delta_C$  21.3 (*q*, C-27) in the HMBC spectrum of **1**. In the HMBC spectrum, the resonance at  $\delta_H$  4.15 (*s*, H-22) showed cross peaks to  $\delta_C$  201.4 (C-23), 39.6 (*d*, C-20) and 12.0 (*q*, C-21), respectively, which revealed a hydroxyl substituent at C-22. The spectral data of the side chain were in good agreement with those of 22*S*-dihydroxytirucalla-7,24-dien-3,23-dione (Liang et al., 1988, 1989), the structure of which was confirmed by X-ray diffraction. Thus **1** was determined to be  $3\beta,22S$ -dihydroxytirucalla-7,24-dien-23-one.

HR-FABMS of compound **2** suggested the molecular formula  $\text{C}_{30}\text{H}_{50}\text{O}_4$ . The  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of **2** were similar to those of **1**, except for the side chain data. A singlet at  $\delta_H$  1.22 (6H) was attributed to protons of two methyl groups, suggesting attachment to an oxygenated carbon (C-25). Furthermore, signals for an oxymethine ( $\delta_C$  74.1) and an oxirane group ( $\delta_C$  60.4, 58.9) were also evident, and were attributed to the side chain. The observation of HMBC cross peaks between  $\delta_H$  1.02 (*d*, 6.6, H-21) and  $\delta_C$  60.4 (*d*, C-22),  $\delta_H$  3.46 (*d*, 8.4, H-24) and  $\delta_C$  25.5 (*q*, C-26, C-27), and between the former and 72.8 (*s*, C-25), indicated the side chain of **2** to be 22,23-epoxy-24,25-dihydroxy substituted. It was presumed that the C-20 configuration belongs to the tirucallane rather than the euphane series, since tirucallane derivatives occur widely in the Meliaceae while euphanes are restricted to *Melia* species (Purushothaman et al., 1985), and in light of the co-occurrence of **2** with compounds **1**, **5** and **6**. Thus **2** was deduced to be 22,23-epoxytirucalla-7-ene- $3\beta,24,25$ -triol.

Compound **3** possessed the molecular formula  $\text{C}_{30}\text{H}_{50}\text{O}_2$  as determined by HR-FABMS. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3** were similar to those of **2**, with the exception of the side chain resonances. The  $^1\text{H}$  NMR spectrum showed a singlet for two methyl groups which resonated at  $\delta_H$  1.30 (6H), suggesting attachment to an oxygenated carbon (C-25). This was supported by the presence of cross peaks between  $\delta_H$  1.30 (6H, H-26, H-27) and  $\delta_C$  70.7 (*s*, C-25) in the HMBC spectrum. The HMBC spectrum also exhibited cross signals between an olefinic proton  $\delta_H$  5.57 (*d*,

$J = 8.0$  Hz, H-24) and  $\delta_C$  70.7 (*s*, C-25), which indicated a double bond between C-23 and C-24. The small coupling constant ( $J = 8.0$  Hz) between H-23 and H-24 suggested a *Z*-type olefinic bond. Taking into account the co-occurrence of compounds **1**, **5** and **6** which also possess a tirucallane skeleton, compound **3** was determined to be  $3\beta,25$ -dihydroxytirucalla-7,23-diene.

Compound **4** was assigned the molecular formula  $\text{C}_{30}\text{H}_{48}\text{O}_3$  by HR-FABMS. The IR spectrum revealed absorptions for a hydroxyl group stretch at  $3341\text{ cm}^{-1}$ , a carbonyl group stretch at  $1713\text{ cm}^{-1}$  and an olefinic stretch at  $1632\text{ cm}^{-1}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **4** displayed the presence of six tertiary methyls, one secondary methyl, nine methylenes, characteristic methines at  $\delta_C$  53.7, 52.3, 48.4, 33.0, quaternary carbons at  $\delta_C$  51.3, 47.8, 43.5, 35.0, four olefinic carbons including two at  $\delta_C$  145.8 (*s*) and 117.9 (*d*), and a ketonic carbonyl ( $\delta_C$  216.7). These signals were the characteristic of the tirucallane-7-ene system with a 3-ketone (Mulholland and Taylor, 1988; Mondon et al., 1981).

