Three New Triterpenoids from *Azadirachta indica*

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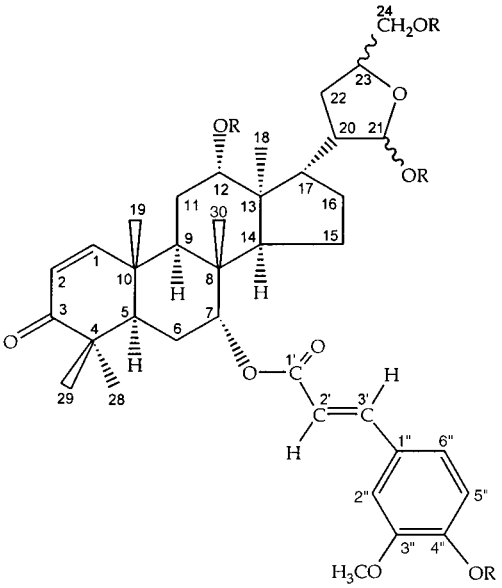
A new trinortriterpene, meliacinolactol (**1**), and two new tetranortriterpenes, limocin C (**2**) and limocin D (**3**), along with a known constituent, azadiradionolide, were isolated from the fresh fruit coats of *Azadirachta indica* and were characterized by chemical transformation and spectroscopic experiments, including 2D-NMR techniques.

1. Introduction. – The motivation for the continuous studies on the chemical constituents of various parts of *Azadirachta indica* A. JUSS (neem), a member of the family Meliaceae, is the well-known therapeutic and pesticidal activities of its constituents for which the tree has been reputed for decades [1–6]. The present study on the terpenoid constituents of the MeOH extract of fresh fruit coats of *A. indica* resulted in the isolation and characterization of three new constituents, *i.e.*, the tetracyclic trinortriterpenoid **1** and the tetracyclic tetranortriterpenoids **2** and **3** (characterized as the isomer mixture), along with a known compound, azadiradionolide [7].

2. Results and Discussion. – Compound **1**, called meliacinolactol, was obtained as an amorphous powder. The IR spectrum of **1** exhibited absorptions at 3600–3200 cm^{-1}, with a shoulder at 3520 cm^{-1} (OH), and at 1710 and 1692 cm^{-1} (CO groups of RCH=CHCOOR and RCH=CHCOR). The structure of meliacinolactol (**1**) was established as 21,23-epoxy-7α-[(*E*)-feruloyloxy]-12α,21ξ,24-trihydroxy-25,26,27-trinorapotirucall-1-en-3-one[1]) by ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*), ^{1}H,^{1}H-COSY-45°, NOESY, and MS data, and by its transformation to tetraacetate **1a**.

The ^{1}H-NMR spectrum (*Table 1*) of **1** indicated the apotirucallane[1]) skeleton with five Me groups at quaternary C-atoms (Me(18), Me(19), Me(28), Me(29), and Me(30)) and characteristic signals at δ 7.09 (H–C(1)) and 5.81 (H–C(2)) with $J(1,2) = 10.2$, for the enone moiety of ring A. This ring system was also supported by the diagnostic mass fragment ions **a**–**d** (*Fig. 2* and *Exper. Part*) in the HR-EI-MS [6–10]. The molecular-ion peak M^+ was not observed in the EI-MS and HR-EI-MS, but the fragment *m*/*z* 445.2944 ($C_{27}H_{41}O_5^+$, **e**) and its intense counterpart *m*/*z* 194.0570 ($C_{10}H_{10}O_4^+$, **f**) furnished the molecular formula of M^+ as $C_{37}H_{50}O_9$ (M_r 638). It was further confirmed by a quasi-molecular ion at *m*/*z* 639 in the FAB-MS (positive-ion mode). These observations also indicated the presence of an (*E*)-feruloyloxy[1]) moiety in the molecule. The (*E*) configuration of its C=C bond and the *meta*/*para* disubstitution were confirmed by the δ(H)s and characteristic *J* values (*Table 1*) [8][11]. The interaction of the MeO group with H–C(2″) in the NOESY experiment established the position of the MeO and OH group at C(3″) and C(4″), respectively (*Fig. 1*). A characteristic ^{1}H-NMR signal of H_β–C(7) at δ 5.29 (*dd*) was observed, allowing us to assign the 7-position to the feruloyloxy

