

## TIRUCALLANE DERIVATIVES FROM *PARAMIGNYA MONOPHYLLA* FRUITS

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**Key Word Index** *Paramignya monophylla*; Rutaceae; fruit; triterpenoids; tirucalladienes; flindissone.

**Abstract**—*Paramignya monophylla* fruits contain flindissone, deoxyflindissone and four new tirucalladienes, 3-oxotirucalla-7,24-dien-23-ol, 3-oxotirucalla-7,24-diene-21,23-diol and their 3 $\beta$ -hydroxy derivatives.

### INTRODUCTION

*Paramignya monophylla* is a woody climber growing at low or moderate altitudes in Sri Lanka and South Asia. Its fruits are spherical and contain several large seeds [1]. There has been no previous work on plants belonging to the genus *Paramignya*.

### RESULTS AND DISCUSSION

The hexane extract of fresh fruits of *P. monophylla* contained flindissone (1) [2] and two new triterpenoids 2 ( $C_{30}H_{48}O_2$ ) and 3 ( $C_{30}H_{50}O_2$ ), the IR spectra of which suggested that they are a keto-alcohol and an alcohol respectively. Their  $^1H$  NMR spectra contained signals for two vinyl protons at  $\delta$  5, a  $\dot{C}HOH$  proton at  $\delta$  4.5 and two vinyl methyls at  $\delta$  1.7. In addition the spectrum of 3 contained a signal for a second  $\dot{C}HOH$  proton at  $\delta$  3.25.

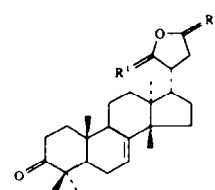
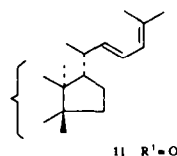
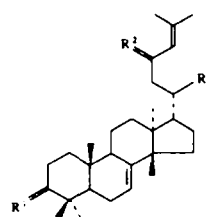
Acetylation of 2 gave a monoacetate 4, whose lithium ethylenediamine reduction gave tirucalla-7,24-dien-3 $\alpha$ -ol (5) and the known tirucalla-7,24-dien-3 $\beta$ -ol (6) [3]. Both 5 and 6 were oxidized to tirucalla-7,24-dien-3-one (7) [3] by pyridinium chlorochromate (PCC). Triterpenoid 2 is therefore a 3-oxotirucalla-7,24-dienol.

The PCC oxidation of 2 gave a diketone 8, whose IR spectrum showed an  $\alpha,\beta$ -unsaturated carbonyl group. The  $^1H$  NMR chemical shift of the vinyl methyl proton signals ( $\delta$  1.97 and 2.17) and the shift on oxidation of the vinyl proton at  $\delta$  5.12 to 6.07 suggested that 8 has a 23-oxo group. Further confirmation that 8 is tirucalla-7,24-diene-3,23-dione came from its mass spectrum whose base peak at  $m/z$  83 could be assigned to the ion formed by  $\alpha$ -cleavage of the  $\Delta^{22}$  bond and the UV  $\lambda_{max}$  at 238 nm, which agreed with the calculated value (239 nm). A 23-hydroxy group is therefore present in 2, whose structure must be that of 3-oxotirucalla-7,24-dien-23-ol.

The PCC oxidation of 3 gave 2 and 8, confirming that 3 is the 3-hydroxy derivative of 2. Its  $^1H$  NMR  $\dot{C}HOH$  signal appeared as a double doublet with  $J = 5$  and 11 Hz indicating that the hydroxyl group has 3 $\beta$  stereochemistry and that 3 is tirucalla-7,24-diene-3 $\beta$ ,23-diol.

Reduction of both flindissone (1) and 2 under Huang-Minlon conditions gave the same product, tirucalla-7,24-dien-23-ol (9), confirming that the stereochemistry at C-17 and C-23 is the same in both compounds. Ketalization of 2 with ethylene glycol gave a ketal (10) in which the 23-hydroxyl group has been eliminated. Removal of the ketal function from 10 gave tirucalla-7,22,24-trien-3-one (11).