An olefinic linkage was placed between C-24 and C-25 based on the observation that one methyl proton resonance was shifted downfield to  $\delta_H$  1.66 and the oxymethylene protons [ $\delta_H$  3.95 (2H, H-26)] appeared as a singlet peak in the  $^1\text{H}$  NMR spectrum of **4**. The assumption was confirmed by the presence of cross peaks between  $\delta_H$  5.31 (H-24) and  $\delta_C$  67.9 (*t*, C-26), and H-24 and  $\delta_C$  14.1 (*q*, C-27) in the HMBC spectrum, in which a correlation between H-24 and  $\delta_C$  66.7 (*d*, C-23) also confirmed a hydroxyl group at C-23. The NOE interaction between H-24 ( $\delta_H$  5.31) and H-26 ( $\delta_H$  3.95) in the NOESY spectrum indicated that the olefinic bond was *E*-type. Compound **4** was deduced to be a tirucallane on the basis of co-occurrence, and was determined to be 23,26-dihydroxytirucalla-7,24-dien-3-one.

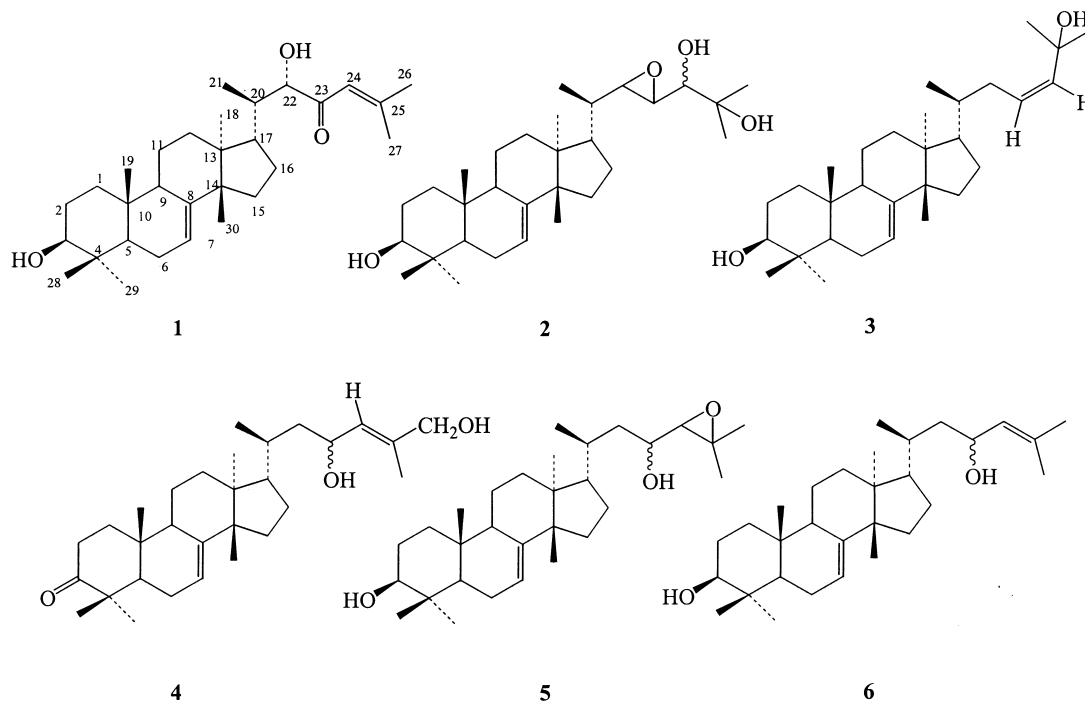
### 3. Experimental

#### 3.1. General

Mps: uncorrected; UV: MeOH; IR: KBr;  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and 2D-NMR spectra were recorded on Bruker AM-400 MHz and a DRX-500 spectrometers with TMS as internal standard and  $\text{CDCl}_3$  as solvent; chemical shift values ( $\delta$ ) were reported in ppm and coupling constants ( $J$ ) in Hz; FABMS data were recorded on a VG Autospec-3000 spectrometer; EIMS: 70 eV.

#### 3.2. Plant material

The bark of *D. hainanense* Merr. was collected from



Xishuangbangna, Yunnan province, P. R. China, in December 1996. The plant was identified by Prof. G.-D. Tao of the Xishuangbangna Botany Garden, Academia sinica. A voucher specimen was deposited in the herbarium of the Department of Taxonomy, Kunming Institute of Botany, Academia sinica, Kunming, P. R. China.