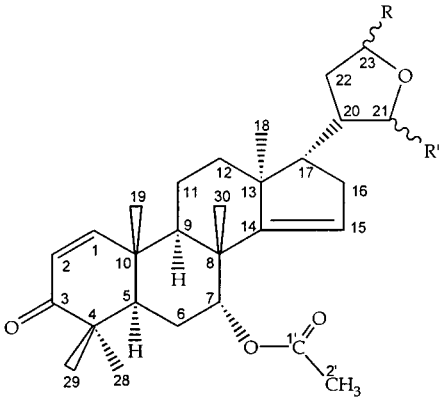
1) The parent tirucallane is identical to the parent euphane except the configuration at C(20). The systematic name of former is (13α,14β,17α,20*S*)-lanostane. When 14β-Me migrates to the 8β-position, parent apotirucallane is formed. The systematic name of ferulic acid is 3-(4-hydroxy-3-methoxyphenyl)prop-2-enoic acid.



NOEs:
H_β–C(12)/Me(30)
Me(18)/H–C(3′)
Me(19)/Me(29), Me(30)
H–C(21)/CH_2(24)
Me(28)/H–C(3′)
H–C(2′)/H–C(2″)
H–C(2″)/MeO

$^1H,^1H$–COSY-45°:
H–C(1)/H–C(2)
CH_2(6)/H_α–C(5), H_β–C(7)
CH_2(11)/H_α–C(9), H_β–C(12)
CH_2(15)/H_α–C(14), CH_2(16)
H–C(17)/CH_2(16), H–C(20)
H–C(20)/H–C(21), CH_2(22)
H–C(23)/CH_2(22), CH_2(24)

1 R = H meliacinolactol
1a R = MeCO



NOEs:
H_β–C(7)/Me(30)
H–C(15)/Me(30)
Me(19)/Me(29), Me(30)

$^1H,^1H$–COSY-45°:
H–C(1)/H–C(2)
CH_2(6)/H_α–C(5), H_β–C(7)
CH_2(16)/H–C(15), H–C(17)
H–C(20)/H–C(21) or CH_2(21) CH_2(22)
H–C(23) or CH_2(23)/CH_2(22)

2 R = H, R' = $^{2'''}Me\overset{1'''}{C}H_2O$ limocin C
3 R = $^{2'''}Me\overset{1'''}{C}H_2O$, R' = H limocin D

Fig. 1. *Isolated compounds* **1**–**3**

moiety, which was confirmed by the $^1H,^1H$ COSY-45° interactions of CH_2(6) with H_β–C(7) and H_α–C(5) [8]. The α-orientation of the feruloyloxy group was supported by the multiplicity (*dd*) and coupling constants of H_β–C(7) ($J(7\beta,6a) = 3.5$ and $J(7\beta,6b) = 3.0$ Hz) and the NOESY correlations of Me(18) and Me(28) with H–C(3′) (*Fig. 1*).

Table 1. *^{1}H-NMR Data* ($CDCl_3$) *of Triterpenes* **1**–**3**. δ in ppm, J in Hz.