The dichloromethane extract of the fruit gave deoxyflindissone (12) [2], 1–3 and two new triterpenoids, 13 and 14. The IR spectra of 13,  $C_{30}H_{48}O_3$ , and 14,  $C_{30}H_{50}O_3$ , suggested that they are a keto-alcohol and an alcohol respectively. Their  $^1H$  NMR spectra were similar to those of 2 and 3 except for the presence of two new



- 2  $R^1 = O, R^2 = OH, H, R^3 = Me$
- 3  $R^1 = \beta OH, \alpha H, R^2 = OH, H, R^3 = Me$
- 4  $R^1 = O, R^2 = OAc, H, R^3 = Me$
- 5  $R^1 = \alpha OH, \beta H, R^2 = H, H, R^3 = Me$
- 6  $R^1 = \alpha H, \beta OH, R^2 = H, H, R^3 = Me$
- 7  $R^1 = O, R^2 = H, H, R^3 = Me$
- 8  $R^1 = O, R^2 = O, R^3 = Me$
- 9  $R^1 = H, H, R^2 = OH, H, R^3 = Me$
- 10  $R^1 = -OCH_2CH_2O-, R^2 = H, H, R^3 = Me$
- 13  $R^1 = O, R^2 = OH, H, R^3 = CH_2OH$
- 14  $R^1 = \beta OH, \alpha H, R^2 = OH, H, R^3 = CH_2OH$
- 15  $R^1 = O, R^2 = OAc, H, R^3 = CH_2OAc$
- 16  $R^1 = \beta OAc, \alpha H, R^2 = OAc, H, R^3 = CH_2OAc$

- 1  $R^1 = H, OH, R^2 = H, CH = CMe_2$
- 12  $R^1 = H, H, R^2 = H, CH = CMe_2$
- 17  $R^1 = O, R^2 = H, CH = CMe_2$
- 18  $R^1 = H, H, R^2 = O$

double doublets at  $\delta$ 3.87 and 3.40, each due to a single proton, and a reduction in the number of methyl signals. The IR spectrum of **14** did not show carbonyl absorption and its  $^1\text{H}$  NMR spectrum contained a signal for an additional  $\text{CHOH}$  proton at  $\delta$ 3.20, suggesting that it is derived from **13** by the reduction of the carbonyl group.

Acetylation of **13** and **14** gave a diacetate (**15**) and a triacetate (**16**) respectively, while PCC oxidation of **13** gave deoxyflindissone (**12**) [2], flindissone lactone (**17**) [2] and another lactone **18** [4].

The formation of these oxidation products and the spectral data of **13** suggested it to be 3-oxotirucalla-7,24-diene-21,23-diol. Compound **14** is then the 3 $\beta$ -hydroxy derivative of **13**, the stereochemistry at C-3 being derived from the nature of the  $^1\text{H}$  NMR signal of the 3 $\alpha$  proton. Lithium aluminum hydride reduction of **13** gave **14** confirming that **14** is tirucalla-7,24-dien-3 $\beta$ ,21,23-triol.

## EXPERIMENTAL

Mps: uncorr. Optical rotations:  $\text{CHCl}_3$ ,  $25^\circ$ . IR: KBr; UV: MeOH.  $^1\text{H}$  NMR: 60 MHz,  $\text{CDCl}_3$ , TMS int. standard. MS: 70 eV. TLC Merck Silica Gel PF $_{254 \times 366}$ ; MPLC Merck Kieselgel 9385. Identities of compounds were established by comparison of physical constants, IR and  $^1\text{H}$  NMR unless otherwise stated.

*Paramignya monophylla* fruits were collected from Mooloya in central Sri Lanka and a voucher specimen is deposited in the University Herbarium.

**Extraction.** Fresh *P. monophylla* fruits (1.2 kg) were chopped and extracted successively with hexane and  $\text{CH}_2\text{Cl}_2$  at  $27^\circ$  for two 24 hr periods. Concn *in vacuo* of the hexane soln at  $40^\circ$  gave 28 g of hexane extract which was separated into a solid (5 g) and an oil (23 g). Extraction with  $\text{CH}_2\text{Cl}_2$  gave organic and aq. layers which on concn gave 45 and 11.6 g of extracts.

