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TETRACYCLIC TRITERPENOIDS OF THE FRUIT COATS OF *AZADIRACHTA INDICA*

BINA SHAHEEN SIDDIQUI,* GHIASUDDIN and SHAHEEN FAIZI

H.E.J. Research Institute of Chemistry, University of Karachi, Karachi-75270, Pakistan

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Key Word Index—*Azadirachta indica*; Meliaceae; fruit coats; tetracyclic triterpenoids; salimuzzalin; azadirolic acid; azadiradionol; azadironol.

Abstract—From the ethanolic extract of the fresh fruit coats of *Azadirachta indica* (neem), four new tetracyclic triterpenoids salimuzzalin [24,25,26,27-tetranorapotirucalla(apoeupha)-7α-hydroxy-21ξ,23ξ-diacetoxy-21,23-epoxy-1,14,20(22)-trien-3-one], azadirolic acid [26,27-dinorapotirucalla(apoeupha)-6β-acetoxy-7α-hydroxy-1,14,20(22)-trien-3-one-25-oic acid], azadiradionol [26,27-dinorapotirucalla(apoeupha)-7α-acetoxy-24ξ-hydroxy-1,14-dien-3,16-dione] and azadironol [4,4,8-trimethyl-5α-(13αMe)-androst-17α-hydroxy-1-en-7α(*p*-methoxy, *m*-hydroxy *trans* cinnamoyloxy)-3-one], were isolated. Their structures were elucidated through spectroscopic techniques.

INTRODUCTION

In continuation of our studies on the constituents of the fresh fruit coats of *Azadiracta indica* A. Juss [1, 2], four new tetracyclic triterpenoids salimuzzalin, azadirolic acid, azadiradionol and azadironol have been isolated. Their structures have been elucidated by spectral studies including 2D NMR techniques.

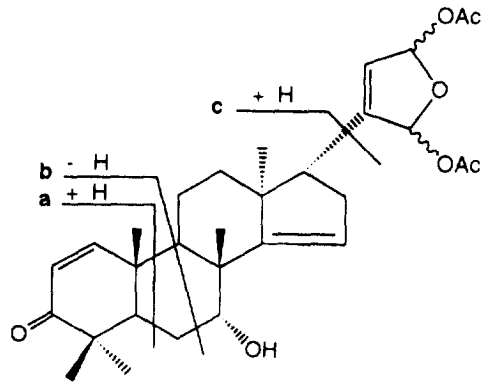
RESULTS AND DISCUSSION

Four new tetracyclic triterpenoids **1–4** were obtained from the neutral part of the ethanolic extract of the fresh ripe neem fruit coats (see Experimental).

The EI- and FD-mass spectra of salimuzzalin (**1**) showed a molecular ion peak at *m/z* 512, corresponding to the molecular formula $C_{30}H_{40}O_7$ (HRMS *m/z* 512.2816 calc. for $C_{30}H_{40}O_7$, 512.2773). A pair of AB doublets at δ 7.13 (J = 10.14 Hz; H-1) and 5.88 (J = 10.14 Hz; H-2) and five quaternary methyl singlets at δ 1.00 (H-18), 1.19 (H-19), 1.08 (6H; H-28 and H-29) and 1.23 (H-30) in the ^{1}H NMR spectrum (Table 1) and the signals at δ 156.8 (C-1), 126.0 (C-2) and 204.1 (C-3) in the ^{13}C NMR spectrum (Table 2) indicated a 1-en-3-one system in ring A [3]. This was supported by mass fragments **a** (*m/z* 137.0973; $C_9H_{13}O$) and **b** (*m/z* 149.1019; $C_{10}H_{13}O$), which also supported a triterpenoid nucleus.Three one-proton double doublets related to H-5, H-7 and H-9 resonated at δ 2.31 (J = 13.33, J = 2.70 Hz), 3.96 (J = 3.60, J = 1.90 Hz) and 2.17 (J = 11.98, J = 5.49 Hz) respectively. A one-proton multiplet at δ 5.49 and two one-proton *ddd* at δ 2.50 (J = 15.40, J = 7.39, J = 2.06 Hz) and 2.63 (J = 15.40, J = 7.11, J = 2.06 Hz) (Table 1) were attributed to H-15, H-16a and H-16b respectively. The ^{13}C NMR spectrum (Table 2) and mass fragment **c** demonstrated that **1** had the same carbocyclic skeleton as that of azadirone [3]. However, the signals of the furan ring, a characteristic feature of meliacins, and those of the acetoxy group were missing in the NMR spectra (^{1}H and ^{13}C NMR). Instead, a hydroxy group at C-7 and a 21,23-diacetoxy-but-20(22)-ene-21,23 ether moiety were indicated by the carbinylic proton signals at δ 3.96 (*dd*, J = 3.60, J = 1.90 Hz, H-7), 4.75 (*d*, J = 4.22 Hz), 4.78 (*m*) and the vinyl proton signal at δ 5.48 (*br s*) which were assigned to H-7, H-21, H-23 and H-22, respectively. This was supported by the presence of the signals at δ 72.0 (C-7), 104.6 (C-21), 109.2 (C-23), 119.6 (C-22) and 158.2 (C-20) in the ^{13}C NMR spectrum (BB and DEPT) and a diagnostic fragment **c** in the mass spectrum of **1**, resulting from the loss of the side chain ($C_8H_9O_5$). All these assignments were made through heteroCOSY and comparison of shifts with those of similar reported meliacins [3–5]. In the light of above noted spectral data, the structure of salimuzzalin has been deduced as 24,25,26,27-tetranorapotirucalla (apoeupha)-7α-hydroxy-21ξ,23ξ-diacetoxy-21,23-epoxy-1,14,20(22)-trien-3-one (**1**).