	δ(H)		
	1	**2**	**3**
H–C(1)	7.09 (d, J = 10.2)	7.14 (d, J = 10.1)	
H–C(2)	5.81 (d, J = 10.2)	5.84 (d, J = 10.1)	
H_α–C(5)	2.30 (m)	2.18 (dd, J = 12.8, 2.2)	
CH_2(6)	1.87–1.95 (m)	1.86–2.26 (m)	
H_β–C(7)	5.29 (dd, J = 3.5, 3.0)	5.26 (br. d)	
H_α–C(9)	2.18 (m)	1.98 (dd, J = 12.8, 7.0)	
CH_2(11)	1.87–1.95 (m)	1.45–2.26 (m)	
H_α–C(12)[a])	–	1.45–2.26 (m)	
H_β–C(12)[a])	4.13 (dd, J = 11.8, 5.9)	1.45–2.26 (m)	
H_α–C(14)	2.12 (t, J = 7.8, 7.8)	–	
H_a–C(15)	2.30–2.45 (m)	5.22 (dd, J = 5.0, 3.6)	
H_b–C(15)	2.30–2.45 (m)	–	
CH_2(16)	1.87–1.95 (m)	1.70–1.95 (m)	
H_β–C(17)	1.65 (m)	1.90 (m)	1.72 (m)
Me(18)	1.25 (s)	1.00 (s)	0.97 (s)
Me(19)	1.15 (s)	1.15 (s)	
H_ξ–C(20)	2.30 (m)	1.54 (m)	1.50 (m)
H_a–C(21)	5.55 (br. d)	5.03 (br. d, J = 5.0)	3.90 (m)
H_b–C(21)	–	–	3.45 (m)
H_a–C(22)	1.45 (m)	1.50 (m)	1.60 (m)
H_b–C(22)	2.33 (m)	2.10 (m)	2.28 (m)
H_a–C(23)	3.58 ($dddd$, J = 6.8, 5.0, 4.2, very small)	4.11 (dt, J = 8.0, 8.0, very small)	5.10 (br. t, J = 5.0)
H_b–C(23)	–	3.65 (m)	
H_a–C(24)	4.20 (dd, J = 11.8, 5.0)	–	–
H_b–C(24)	3.68 (dd, J = 11.8, 4.2)	–	–
Me(28)	1.23 (s)	1.06 (s)	
Me(29)	1.06 (s)	1.06 (s)	
Me(30)	1.29 (s)	1.16 (s)	
OH–C(12)	3.88 (br. s)	–	
OH–C(21)	3.17 (br. s)	–	
H–C(2′)	6.27 (d, J = 15.9)	1.94 (s)	
H–C3′)	7.58 (d, J = 15.9)	–	
H–C(2″)	7.02 (d, J = 1.9)	–	
H–C(5″)	6.89 (d, J = 8.2)	–	
H–C(6″)	7.06 (d, J = 8.2, 1.9)	–	
MeO	3.93 (s)	–	
H_a–C(1‴)	–	3.42 (dt, J = 9.6, 7.2)	3.47 (dt, J = 9.6, 7.2)
H_b–C(1‴)	–	3.70 (dt, J = 9.6, 7.2)	3.74 (dt, J = 9.6, 7.2)
Me(2‴)	–	1.18 (t, J = 7.2)	1.20 (t, J = 7.2)

[a]) Indistinguishable for compounds **2** and **3**

The fragment ion at m/z 522.2972 (**g**) represented the basic tetracyclic skeleton substituted by a feruloyloxy group. The fragment ions at m/z 504.2866 and 328.2393, due to the loss of H_2O and the feruloyloxy moiety from **g**, respectively, and other fragment ions at m/z 311.2002 and 295.2052 suggested the presence of an OH function at ring C or D of the skeleton (*Fig. 2* and *Exper. Part*). A CH proton of a secondary-alcohol moiety at δ 4.13 (dd) in the ^{1}H-NMR (*Table 1*), with $J(12,11\alpha) = 11.8$ and $J(12,11\beta) = 5.9$ Hz, was attributed to H_β–C(12), with OH–C(12) on the α-side. This position was confirmed by the interactions of CH_2(11) with H_α–C(9) and H_β–C(12) observed in the ^{1}H,^{1}H COSY-45° experiment. The α-orientation of the OH function was also

Table 2. *^{13}C-NMR Data* ($CDCl_3$) *of Triterpenes* **1**–**3**. δ in ppm.