**Chromatography of the hexane extract of *P. monophylla* fruit.** The extract (4 g) was chromatographed on silica gel (120 g) at medium pressure using hexane- $\text{CH}_2\text{Cl}_2$ -MeOH mixts as eluents. Elution with  $\text{CH}_2\text{Cl}_2$ -hexane (7:3) gave 3-oxotirucalla-7,24-dien-23-ol (**2**) (850 mg), needles from  $\text{CH}_2\text{Cl}_2$ -hexane, mp  $169\text{--}171^\circ$ ,  $[\alpha]_D -67^\circ$  (c 0.5) (Found C: 82.0, H: 10.5;  $\text{C}_{30}\text{H}_{48}\text{O}_2$  requires C: 81.8, H 11.0); IR  $\nu_{\text{max}} \text{ cm}^{-1}$ : 3510, 1702, 1442 and 1107;  $^1\text{H}$  NMR (200 MHz):  $\delta$ 0.80, 1.02, 1.03, 1.07 and 1.13 (s, Me), 0.91 (d,  $J = 6$  Hz, 3H, 21-H), 1.73 and 1.76 (each d,  $J = 1$  Hz, 3H, 26-H and 27-H), 4.48 (m,  $W_{1:2} = 24$  Hz, 1H, 23-H), 5.10 (br d,  $J = 9$  Hz, 1H, 24-H) and 5.32 (dt,  $J = 4$  and 10 Hz, 1H, 7-H); MS  $m/z$  (rel. int.): 440 [ $\text{M}]^+$  (6), 425 (6) 422 (15), 407 (87), 351 (9), 341 (33), 325 (100), 313 (68) and 311 (68).

Elution with  $\text{CH}_2\text{Cl}_2$ -hexane (9:1) followed by further purification using MPLC gave on recrystallization from  $\text{CH}_2\text{Cl}_2$ -hexane needles of tirucalla-7,24-diene-3 $\beta$ ,23-diol (**3**) (100 mg), mp  $151\text{--}152^\circ$ ,  $[\alpha]_D -29^\circ$  (c 0.5); (HRMS 442.3799 [ $\text{M}]^+$ ; calc. for  $\text{C}_{30}\text{H}_{50}\text{O}_2$ : 442.3811) IR  $\nu_{\text{max}} \text{ cm}^{-1}$ : 3510, 1657 and 1442;  $^1\text{H}$  NMR (200 MHz):  $\delta$ 0.74, 0.78, 0.86, 0.88 and 0.97 ( $\times 2$ ) (s, Me), 0.89 (d,  $J = 6$  Hz, 3H, 21-H), 1.70 and 1.74 (each d,  $J = 1$  Hz, 3H, 26-H and 27-H), 3.25 (dd,  $J = 5$  and 11 Hz, 1H, 3 $\alpha$ -H), 4.45 (dt,  $J = 4$  and 10 Hz, 1H, 23-H), 5.10 (br d,  $J = 9$  Hz, 1H, 24-H) and 5.25 (m,  $W_{1:2} = 8$  Hz, 1H, 7-H); MS  $m/z$  (rel. int.): 442 [ $\text{M}]^+$  (9), 427 (9), 424 (16), 409 (64), 391 (11), 327 (100), 309 (41) and 187 (56).

Elution with  $\text{CH}_2\text{Cl}_2$ -MeOH (97:3) gave on recrystallization from  $\text{CH}_2\text{Cl}_2$ -hexane needles of flindissone (**1**) (600 mg), mp  $148\text{--}150^\circ$ ,  $[\alpha]_D -49^\circ$  (c 0.2) (lit. [2], mp  $147^\circ$ ,  $[\alpha]_D -45^\circ$ );  $^1\text{H}$  NMR (200 MHz):  $\delta$ 0.85, 0.90, 1.01, 1.04, 1.11 (s, Me), 1.69 and 1.70 (each d,  $J = 1$  Hz, 3H, 26-H and 27-H), 4.77 (m,  $W_{1:2} = 46$  Hz, 1H, 23-H), 5.14 (br d,  $J = 8$  Hz, 1H, 24-H), 5.26 (m,  $W_{1:2} = 12$  Hz,

1H, 7-H) and 5.30 (m,  $W_{1:2} = 8$  Hz, 1H, 7-H); MS  $m/z$  (rel. int.): 454 [ $\text{M}]^+$  (12), 436 (38), 421 (23), 393 (10), 297 (12), 150 (99) and 95 (100).