Azadirolic acid (**2**) was assigned the molecular formula $C_{30}H_{42}O_6$ (EI-HRMS *m/z* 498.2953 calc. $C_{30}H_{42}O_6$; 498.2980). Its ^{1}H NMR spectrum (Table 1)

*Author to whom correspondence should be addressed.



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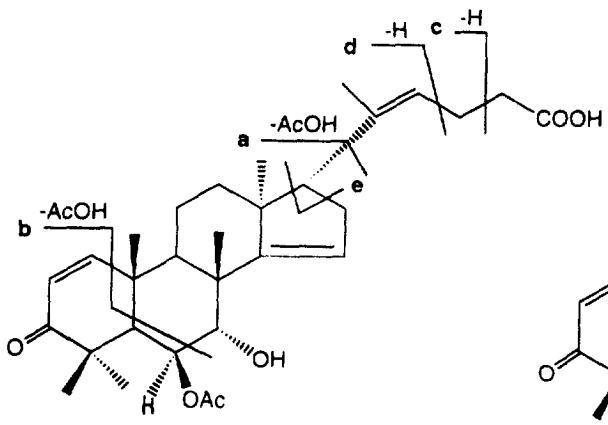

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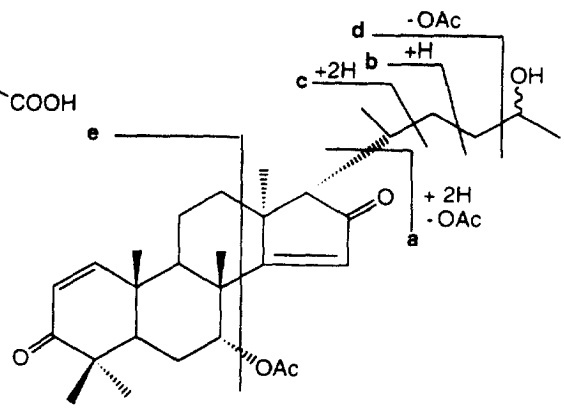

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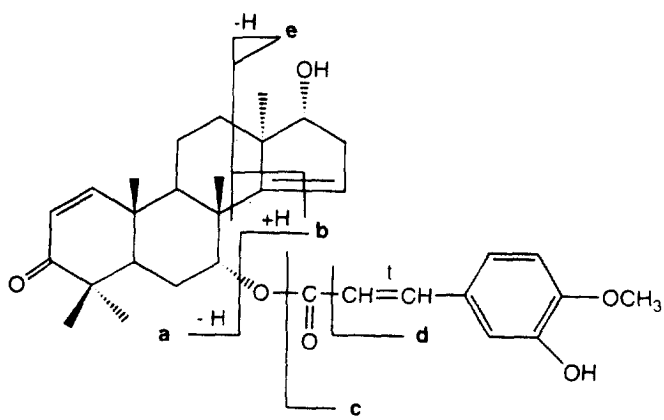