	δ(C)				δ(C)		
	1	**2**	**3**		**1**	**2**	**3**
C(1)	158.2	158.4[h])		C(21)	101.6	104.0[p])	72.0[j])
C(2)	125.5	125.6		C(22)	37.0[c])	38.6[k])	38.9[k])
C(3)	205.0	[t])		C(23)	70.4[b])	73.2	103.2[p])
C(4)	44.3[a])	44.2[i])		C(24)	65.4	–	–
C(5)	46.2	46.3		C(28)	21.3[e])	21.0[o])	
C(6)	29.6	23.8		C(29)	27.2[f])	27.1[q])	
C(7)	71.6[b])	74.6[j])		C(30)	26.6[f])	27.4[q])	
C(8)	44.6[a])	[t])		C(1′)	165.0	168.0	
C(9)	37.1[c])	38.4[k])		C(2′)	116.0[g])	21.3[o])	
C(10)	40.3[s])	39.9[s])		C(3′)	144.6[s])	–	
C(11)	16.4	16.5		C(1″)	129.5	–	
C(12)	71.0[b])	39.9[s])		C(2″)	109.5	–	
C(13)	44.9[a])	44.8[i])		C(3″)	[t])	–	
C(14)	56.0[d])	159.0[h])		C(4″)	[t])	–	–
C(15)	24.4	119.2[t])	119.8[t])	C(5″)	115.0[g])	–	
C(16)	34.2	35.2[m])	35.5[m])	C(6″)	123.0	–	
C(17)	55.3[d])	58.4[n])	69.5[n])	C(1‴)	–	68.2[r])	68.8[r])
C(18)	21.5[e])	20.6[o])		C(2‴)	–	29.7[s])	29.7[s])
C(19)	18.9	18.2		MeO	57.6	–	
C(20)	40.3[s])	39.9[s])					

[a–r]) Assignments interchangeable. [s]) Observed with shoulder peaks. [t]) Not observed.

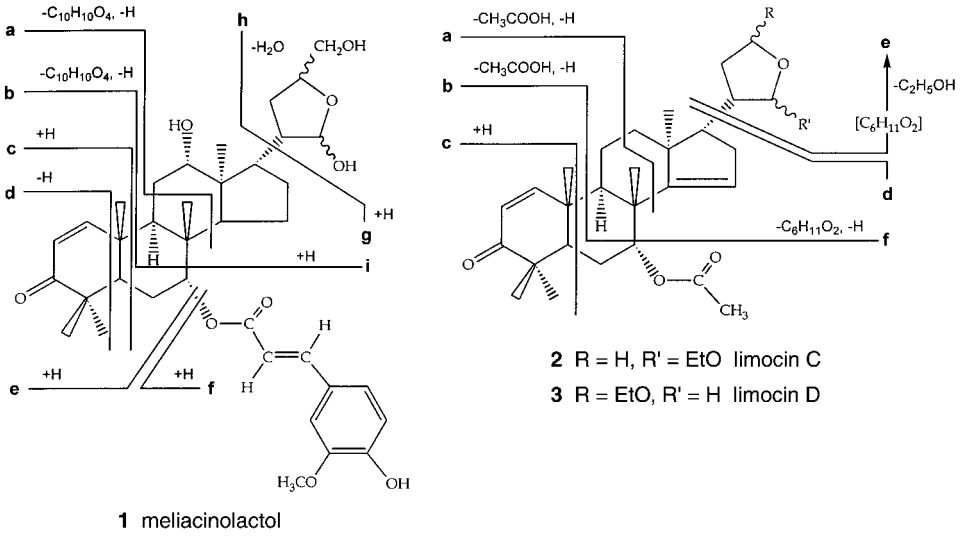


Fig. 2. *Mass fragments of* **1**–**3**

supported by the NOESY interaction H_β–C(12)/Me(30). Me(30) also interacted with Me(19), which in turn interacted with Me(29) (*Fig. 1*).

The ^{13}C-NMR spectrum of **1** (*Table 2*) showed 35 out of 37 C-atoms, the quaternary C(3″) and C(4″) were not observed. Of these, 30 C-atoms accounted for the basic skeleton and feruloyloxy group; therefore, a side chain with an elemental composition of $C_5H_9O_3$ had to be attributed. A fragment ion at *m*/*z* 99.0437 ($C_5H_7O_2^+$, **h**)