### 3.3. Extraction and isolation

The dried and powdered bark (4.2 kg) of *D. hainanense* was extracted with EtOH under reflux, and the solvent was evaporated in vacuo. The residue was partitioned in H<sub>2</sub>O and extracted with EtOAc. The EtOAc extracts were concentrated in vacuo to afford 72 g of residue, which was subjected to silica gel column chromatography, using CHCl<sub>3</sub>–Me<sub>2</sub>CO (from CHCl<sub>3</sub> to CHCl<sub>3</sub>–Me<sub>2</sub>CO, 1:1) as eluent. The fractions were monitored by TLC and combined. Fractions 2–5 were further purified on silica gel CC with petrol–Me<sub>2</sub>CO (9:1–2:1) as eluent followed by recrystallization to yield **1** (40 mg), **2** (25 mg), **3** (38 mg), **4** (36 mg), **5** (16 mg), **6** (10 mg).

### 3.4. 3β,22S-Dihydroxy-tirucalla-7,24-dien-23-one (**1**)

C<sub>30</sub>H<sub>48</sub>O<sub>3</sub>, white powder; mp 80–82°C; [α]<sub>D</sub><sup>26</sup> +33.3° (c 0.45, CH<sub>3</sub>OH); UV (MeOH) λ<sub>max</sub> (log ε): 240 (3.71) nm; IR (KBr) ν<sub>max</sub>: 3448, 2935, 2875, 1711, 1622, 1460, 1384, 1248, 1183, 1107, 1034, 993 and 822 cm<sup>-1</sup>;

Table 1  
<sup>13</sup>C NMR spectral data of compounds 1–6 (CDCl<sub>3</sub>, 100 MHz)

C	1	2	3	4	5	6
1	37.2 t	37.2 t	37.2 t	38.4 t	37.2 t	37.3 t
2	27.6 t	27.7 t	27.7 t	34.8 t	27.7 t	27.7 t
3	79.3 d	79.2 d	79.3 d	216.7 s	79.2 d	79.3 d
4	39.0 s	39.0 s	39.0 s	47.8 s	39.0 s	39.0 s
5	50.7 d	50.7 d	50.7 d	52.3 d	50.7 d	50.7 d
6	24.0 t	24.0 t	24.0 t	24.3 t	23.9 t	24.0 t
7	118.0 d	118.3 d	117.9 d	117.9 d	118.1 d	117.9 d
8	145.7 s	145.3 s	145.8 s	145.8 s	145.6 s	145.8 s
9	49.1 d	49.0 d	49.0 d	48.4 d	49.0 d	49.0 d
10	35.0 s	35.0 s	35.0 s	35.0 s	35.0 s	35.0 s
11	18.1 t	18.0 t	18.1 t	18.3 t	18.1 t	18.1 t
12	33.6 t	33.5 t	33.7 t	33.8 t	33.8 t	33.9 t
13	43.4 s	44.0 s	43.6 s	43.5 s	43.6 s	43.6 s
14	51.4 s	50.8 s	51.2 s	51.3 s	51.2 s	51.2 s
15	34.0 t	34.2 t	34.1 t	34.1 t	34.0 t	34.0 t
16	28.1 t	27.3 t	28.1 t	28.2 t	28.7 t	28.5 t
17	49.0 d	50.5 d	52.6 d	53.7 d	53.3 d	53.6 d
18	21.9 q	21.9 q	21.9 q	22.2 q	21.7 q	21.8 q
19	13.1 q	13.1 q	13.1 q	12.7 q	13.1 q	13.1 q
20	39.6 d	38.8 d	36.5 d	33.0 d	33.6 d	33.7 d
21	12.0 q	16.4 q	18.4 q	19.2 q	19.9 q	19.4 q
22	80.7 d	60.4 d	38.9 t	43.2 t	40.8 t	44.4 t
23	201.4 s	58.9 d	125.6 d	66.7 d	69.3 d	67.3 d
24	119.3 d	74.1 d	139.4 d	127.9 d	68.5 d	128.5 d
25	159.3 s	72.8 s	70.7 s	138.2 s	60.3 s	135.6 s
26	26.7 q	25.5 q	29.9 q	67.9 t	24.8 q	25.8 q
27	21.3 q	25.5 q	29.9 q	21.5 q	19.8 q	22.4 q
28	27.2 q	27.5 q	27.6 q	24.5 q	27.6 q	27.6 q
29	14.7 q	14.7 q	14.7 q	14.1 q	14.7 q	14.7 q
30	27.4 q	27.6 q	27.2 q	27.4 q	27.2 q	27.2 q