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contained a pair of AB doublets at δ 7.15 (J = 10.21 Hz; H-1) and 5.87 (J = 10.21 Hz; H-2), while the ^{13}C NMR spectrum (Table 2) contained signals at δ 157.9 (C-1), 125.8 (C-2) and 203.5 (C-3) characteristic of a 1-en-3-one system in ring A [3]. The spectral data (^1H *and* ^{13}C *NMR*) revealed that rings A-D of **2** were similar to those of **1** and other reported meliacins [3, 4]. However, in azadirone [3], the 7β proton appears as a triplet at δ 5.35 in the ^1H NMR spectrum whereas the signal corresponding to the same proton in **2** was observed as a doublet (δ 4.77, J = 3.62 Hz) indicating the presence of a substituent at C-6, which was further

Table 1. ^{1}H NMR spectral data of triterpenoids **1–4**

H	1	2	3	4
1	7.13 *d* $J_{1,2}$ 10.14	7.15 *d* $J_{1,2}$ 10.21	7.10 *d* $J_{1,2}$ 10.10	7.14 *d* $J_{1,2}$ 10.10
2	5.88 *d* $J_{2,1}$ 10.14	5.87 *d* $J_{2,1}$ 10.21	5.80 *d* $J_{2,1}$ 10.10	5.84 *d* $J_{2,1}$ 10.10
5	2.31 *dd* $J_{5,6\beta}$ 13.33 $J_{5,6\alpha}$ 2.70	2.17 *d* $J_{5,6\alpha}$ 6.09	2.69 *dd* $J_{5,6\beta}$ 14.15 $J_{5,6\alpha}$ 5.32	2.18 *dd* $J_{5,6\beta}$ 11.41 $J_{5,6\alpha}$ 5.66
6α	1.78 *m*	5.30 *dd* $J_{6\alpha,5\beta}$ 6.09 $J_{6\alpha,7}$ 3.62	1.71–2.11 *m*	1.50–2.15 *m*
6β	1.95 *m*	—	1.71–2.11 *m*	1.50–2.15 *m*
7	3.96 *dd* $J_{7,6\beta}$ 3.60 $J_{7,6\alpha}$ 1.90	4.77 *d* $J_{7,6\alpha}$ 3.62	5.26 *t* $J_{7,6\alpha} = J_{7,6\beta}$ 1.91	5.35 *m*
9	2.17 *dd* $J_{9,11\beta}$ 11.98 $J_{9,11\alpha}$ 5.49	2.73 *dd* $J_{9,11\beta}$ 12.94 $J_{9,11\alpha}$ 5.61	2.34 *dd* $J_{9,11\beta}$ 11.51 $J_{9,11\alpha}$ 4.32	2.33 *dd* $J_{9,11\beta}$ 10.98 $J_{9,11\alpha}$ 3.79
11α	1.60–1.90 *m*	1.73 *m*	1.71–2.11 *m*	1.50–2.15 *m*
11β	1.60–1.90 *m*	1.92–2.11 *m*	1.71–2.11 *m*	1.50–2.15 *m*
12α	1.60–1.90 *m*	1.57 *m*	1.71–2.11 *m*	1.50–2.15 *m*
12β	1.60–1.90 *m*	1.92–2.11 *m*	1.71–2.11 *m*	1.50–2.15 *m*
15	5.49 *m*	5.59 *br d* $J_{15,16a}$ 2.57	5.46 *s*	1.50–2.15 *m*
16a	2.50 *ddd* J_{gem} 15.40 $J_{16a,17}$ 7.39 $J_{16a,15}$ 2.06	2.53 *ddd* J_{gem} 16.02 $J_{16a,17}$ 7.60 $J_{16a,15}$ 2.57	—	1.50–2.15 *m*
16b	2.63 *ddd* J_{gem} 15.40 $J_{16b,17}$ 7.11 $J_{16b,15}$ 2.06	2.45 *m*	—	1.50–2.15 *m*
17	1.60–1.90 *m*	1.92–2.11 *m*	1.88 *d* $J_{17,20}$ 4.45	4.14 *dd* $J_{17\beta,16a}$ 10.83 $J_{17\beta,16b}$ 6.71
18	1.00 *s*	1.00 *s*	1.01 *s*	1.24 *s*
19	1.19 *s*	1.11 *s*	1.17 *s*	1.19 *s*
20	—	—	1.71–2.11 *m*	—
21	4.75 *br d* $J_{21,20}$ 4.22	2.07 *br s*	0.98 *d* $J_{21,20}$ 7.54	—
22	5.48 *br s*	4.21 *ddd* $J_{22,23a}$ 10.58 $J_{22,23b}$ 5.04 $J_{22,21}$ 1.70	1.71–2.11 *m*	—
23	4.78 *m*	1.92–2.11 *m*	1.71–2.11 *m*	—
24a	—	2.24 *dt* J_{gem} 14.15 $J_{24a,23b}$ 3.74	3.60 *m*	—
24b	—	2.23 *ddd* J_{gem} 14.15 $J_{24b,23b}$ 3.74 $J_{24b,23a}$ 7.07	—	—
25	—	—	1.39 *d* $J_{25,24}$ 6.50	—
28	1.08 *s*	1.07 *s*	1.04 *s*	1.06 *s*
29	1.08 *s*	1.04 *s*	1.04 *s*	1.07 *s*
30	1.23 *s*	1.25 *s*	1.26 *s*	1.24 *s*
2′	—	—	—	6.27 *d* $J_{2',3'}$ 15.80
3′	—	—	—	7.58 *d* $J_{3',2'}$ 15.80
5′	—	—	—	7.01 *d* $J_{5',9'}$ 1.89