was assessed as the dehydrated fragment of the side chain $C_5H_9O_3$ at C(17). The ^{1}H-NMR further showed a CH_2 group at δ 3.68 (*dd*, $^2J = 11.8$, J(24a,23) = 4.2 Hz) and 4.20 (*dd*, $^2J = 11.8$, J(24b,23) = 5.0 Hz). The protons of this CH_2 group showed ^{1}H,^{1}H COSY-45° interactions with each other as well as with a vicinal proton at δ 3.58; the former were assigned to a CH_2OH group which was supported by the fragment ion at *m/z* 69.0331 arising by loss of CH_2OH from fragment ion **h** (*Fig. 2*). The ^{13}C-NMR spectrum (*Table 2*) showed six sp^3-hybridized O-substituted C-atoms; those at δ 57.6 and 65.4 were assigned to MeO and CH_2OH respectively, while three C-atoms at δ 70.4, 71.0, and 71.6 were attributed to C(23), C(12), and C(7) (values interchangeable). The signal at δ 101.6 was assigned to the hemi-acetal atom C(21). Further, the molecular formula showed 13 double-bond equivalents, 12 of these were accounted for by the basic skeleton and the feruloyloxy group, and the remaining one was justified by the ring of the side chain. The CH_2OH group was placed at C(23) because of the ^{1}H,^{1}H COSY-45° interactions of H_ξ–C(23) with CH_2(24). A broad doublet at δ 5.55 was assigned to H_ξ–C(21). Therefore, the side chain at C(17) was established as the 21,23-epoxy-21-hydroxy-23-(hydroxymethyl) moiety.

The presence of the OH groups in **1** was further confirmed by the ^{1}H-NMR spectrum of **1a**, exhibiting 4 distinct signals of acetyl groups at δ 1.93, 2.06, 2.08, and 2.30.

After a combination of various chromatographic techniques, compounds **2** and **3** were finally obtained by prep. TLC as a 2:1 isomer mixture (by ^{1}H-NMR). They were characterized as the mixture, similarly to the earlier reported isomer mixture limocin A limocin B [10]. Due to the close similarities in the spectral data of **2** and **3** (*Tables 1* and *2* and *Exper. Part*) with limocin A and B, the trivial names limocin C and D, respectively, were proposed for these compounds. The structures of limocin C (**2**) and limocin D (**3**) were established as 7α-(acetyloxy)-21,23-epoxy-21ξ-ethoxy- and 7α-(acetyloxy)-21,23-epoxy-23ξ-ethoxy-24,25,26,27-tetranorapotirrucalla-1,14-dien-3-one, respectively, by their spectral data and comparison of the latter with those of limocin A/limocin B.

The IR spectrum of **2/3** exhibited absorptions at 1725 and 1665 cm^{-1} for various vibrational modes of RHC=CCOR and RCOOR. The M^+ was observed at *m/z* 484 and 484.3158 in the EI-MS and HR-EI-MS, respectively, corresponding to the molecular formula $C_{30}H_{44}O_5$. The characteristic signals in the ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*) and the fragment ions **a**–**d** in the HR-EI-MS, particularly *m/z* 369.2401 (**d**, *Fig. 2* and *Exper. Part*) confirmed that **2** and **3** possess the same basic tetracyclic 7α-(acetyloxy)apotirrucalla-1,14-dien-3-one skeleton as limocin A and B [10]. Thus, the difference of M^+ of **2/3** and limocin A/B, corresponding to a methylene unit, was accounted for by the side chain of the composition $C_6H_{11}O_2$. Like various common signals and coupling constants in the ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*), the mixture **2/3**, when compared with limocin A/B, also showed two acetal functions in the ratio 2:1 for the tetrahydrofuran-ring residue at C(17). Each was identified by its characteristic signals, *i.e.*, δ 5.03 (br. *d*, J (21ξ,20ξ) = 5.0 Hz) for H–C^2(21)[2]) and δ 5.10 (br. *t*, J(22a,23ξ) = J(22b,23ξ) = 5.0 Hz) for H–C^3(23)[2]). The corresponding C-atoms resonated in the ^{13}C-NMR (*Table 2*) at δ 104.0 and 103.2 (C^2(21) and C^3(23), assignments interchangeable). Assignments of the vicinal protons were confirmed by the ^{1}H,^{1}H COSY-45° interactions of H_ξ–C^2(21) with H_ξ–C^2(20) and H_ξ–C^3(23) with C^{3}H$_2$(22) (*Fig. 1*). The ^{1}H-NMR further showed two sets of signal spreading at δ 3.30–3.55 and 3.63–3.80 in the integration ratio 1:2. By means of a *J*-resolved ^{1}H-NMR experiment, these were found to be 4 identical *dt* resonating at δ 3.42, 3.47, 3.70, and 3.74 and 2 *m* at δ 3.45 and 3.65. The relative ratio and ^{1}H,^{1}H COSY-45° interactions of the protons at δ 3.42 (H_a–C^2(1‴)) and δ 3.70 (H_b–C^2(1‴)) and of the protons at δ 3.47 (H_a–C^3(1‴) and 3.74 (H_b–C^3(1‴)) showed that these belong to two sets of CH_2O protons. Further, the multiplicities and ^{1}H,^{1}H COSY-45° interactions of the protons at δ 3.42 and 3.70 (C^{2}H$_2$(1‴)) with those at δ 1.18 (*t*, J(2‴,1‴) = 7.2 Hz) and of the protons at δ 3.47 and 3.74 (CH$_2^3$(1‴)) with those at δ 1.20 (*t*, J(2‴,1‴) = 7.2 Hz) suggested that **2** and **3** each possess an EtO group of an acetal moiety at the tetrahydrofuran ring. The multiplicities and ratios of the H–C^2(21) and H–C^3(23) signals were compatible with the EtO group at C^2(21) in **2** and at C^3(23) in **3**. This was also supported by the fragment ion **e** at *m/z* 69.0523 (*Fig. 2*) and by other fragment ions at *m/z* 454.2771, 438.2757, and 365.2452 (*Exper. Part*). In the ^{1}H,^{1}H COSY-45° experiment, further