**3-Oxotirucalla-7,24-dien-23-yl acetate (4).** Alcohol (**2**) (220 mg) with  $\text{Ac}_2\text{O}$  (0.1 ml) and pyridine (2 ml) at  $27^\circ$  for 6 hr gave after work-up needles of 3-oxotirucalla-7,24-dien-23-yl acetate (**4**) (200 mg), mp  $172\text{--}174^\circ$ ,  $[\alpha]_D -67^\circ$  (c 0.5); (Found C: 79.7, H: 10.4;  $\text{C}_{32}\text{H}_{50}\text{O}_3$  requires C: 79.6, H 10.4); IR  $\nu_{\text{max}} \text{ cm}^{-1}$ : 1732, 1702, 1442 and 1220;  $^1\text{H}$  NMR:  $\delta$ 0.79, 1.02 ( $\times 2$ ), 1.06 and 1.11 (s, Me), 1.72 and 1.75 (each s, 3H, 26-H and 27-H), 2.00 (s, 3H, OAc), 5.06 (m, 1H, 24-H), 5.33 (m, 1H, 7-H) and 5.66 (m, 1H, 23-H); MS  $m/z$  (rel. int.): 482 [ $\text{M}]^+$  (5), 422 (27), 507 (83), 341 (21), 325 (100), 313 (48) and 311 (40).

**Lithium ethylenediamine reduction of acetate 4.** Acetate **4** (200 mg) and Li (150 mg) in ethylenediamine (10 ml) under  $\text{N}_2$  were refluxed until the soln turned blue and then heated at  $110^\circ$  for 25 min, cooled and BuOH (5 ml) added to destroy excess Li. Acidification (2 M HCl) followed by extraction with  $\text{CH}_2\text{Cl}_2$  gave an extract which was concd. Purification by prep. TLC (hexane-EtOAc, 9:1) gave the less polar tirucalla-7,24-diene-3 $\alpha$ -ol (**5**), needles from MeOH (75 mg), mp  $56\text{--}60^\circ$ ,  $[\alpha]_D -52.4^\circ$  (c 0.5); IR  $\nu_{\text{max}} \text{ cm}^{-1}$ : 3410, 1449 and 1031;  $^1\text{H}$  NMR:  $\delta$ 0.76, 0.83 and 0.99 ( $\times 3$ ) (s, Me), 0.93 (d,  $J = 5$  Hz, 3H, 21-H), 1.62 (br s, 6H, 26-H and 27-H), 3.26 (m,  $W_{1:2} = 6$  Hz, 1H, 3 $\beta$ -H), 5.02 and 5.33 (overlapping m, 1H each, 24-H and 7-H); MS  $m/z$  (rel. int.): 427 [ $\text{M} + 1]^+$  (25), 408 (32), 369 (100), 351 (35), 325 (75), 271 (25) and 245 (25) and the more polar tirucalla-7,24-diene-3 $\beta$ -ol (**6**), needles from MeOH- $\text{CH}_2\text{Cl}_2$  (65 mg), mp  $110\text{--}112^\circ$ ,  $[\alpha]_D -47.5^\circ$  (c 0.5); (lit. [3], mp  $105^\circ$ ,  $[\alpha]_D -49^\circ$ ).

**Tirucalla-7,24-dien-3-one (7).** (i) PCC (50 mg) was added to alcohol **5** (50 mg) in  $\text{CH}_2\text{Cl}_2$  (5 ml) and the mixt. stirred at  $25^\circ$  for 1.5 hr. The usual work-up gave on recrystallization from MeOH-Et $_2$ O needles of tirucalla-7,24-dien-3-one (36 mg), mp  $115\text{--}116^\circ$ ,  $[\alpha]_D -73.1^\circ$  (c 0.1) (lit. [3], mp  $115\text{--}116^\circ$ ,  $[\alpha]_D -70^\circ$ ); (ii) alcohol **6** (50 mg) on similar oxidation with PCC gave tirucalla-7,24-dien-3-one (40 mg), identical with that obtained above.