EIMS  $m/z$  (rel. int.): 456  $[M]^-$  (25), 441 (23), 421 (13), 386 (10), 373 (10), 355 (13), 343 (15), 327 (37), 309 (10), 299 (10), 213 (8), 185 (13), 171 (22), 161 (25), 145 (27), 133 (31), 109 (46), 95 (57) and 83 (100); HR-FABMS  $m/z$  455.3531  $[M - H]^-$  (calculated for  $C_{30}H_{47}O_3$ , 455.3525);  $^1H$  NMR spectral data ( $CDCl_3$ , 400 MHz):  $\delta$  6.06 (1H, *s*, H-24), 5.24 (1H, *br s*, H-7), 4.15 (1H, *s*, H-22), 3.22 (1H, *dd*,  $J = 9.0$  and 4.1 Hz, H-3), 2.19, 1.95 (each 3H, *s*, H-26, H-27), 1.01 (3H, *s*, H-30), 0.94 (3H, *s*, H-28), 0.83 (6H, *s*, H-29, H-18), 0.72 (3H, *s*, H-19), 0.61 (3H, *d*,  $J = 6.6$  Hz, H-21);  $^{13}C$  NMR spectral data: see Table 1.

### 3.5. 22,23-Epoxy-tirucalla-7-ene-3 $\beta$ ,24,25-triol (2)

$C_{30}H_{50}O_4$ , colorless needles ( $Me_2CO$ ); mp 118–120°C;  $[\alpha]_D^{26} -4.7^\circ$  ( $c$  0.95,  $CH_3OH$ ); IR (KBr)  $\nu_{max}$ : 3395, 2965, 2933, 2887, 1642, 1463, 1384, 1245, 1170, 1157, 1117, 1066, 1041, 990, 913, 886 and 731  $cm^{-1}$ ; EIMS  $m/z$  (rel. int.): 474  $[M]^+$  (40), 459 (10), 442 (15), 413 (10), 395 (12), 383 (10), 342 (27), 327 (25), 299 (17), 255 (17), 227 (15), 213 (16), 187 (30), 173 (36), 161 (84), 147 (49), 133 (57), 119 (60), 105 (67), 81 (63) and 59 (100); HR-FABMS  $m/z$ : 473.3541  $[M - H]^-$  (calculated for  $C_{30}H_{49}O_4$ , 473.3630);  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  5.25 (1H, *d*,  $J = 3.1$  Hz, H-7), 3.46 (1H, *d*,  $J = 8.4$  Hz, H-24), 3.22 (1H, *dd*,  $J = 10.7$  and 5.3 Hz, H-3), 3.08 (1H, *d*,  $J = 2.2$  Hz, H-22), 2.74 (1H, *dd*,  $J = 8.0$  and 2.2 Hz, H-23), 1.22 (6H, *s*, H-26, H-27), 1.02 (3H, *d*,  $J = 6.6$  Hz, H-21), 0.97 (3H, *s*, H-30), 0.95 (3H, *s*, H-28), 0.84 (3H, *s*, H-29), 0.79 (3H, *s*, H-18), 0.73 (3H, *s*, H-19);  $^{13}C$  NMR spectral data: see Table 1.

### 3.6. 3 $\beta$ ,25-Dihydroxy-tirucalla-7,23-diene (3)

$C_{30}H_{50}O_2$ , colorless needles ( $Me_2CO$ ); mp 168–170°C;  $[\alpha]_D^{27} -31.0^\circ$  ( $c$  0.45,  $CHCl_3$ ); IR (KBr)  $\nu_{max}$ : 3381, 2966, 2931, 2885, 1719, 1461, 1443, 1383, 1245, 1160, 1102, 1035, 971, 918 and 824  $cm^{-1}$ ; EIMS  $m/z$  (rel. int.): 442  $[M]^+$  (57), 427 (20), 409 (100), 391 (15), 327 (46), 309 (10), 255 (8), 215 (11), 203 (12), 187 (20), 161 (21), 109 (67), 95 (46), 81 (49), 69 (57); HR-FABMS  $m/z$ : 441.3758  $[M - H]^-$  (calculated for  $C_{30}H_{49}O_2$ , 441.3733)  $^1H$  NMR spectral data ( $CDCl_3$ , 400 MHz):  $\delta$  5.57 (1H, *d*,  $J = 8.0$  Hz, H-24), 5.55 (1H, *dd*,  $J = 8.0$  and 5.5 Hz, H-23), 5.23 (1H, *d*,  $J = 3.2$  Hz, H-7), 3.21 (1H, *dd*,  $J = 11.2$  and 4.2 Hz, H-3), 1.30 (6H, *s*, H-26, H-27), 0.94 (6H, *s*, H-28, H-30), 0.85 (3H, *s*, H-29), 0.84 (3H, *d*,  $J = 5.9$  Hz, H-21), 0.79 (3H, *s*, H-18), 0.72 (3H, *s*, H-19),  $^{13}C$  NMR spectral data: see Table 1.