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[2]) The C-atoms of limocin C (**2**) are labelled with a superscript 2 and those of limocin C (**3**) with a superscript 3.

interactions were observed between the signals at δ 3.65 ($H_b-C^2(23)$) and 4.11 ($H_a-C^2(23)$) and between the signals at δ 3.45 ($H_b-C^3(21)$) and δ 3.90 ($H_a-C^3(21)$).

Compound **1** is a trinortriterpenoid with an intact ring D and lacking three C-atoms of the side chain. Prior to this, only one trinortriterpenoid has been obtained from *Azadirachta indica*, but it had a seco ring D [12]. Compounds **2** and **3** possess a 2-ethoxytetrahydrofuran acetal moiety as side chain at C(17), which has lost four C-atoms of the triterpenoid skeleton. Prior to these only three such acetals have been reported [10].

Experimental Part

General. Vacuum liquid chromatography (VLC): silica gel *60 PF_{254}*. Flash column chromatography (FC): *Eyela flash-column EF-10* chromatograph; *Aldrich* column, 100 ml; silica gel *9385* (*Merck*, 0.040–0.063 mm). Prep.TLC: silica gel *60 PF_{254}* (*Merck*). TLC: silica-gel *G-25 UV_{254}* aluminium plates; detection at 254 and 366 nm with *UVKL* UV lamps *H. Jurgens & Co.* and I_2 spray. Optical rotations: *Jasco DIP-360* digital polarimeter. CD Spectra: *Jasco J-600* spectropolarimeter; λ in nm (mdeg). UV Spectra: *Hitachi U-3200* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Jasco-A-302* spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H-NMR, COSY, NOESY, and *J*-resolved: *Bruker* spectrometers, at 300 and 400 MHz; chemical shifts δ in ppm. rel. to $SiMe_4$ as an internal standard, coupling constants *J* in Hz. ^{13}C-NMR: *Bruker* spectrometer, at 75 MHz. EI-MS: *Finnigan-Mat 311A* mass spectrometer; source at 250° and 70 eV; *m/z* (rel.-%). HR-EI-MS and FAB-MS: *Jeol JMS-HX-110* mass spectrometer; EI, source at 250° and 70 eV; *m/z* (rel.-%); FAB, positive-ion mode.