**Tirucalla-7,24-diene-3,23-dione (8).** Keto-alcohol **2** (100 mg) in  $\text{CH}_2\text{Cl}_2$  (5 ml) with PCC (150 mg) at  $0^\circ$  for 2 hr gave crystals of tirucalla-7,24-diene-3,23-dione (**8**) (75 mg) from  $\text{CH}_2\text{Cl}_2$ -MeOH, mp  $112\text{--}114^\circ$ ,  $[\alpha]_D -61.0^\circ$  (c 1.0); UV  $\lambda_{\text{max}} \text{ nm}$ : 238 (log  $\epsilon$  4.19); IR  $\nu_{\text{max}} \text{ cm}^{-1}$ : 1702, 1685, 1617 and 1442;  $^1\text{H}$  NMR:  $\delta$ 0.85, 1.02-1.10 (18H, Me), 1.89 and 2.16 (each br s, 3H, 26-H and 27-H), 5.33 (m,  $W_{1:2} = 7$  Hz, 1H, 7-H) and 6.08 (m,  $W_{1:2} = 3$  Hz, 1H, 24-H); MS  $m/z$  (rel. int.): 438 [ $\text{M}]^+$  (1), 423 (8), 369 (37), 351 (13), 325 (64) and 83 (100).

**Oxidation of tirucalla-7,24-diene-3 $\beta$ ,23-diol (3).** Similar PCC oxidation of diol **3** (100 mg) in  $\text{CH}_2\text{Cl}_2$  (10 ml) gave **2** (22 mg) and **8** (54 mg), identical with those isolated above.

**Tirucalla-7,24-dien-23-ol (9).** (i) Ketoalcohol **2** (200 mg), KOH (250 mg) and  $\text{N}_2\text{H}_4 \cdot 2\text{H}_2\text{O}$  (0.5 ml, 85%) in ethylene glycol (15 ml) was refluxed for 4 hr, distilled to  $200^\circ$  and then heated at  $200^\circ$  for 5 hr to give, on work-up followed by purification on prep. TLC ( $\text{CH}_2\text{Cl}_2$ ), tirucalla-7,24-dien-23-ol (**9**) (130 mg), plates from MeOH, mp  $114\text{--}116^\circ$ ,  $[\alpha]_D -34.3^\circ$  (c 0.6) (HRMS 426.3843 [ $\text{M}]^+$ , calc. for  $\text{C}_{30}\text{H}_{50}\text{O}$  426.3861); IR  $\nu_{\text{max}} \text{ cm}^{-1}$ : 3345 and 1669;  $^1\text{H}$  NMR:  $\delta$ 0.80, 0.81, 0.86-0.91 and 0.98 (18H, Me), 1.74 (br s, 6H, 26-H and 27-H), 4.40 (m,  $W_{1:2} = 24$  Hz, 1H, 23-H), 5.13 (br d,  $J = 10$  Hz, 1H, 24-H) and 5.27 (m, 1H, 7-H); MS  $m/z$  (rel. int.): 426 [ $\text{M}]^+$  (12), 411 (7), 393 (23), 311 (30) and 109 (100). (ii) Flindissone (**1**) (100 mg) in ethylene glycol (10 ml) on similar treatment with KOH (200 mg) and  $\text{N}_2\text{H}_4 \cdot 2\text{H}_2\text{O}$  (0.3 ml, 85%) gave **9** (68 mg) identical with that obtained above.

**3,3-Ethylenedioxytirucalla-7,22,24-triene (10).** Alcohol **2** (400 mg), TsOH (40 mg) and ethylene glycol (0.6 g) in  $\text{C}_6\text{H}_6$  (40 ml) refluxed for 0.5 hr in a Dean-Stark apparatus gave, after work-

up and purification by flash chromatography (hexane-CH<sub>2</sub>Cl<sub>2</sub>, 4:1), 3,3-ethylenedioxytirucalla-7,22,24-triene (384 mg) as an amorphous solid,  $[\alpha]_D -40^\circ$  (c 0.6) (Found C: 82.6, H: 10.4; C<sub>32</sub>H<sub>50</sub>O<sub>2</sub> requires C: 82.4, H 10.7); IR  $\nu_{\max}$  cm<sup>-1</sup>: 1690, 1200, 1109 and 782; <sup>1</sup>H NMR:  $\delta$  0.80, 0.83 ( $\times 2$ ), 0.97 and 1.01 ( $\times 2$ ) (18H, Me), 1.73 (br s, 6H, 26-H and 27-H), 3.94 (s, 4H, -OCH<sub>2</sub>CH<sub>2</sub>O-), 5.23 (m, 1H, 7-H) and 5.50 (m, 3H, 22-H, 23-H and 24-H); MS  $m/z$  (rel. int.): 466 [M]<sup>+</sup> (2), 367 (30), 357 (15), 187 (8), 109 (100) and 99 (95).