Table 1. *continued*

8′	—	—	—	6.89 *d* $J_{8',9'}$ 8.10
9′	—	—	—	7.05 *dd* $J_{9',8'}$ 8.10 $J_{9',8'}$ 1.89
AcO	1.95 *s* 1.92 *s*	1.91 *s*	1.92 *s*	—
COOH	—	10.01 *s*	—	—
OCH_3	—	—	—	3.90 *s*
OH	—	—	3.03 *s* (exchangeable with D_2O)	—

Table 2. ^{13}C NMR spectral data of compounds **1** and **2**

C	1	2	C	1	2
1	156.8	157.9	15	120.1	118.2
2	126.0	125.8	16	34.0	38.5*
3	204.1	203.5	17	52.6	55.6
4	46.0	44.0	18	20.0	12.8
5	44.8	52.4	19	19.1	21.6
6	24.8	76.7	20	158.2	145.6
7	72.0	75.6	21	104.6	24.5
8	44.6	44.7	22	119.6	129.6
9	35.0	47.7	23	109.2	34.9*
10	38.5	41.0	24	—	24.41
11	15.6	17.8	25	—	173.5
12	29.7	31.6	28	27.0	26.4
13	47.5	46.5	29	21.2	24.5
14	161.5	157.7	30	26.3	26.4
			$\underline{O}C\underline{O}CH_3$	189.4 189.2	172.9
			$OCO\underline{C}H_3$	22.4 21.2	21.6

* Assignment may be interchanged.

supported by H-6α giving rise to a double doublet at δ 5.30 (J = 6.09, J = 3.62 Hz). H-5 on the other hand showed a doublet at δ 2.17 (J = 6.09 Hz). The chemical shift of H-7 was upfield as compared to H-7 of azadirone indicating a hydroxyl group instead of an acetoxy group at C-7, whereas the chemical shift of H-6 revealed that C-6 has an acetoxyl group (δ_{CH_3} 1.94). The ^1H NMR spectrum further showed a vinyl methyl at δ 2.07 (*br s*), a one-proton doublet of triplet at δ 2.24 (*dt*, J = 14.15, J = 3.74 Hz), two one-proton doublets of double doublet at δ 2.23 (*ddd*, J = 14.15, J = 7.07, J = 3.74 Hz) and 4.21 (*ddd*, J = 10.58, J = 5.04, J = 1.70 Hz) assigned to H-21, H-24a, H-24b and H-22 respectively, while a proton resonating at δ 10.01 as a singlet and exchangeable with D_2O was assigned to the COOH proton. The mass fragment **c** indicated that the COOH group is at the end of the side chain and the double bond is at C-20.

The above noted functionalities and their locations were confirmed by the mass fragments at m/z 325.2163 [M^+ − side chain − AcOH; $C_{22}H_{29}O_2$; fragment **a**], 121.0864 [C_8H_9O; fragment **b**], 438.2811 [$C_{28}H_{38}O_4$; fragment **c**], 426.2802 [$C_{27}H_{38}O_4$; fragment **d**] and 126.0689 [$C_7H_{10}O_2$; fragment **e**]. In the light of these observations, the structure of azadirolic acid has been elucidated as 26,27-dinorapotirucalla(apoeupha)-6β-acetoxy-7α-hydroxy-1,14,20(22)trien-3-one-25-oic acid (**2**). The ^1H and ^{13}C NMR assignments are based on 2D NMR (J resolved, COSY, NOESY and hetero-COSY) data and comparison with those of similar compounds (see Experimental).