Plant Materiel: Fresh, undried, ripe fruits (50 kg) of *A. indica* were collected in the Karachi region in July, 1999. A voucher specimen (No. NM-1) of the plant material, identified by Prof. Dr. *S. I. Ali*, Department of Botany, University of Karachi, has been deposited in the herbarium of the Department of Botany, University of Karachi. Seeds and coatings of the fruits were separated manually, and coatings were extracted repeatedly (5 ×) with EtOH at r.t.; the extract was then evaporated. The EtOH extract of the uncrushed fruit coats (23 kg) was partitioned between AcOEt and H_2O, the org. phase washed, dried (Na_2SO_4), and evaporated, and the gummy syrup obtained was treated with 4% aq. Na_2CO_3 soln. to ultimately furnish acidic and neutral fractions. The neutral fraction was divided into petroleum-ether-soluble and petroleum-ether-insoluble fractions. The petroleum-ether-insoluble fraction was again divided into Et_2O-soluble and Et_2O-insoluble portions. Then, 189 g of the Et_2O-insoluble portion was subjected to VLC (petroleum ether → petroleum ether/AcOEt → AcOEt → MeOH). The eluates were combined after TLC analysis: *Fractions A–M*.

Fraction L (1.53 g; eluted with 100% AcOEt) was subjected to FC (*Eyela* column, $CHCl_3$ → $CHCl_3$/MeOH → MeOH): *Fr. FC-1–FC-16*. *Fr. FC-6* (293.1 mg; eluted with $CHCl_3$/MeOH 99:1 → 95.5:4.5 by a 5% gradient; elution volume 1600 ml) was resubmitted to FC (*Aldrich* column, $CHCl_3$ → $CHCl_3$/MeOH → MeOH): 22 fractions. *Fr. 8* (eluted with $CHCl_3$ (1200 ml) and $CHCl_3$/MeOH 99:1 (240 ml) was purified by prep. TLC ($CHCl_3$/MeOH 7:3, repeatedly), resulting in two bands. The band with R_f 0.30 afforded 16 mg of **1**.

Fraction H (5.38 g; eluted with petroleum ether/AcOEt 3:7 (3000 ml) was submitted to FC (*Aldrich* column, $CHCl_3$ → $CHCl_3$/MeOH → MeOH): *Fr. H1–H22*. *Fr. H3* (eluted with $CHCl_3$ (800 ml)) was purified by prep. TLC (petroleum ether/AcOEt 92:8, repeatedly). The band with R_f 0.88 afforded 6.5 mg of gummy **2**/**3**. *Fr. H5* (eluted with $CHCl_3$ (1040 ml)) was purified by prep. TLC (petroleum ether/AcOEt 75:25), affording two bands. The band with R_f 0.65, on repeated prep. TLC ($CHCl_3$/MeOH 95:5) furnished 4.8 mg of azadiradionolide (R_f 0.83) [7].

Meliacinolactol (=*21,23-Epoxy-7α-[(*E*)-feruloyloxy]-12α,21ξ,24-trihydroxy-25,26,27-trinorapotirucall-1-en-3-one*[1]); **1**): Amorphous powder, decomposed on standing, even at r.t. $[\alpha]_D^{29} = -0.11$ ($c = 0.16$, $CHCl_3$). CD (MeOH): 318.2 (−40.04), 280.8 (+1.38), 256.2 (−0.12), 240.6 (+0.94), 228.8 (−0.44). UV (MeOH): 318 (3.41), 281 (3.55), 224 (4.24). IR ($CHCl_3$): 3600–3200, 3520, 1736, 1726, 1710, 1692, 1665–1610, 1460, 1450, 1372, 1360, 1160, 1120, 1090. ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. FAB-MS: 638 (M^+). HR-EI-MS: 522.2972 (16, $C_{32}H_{42}O_6^+$, **g**), 504.2866 (21, $C_{32}H_{40}O_5^+$, [**g** − H_2O]$^+$), 445.2944 (13, $C_{27}H_{41}O_5^+$, **e**), 430.2710 (14, $C_{26}H_{38}O_5^+$, [**e** − Me]$^+$), 328.2393 (90, $C_{22}H_{32}O_2^+$, [**g** − $C_{10}H_{10}O_4$]$^+$), 311.2002 (14, $C_{21}H_{27}O_2^+$, [**g** − $C_{10}H_{10}O_4$ − Me − 2 H]$^+$), 295.2052 (17, $C_{21}H_{27}O^+$, [**g** − $C_{10}H_{10}O_4$ − Me − H_2O]$^+$), 282.1822 (16, $C_{16}H_{26}O_4^+$, **i**), 201.1270 (14, $C_{14}H_{17}O^+$, **a**), 194.0570 (38, $C_{10}H_{10}O_4^+$, **f**), 186.1035 (14, $C_{13}H_{14}O^+$, [**a**-Me]$^+$), 177.0542 (100, $C_{10}H_9O_3^+$, acylium ion of **f**), 173.0958 (17, $C_{12}H_{13}O^+$, [**a** − Me − CH]$^+$), 161.0957 (22, $C_{11}H_{13}O^+$, **b**) 149.0593 (24, $C_9H_9O_2^+$, [**f** − CO_2 − H]$^+$),