**Tirucalla-7,22,24-trien-3-one (11).** Ketal **10** (100 mg) and TsOH (50 mg) were refluxed in Me<sub>2</sub>CO (100 ml) for 12.5 hr. Work-up followed by prep. TLC (CH<sub>2</sub>Cl<sub>2</sub>-hexane, 3:2) gave tirucalla-7,22-24-trien-3-one as an amorphous solid, mp 110–116°,  $[\alpha]_D -41^\circ$  (c 0.5); (Found C: 85.9, H: 10.7; C<sub>30</sub>H<sub>46</sub>O requires C: 85.3, H: 11.0); IR  $\nu_{\max}$  cm<sup>-1</sup>: 1710, 1690 and 1388; <sup>1</sup>H NMR:  $\delta$  0.80, 0.83 ( $\times 2$ ), 0.97 and 1.01 (s, 15H, Me), 0.91 (d,  $J = 5$  Hz, 3H, 21-H), 1.73 (br s, 6H, 26-H and 27-H), 5.23 (m,  $W_{1/2} = 8$  Hz, 1H, 7-H) and 5.50 (m, 3H, 22-H, 23-H and 24-H); MS  $m/z$  (rel. int.): 423 [M+1]<sup>+</sup> (9), 407 (5), 340 (18), 325 (45), 313 (100), 297 (46), 271 (27) and 187 (49).

**Chromatography of the CH<sub>2</sub>Cl<sub>2</sub> extract of *P. monophylla* fruit.** The extract (25 g) was chromatographed on silica gel (350 g) at medium pressure using hexane-CH<sub>2</sub>Cl<sub>2</sub>-MeOH mixts as eluents. Elution with CH<sub>2</sub>Cl<sub>2</sub>-hexane (1:4) gave after prep. TLC (Et<sub>2</sub>O-hexane, 1:4) and recrystallization from Et<sub>2</sub>O, prisms of deoxyflindissone (**12**) (156 mg), mp 162–164° (needles from CH<sub>2</sub>Cl<sub>2</sub>-MeOH, mp 144–145°),  $[\alpha]_D -72.5^\circ$  (c 0.5) (lit. [2] mp 168–170°,  $[\alpha]_D -73^\circ$ ); <sup>1</sup>H NMR:  $\delta$  0.83, 1.00 ( $\times 3$ ), 1.08 (s, 15H, Me), 1.66 (br s, 6H, 26-H and 27-H), 3.08 (t,  $J = 8.5$  Hz, 1H, 21-H), 3.84 (dd,  $J = 8.5$  and 6.2 Hz, 1H, 21-H), 4.30 (m,  $W_{1/2} = 11$  Hz, 1H, 23-H), 5.11 (br d,  $J = 8$  Hz, 1H, 24-H) and 5.30 (m,  $W_{1/2} = 7$  Hz, 1H, 7-H); MS  $m/z$  (rel. int.): 438 [M]<sup>+</sup> (13), 423 (100), 405 (3), 285 (10) and 125 (36).

Elution with CH<sub>2</sub>Cl<sub>2</sub>-MeOH (99:1–97:3) gave 3-oxotirucalla-7,24-dien-23-ol (**2**) (536 mg), tirucalla-7,24-diene-3 $\beta$ ,23-diol (**3**) (200 mg) and flindissone (**1**) (400 mg), identical with those isolated above.