### 3.7. 23,26-Dihydroxy-tirucalla-7,24-dien-3-one (4)

$C_{30}H_{48}O_3$ , colorless needles ( $Me_2CO$ ); mp 138–

140°C  $[\alpha]_D^{19} -72.5^\circ$  ( $c$  0.29,  $CH_3OH$ ); IR (KBr)  $\nu_{max}$ : 3341, 2952, 2861, 1713, 1632, 1462, 1452, 1388, 1371, 1310, 1263, 1013, 1008, 970 and 838  $cm^{-1}$ ; EIMS  $m/z$  (rel. int.): 456  $[M]^+$  (33), 438 (55), 423 (90), 405 (15), 380 (12), 340 (28), 325 (100), 313 (45), 271 (47), 245 (35), 203 (28), 189 (34), 173 (48), 161 (56), 147 (60), 135 (65), 119 (72), 107 (75) and 95 (81); HR-FABMS  $m/z$ : 455.3600  $[M - H]^-$  (calculated for  $C_{30}H_{47}O_3$ , 455.3525);  $^1H$  NMR spectral data ( $CDCl_3$ , 400 MHz):  $\delta$  5.31 (1H, *d*,  $J = 9.1$  Hz, H-24), 5.24 (1H, *d*,  $J = 2.7$  Hz, H-7), 4.44 (1H, *dt*,  $J = 3.9$  and 9.1 Hz, H-23), 3.95 (2H, *s*, H-26), 2.70 (1H, *dt*,  $J = 4.4$  and 14.5 Hz, H-2a), 2.18 (*br d*,  $J = 14.1$  Hz, H-2b), 1.66 (3H, *s*, H-27), 1.05 (3H, *s*, H-29), 0.99 (3H, *s*, H-28), 0.94 (3H, *s*, H-30), 0.95 (3H, *s*, H-19), 0.80 (3H, *d*,  $J = 5.6$  Hz, H-21), 0.72 (3H, *s*, H-18);  $^{13}C$  NMR spectral data: see Table 1.

### 3.8. 24,25-Epoxy-3 $\beta$ ,23-dihydroxy-7-tirucallene (5)

Prisms ( $Me_2CO$ ); mp 155–157°C; IR (KBr)  $\nu_{max}$ : 3480, 2953, 2880, 1684, 1460, 1381, 1335, 1302, 1278, 1252, 1163, 1147, 1035 and 990  $cm^{-1}$ ; EIMS  $m/z$  (rel. int.): 458  $[M]^+$  (35), 443 (12), 425 (13), 386 (10), 371 (100), 353 (45), 335 (10), 327 (28), 309 (15), 187 (30), 147 (33), 135 (45), 121 (52), 107 (55), 95 (52), 81 (48) and 69 (51);  $^1H$  NMR spectral data correspond to those of Mulholland and Taylor (1988);  $^{13}C$  NMR spectral data: see Table 1.

### 3.9. 3 $\beta$ ,23-Dihydroxy-tirucalla-7,24-diene (6)

White powder: mp 80–83°C; IR (KBr)  $\nu_{max}$ : 3445, 2935, 2873, 1720, 1461, 1380, 1252, 1180, 1036, 990, 891 and 549  $cm^{-1}$ ; EIMS  $m/z$  (rel. int.): 442  $[M]^+$  (20), 424 (12), 409 (30), 371 (12), 327 (35), 302 (10), 255 (14), 203 (17), 187 (25), 159 (30), 147 (35), 121 (65), 109 (100), 91 (78), 81 (82) and 69 (68);  $^1H$  NMR spectral data are in agreement with those of Kumar et al. (1991);  $^{13}C$  NMR spectral data: see Table 1.

## Acknowledgements

The authors wish to thank the Yunnan Committee of Science and Technology for financial support, and the members of the analytical group in the Laboratory of Phytochemistry, Kunming Institute of Botany, for the spectral measurements.

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