137.0958 (41, $C_9H_{13}O^+$, **c**), 123.0437 (13, $C_7H_7O_2^+$, [**f** – $C_3H_3O_2$]$^+$), 121.0645 (24, $C_8H_9O^+$, [**c** – Me + H]$^+$), 105.0331 (32, $C_7H_5O^+$, [**c** – 2Me]$^+$), 99.0437 (13, $C_5H_7O_2^+$, **h**), 95.0487 (24, $C_6H_7O^+$, **d**), 81.0331 (18, $C_5H_5O^+$, [**h** – H_2O]$^+$), 69.0331 (16, $C_4H_5O^+$, [**h** – CH_2OH + H]$^+$).

Acetylation of **1**. A mixture of **1** (6 mg) Ac_2O (1.4 ml), and pyridine was stirred overnight. After partition between AcOEt and H_2O, the AcOEt extract yielded, on prep. TLC, 3.6 mg of **1a**.

^{1}H-NMR ($CDCl_3$): 2.30 (AcO–C(4″)); 2.08, 2.06, 1.93 (3*s*, AcO–C(12), AcO–C(21), AcO–C(24)).

Limocin C and D (= *7α-(Acetyloxy)-21,23-epoxy-21ξ-ethoxy-* and *7α-(Acetyloxy)-21,23-epoxy-23ξ-ethoxy-24,25,26,27-tetranorapotirucalla-1,14-dien-3-one*[1]); **2** and **3**, resp.): Yellowish gum. $[\alpha]_D^{29} = -0.04$ ($c = 0.13$, $CHCl_3$). UV (MeOH): 229.0, 198.2. IR ($CHCl_3$): 1725, 1665, 1610, 1440, 1335, 1110, 1080, 1020. ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. HR-EI-MS: 484.3158 (21, M^+), 454.2771 (21, $C_{28}H_{38}O_5^+$, [$M - C_2H_5$ – H]$^+$), 440.2881 (15, $C_{28}H_{40}O_4^+$, [M – MeCO – H]$^+$), 438.2757 (100, $C_{28}H_{38}O_4^+$, [$M - C_2H_5OH$]$^+$), 369.2401 (39, $C_{24}H_{33}O_3^+$, **d**), 365.2452 (43, $C_{25}H_{33}O_2^+$, [$M - OC_2H_5$ – MeCOO – Me]$^+$), 310.2279 (95, $C_{22}H_{30}O^+$, [**d**-MeCOO]$^+$), 295.2029 (29, $C_{21}H_{27}O^+$, [**d**-MeCOO – Me]$^+$), 215.1385 (22, $C_{15}H_{19}O^+$, **a**), 201.1351 (21, $C_{14}H_{17}O^+$, [**a** – CH_2]$^+$), 162.1074 (22, $C_{11}H_{14}O^+$, **b**), 145.0984 (31, $C_{11}H_{13}^+$, **f**), 137.0947 (46, $C_9H_{13}O^+$, **c**), 131.0827 (26, $C_{10}H_{11}^+$, [**f** – CH_2]$^+$), 120.0635 (36, $C_8H_8O^+$, [**c** – Me – 2 H]$^+$), 107.0786 (26, $C_7H_7O^+$, [**c** – 2Me]$^+$), 69.0523 (21, $C_4H_5O^+$, **e**).

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