Elution with CH<sub>2</sub>Cl<sub>2</sub>-MeOH (23:2) gave 3-oxotirucalla-7,24-diene-21,23-diol (**13**) (4.4 g), needles from CH<sub>2</sub>Cl<sub>2</sub>-MeOH, mp 150–152°,  $[\alpha]_D -65^\circ$  (EtOH; c 1.0) (Found C: 75.8, H: 10.6; C<sub>30</sub>H<sub>48</sub>O<sub>3</sub>·H<sub>2</sub>O requires C: 75.4, H: 10.5) IR  $\nu_{\max}$  cm<sup>-1</sup>: 3375, 3175 and 1709; <sup>1</sup>H NMR (200 MHz):  $\delta$  0.87, 1.03, 1.04, 1.06 and 1.24 (s, 15H, Me), 2.05 (two s, each 3H, 26-H and 27-H), 3.40 (dd,  $J = 6.5$  and 12 Hz, 1H, 21-H), 3.87 (dd,  $J = 2$  and 12 Hz, 1H, 21-H), 4.55 (dt,  $J = 9$  and 7 Hz, 1H, 23-H), 5.18 (br d,  $J = 9$  Hz, 1H, 24-H) and 5.33 (m,  $W_{1/2} = 3$  Hz, 1H, 7-H); MS  $m/z$  (rel. int.): 456 [M]<sup>+</sup> (5), 438 (31), 423 (100), 405 (9), 323 (15) and 313 (15).

Elution with CH<sub>2</sub>Cl<sub>2</sub>-MeOH (22:3) followed by further purification using flash chromatography (hexane-EtOAc, 3:2) gave on recrystallization from hexane-EtOAc, needles of tirucalla-7,24-diene-3 $\beta$ ,21,23-triol (**14**) (250 mg), mp 142–144°,  $[\alpha]_D -34^\circ$  (EtOH; c 0.7) (HRMS 440.3638 [M–18]<sup>+</sup>, calc. for C<sub>30</sub>H<sub>48</sub>O<sub>2</sub> 440.3655) IR  $\nu_{\max}$  cm<sup>-1</sup>: 3100–3600, 1690, 1250 and 1049; <sup>1</sup>H NMR:  $\delta$  0.67, 0.86 ( $\times 2$ ), 0.97 ( $\times 2$ ) (s, 15H, Me), 1.69 (br s, 6H, 26-H and 27-H), 2.75 (br s, D<sub>2</sub>O exchangeable, 1H, OH), 3.24 (dd,  $J = 5$  and 9 Hz, 1H, 3 $\alpha$ -H), 3.39 (m,  $W_{1/2} = 4$  Hz, 1H, 21-H), 3.94 (m,  $W_{1/2} = 3$  Hz, 1H, 21-H), 4.33 (m,  $W_{1/2} = 16$  Hz, 1H, 23-H), 5.13 (m,  $W_{1/2} = 6$  Hz, 1H, 24-H) and 5.30 (m,  $W_{1/2} = 5$  Hz, 1H, 7-H); MS  $m/z$  (rel. int.): 458 [M]<sup>+</sup> (0.8), 440 (21), 425 (100), 407 (15), 285 (27) and 125 (42).

**3-Oxotirucalla-7,24-diene-21,23-diol, diacetate (15).** Diol **13** (100 mg) with Ac<sub>2</sub>O (0.25 ml) and pyridine (2.5 ml) at 27° for 5.5 hr gave after work-up, 3-oxotirucalla-7,24-diene-21,23-diacetate, needles from CH<sub>2</sub>Cl<sub>2</sub>-MeOH (80 mg), mp 114–116°,  $[\alpha]_D -53^\circ$  (c 0.9); (Found C: 75.8, H: 9.7; C<sub>34</sub>H<sub>52</sub>O<sub>5</sub> requires C: 75.5, H: 9.7); IR  $\nu_{\max}$  cm<sup>-1</sup>: 1735, 1707, 1470, 1442 and 1239; <sup>1</sup>H NMR:  $\delta$  0.82, 1.03 ( $\times 3$ ) and 1.18 (s, 15H, Me), 1.76 (br s, 6H, 26-H and 27-H), 2.07 and 2.17 (each s, 3H, OAc), 4.06 (m,  $W_{1/2} = 14$  Hz, 2H, 21-H), 5.09 (br d,  $J = 9$  Hz, 1H, 24-H), 5.33 (m,  $W_{1/2} = 8$  Hz, 1H, 7-H) and 5.66 (m,  $W_{1/2} = 12$  Hz, 1H, 23-H); MS  $m/z$  (rel. int.): 540 [M]<sup>+</sup> (74), 525 (2), 497 (19), 480 (21), 465 (100), 420 (45), 405 (81), 313 (60) and 323 (50).

**Tirucalla-7,24-diene-3 $\beta$ ,21,23-triol, triacetate (16).** Triol **14** (50 mg) with Ac<sub>2</sub>O (0.15 ml) and pyridine (0.6 ml) at 27° for 17 hr gave after prep. TLC [CH<sub>2</sub>Cl<sub>2</sub>], tirucalla-7,24-diene-3 $\beta$ ,21,23-triol, triacetate (40 mg), plates from CH<sub>2</sub>Cl<sub>2</sub>-MeOH, mp 125–127°,  $[\alpha]_D -12^\circ$  (c 0.9); (Found C: 73.8, H: 9.4; C<sub>36</sub>H<sub>56</sub>O<sub>6</sub> requires C: 73.9, H: 9.4); IR  $\nu_{\max}$  cm<sup>-1</sup>: 1740, 1723, 1670, 1220 and 826; <sup>1</sup>H NMR:  $\delta$  0.77, 0.80, 0.83, 0.93 and 0.94 (s, 15H, Me), 1.72 (br s, 6H, 26-H and 27-H), 1.97, 2.03 and 2.06 (each s, 3H, OAc), 4.03 (m,  $W_{1/2} = 12$  Hz, 2H, 21-H), 4.51 (dt,  $J = 9$  and 5 Hz, 1H, 3 $\alpha$ -H), 5.03 (br d,  $J = 10$  Hz, 1H, 24-H), 5.30 (m,  $W_{1/2} = 6$  Hz, 1H, 7-H) and 5.60 (m,  $W_{1/2} = 16$  Hz, 1H, 23-H); MS  $m/z$  (rel. int.): 584 [M]<sup>+</sup> (6), 524 (15), 509 (41), 464 (100), 449 (77), 427 (32), 421 (17), 408 (34), 389 (94), 367 (53), 357 (66), 341 (56), 335 (19) and 297 (84).

**Oxidation of 3-oxotirucalla-7,24-diene-21,23-diol (13).** Diol **13** (300 mg) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) on oxidation with PCC (500 mg) for 13.5 hr gave on work-up followed by prep. TLC (hexane-Et<sub>2</sub>O, 5:1) the least polar deoxyflindissone (**12**) (50 mg), identical with that obtained above, flindissone lactone (**17**) (35 mg), needles from EtOAc, mp 187–189°,  $[\alpha]_D -87.5^\circ$  (c 0.5) (lit. [2], mp 193–195°,  $[\alpha]_D -87^\circ$ ); <sup>1</sup>H NMR (200 MHz):  $\delta$  0.84, 1.04, 1.06, 1.08 and 1.13 (s, Me), 1.75 and 1.76 (each d,  $J = 1$  Hz, 3H, 26-H and 27-H), 5.03 (dt,  $J = 5$  and 9 Hz, 1H, 23-H), 5.21 (br d,  $J = 10$  Hz, 1H, 24-H) and 5.33 (m,  $W_{1/2} = 9$  Hz, 7-H); MS  $m/z$  (rel. int.): 452 [M]<sup>+</sup> (7), 437 (100), 419 (6), 391 (11), 311 (11), 295 (20) and 187 (10), and the most polar  $\gamma$ -lactone **18** (35 mg), needles from Et<sub>2</sub>O, mp 188–189°,  $[\alpha]_D -61.5^\circ$  (c 0.4) (lit. [4] mp 188–189°); <sup>1</sup>H NMR:  $\delta$  0.84, 1.04 ( $\times 3$ ) and 1.12 (s, Me), 3.93 (dd,  $J = 8$  and 9 Hz, 1H, 21-H), 4.35 (dd,  $J = 9$  and 6 Hz, 1H, 21-H) and 5.36 (br d,  $J = 4$  Hz, 1H, H-7); MS  $m/z$  (rel. int.): 398 [M]<sup>+</sup> (20), 383 (100), 364 (28) and 185 (20).

**Tirucalla-7,24-dien-3,21,23-triol (14).** Diol **13** (135 mg) refluxed with LiAlH<sub>4</sub> in THF (15 ml) for 0.5 hr gave on work-up tirucalla-7,24-dien-3,21,23-triol (105 mg), identical with **14** obtained above.

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