Azadiradionol (**3**) was assigned the molecular formula $C_{30}H_{44}O_5$ (EI-HRMS m/z 484.3183 calc. 484.3188). Its ^1H NMR spectrum showed five quaternary methyl singlets, at δ 1.01 (H-18), 1.04 (6H, H-28 and H-29), 1.17 (H-19) and 1.26 (H-30) along with two secondary methyls resonating at δ 0.98 (*d*, J = 7.54 Hz) and 1.39 (*d*, J = 6.50) indicating its triterpenoid nature. A pair of AB doublets at δ 7.10 (J = 10.10 Hz; H-1) and 5.80 (J = 10.10 Hz; H-2), two one-proton double doublets at δ 2.69 (J = 14.15, J = 5.32 Hz; H-5) and 2.34 (J = 11.51, J = 4.32 Hz;

H-9), a one-proton singlet at δ 5.46 (H-15) and a one-proton triplet at δ 5.26 (J = 1.91 Hz; H-7) along with an acetoxy singlet at δ 1.92 demonstrated that compound **3** had the same tetracyclic skeleton as that of azadiradione [3] which was further supported by the diagnostic mass fragment **a**. However, the signals of the furan ring which is a common feature of meliacins [3–5] were missing in the ^{1}H NMR spectrum. Fragment **a** further indicated the composition of the side chain as $C_6H_{13}O$. A carbinylic proton at δ 3.60 (*m*) suggested the presence of a hydroxyl group which was placed at C-24 as H-25 appeared as a doublet and its placement was supported by the mass fragments **b–d** (see Experimental). The observations noted above led to the elucidation of the structure of azadiradionol as 26,27-dinorapotirucalla (apoeupha)-7α-acetoxy-24ξ-hydroxy-1,14-dien-3,16-dione (**3**).

The mass spectra (EI and FD) of azadironol (**4**) showed the $[M]^+$ peak at m/z 522, corresponding to the molecular formula $C_{32}H_{42}O_6$ (through peak matching 522.2976; calc. for $C_{32}H_{42}O_6$, 522.2980). The ^{1}H NMR spectrum indicated that again the signals of the furan ring were missing and the double doublet of H-17 of azadirone at δ 2.78 was replaced by a downfield signal at δ 4.14 showing that C-17 has a hydroxyl group (IR ν_{max} 3450 cm^{-1}). The signal of the acetoxy group at C-7 of azadirone [3] was also missing in the ^{1}H NMR spectrum although a downfield multiplet at δ 5.35 was noted which suggested an ester function at C-7. It was identified as a *p*-methoxy-*m*-hydroxy-*trans*-cinnamoyloxy group by the ^{1}H NMR data. Thus a set of AB doublets at δ 6.27 and 7.58 (J = 15.80 Hz), and a double doublet at δ 7.05 (J = 8.10, J = 1.89), and a doublet at δ 6.89 (J = 8.10 Hz) were attributable to H-2′, H-3′, H-9′ and H-8′, respectively, while H-5′ resonated as a narrow doublet at δ 7.01 (J = 1.89). The methoxyl protons resonated at δ 3.90 as a singlet. This ester group was also supported by mass fragment **b**. In the light of these spectral data the structure of azadironol has been deduced as 4,4,8-trimethyl5α(13αMe)-androst-17α-hydroxy-1-en-7α-(*p*-methy-oxy, *m*-hydroxy-cinnamoyloxy)-3-one (**4**). The structure was substantiated by mass fragments **a** [M^+-$C_{10}H_{10}O_4$, $C_{22}H_{32}O_2$], **c** [$C_{10}H_9O_3$], **d** [$C_9H_9O_2$] and **e** [C_5H_7O].

EXPERIMENTAL

General

IR and UV: $CHCl_3$ and MeOH, respectively; ^{1}H NMR: 400 and 300 MHz, $CDCl_3$; ^{13}C NMR (BB and DEPT): 75 (**1**) and 100 MHz $CDCl_3$ (**2**). Assignments of chemical shifts of the methyl groups of **1**, **2**, **3** and **4** are based on comparison with those reported for compounds bearing similar parent tetracyclic skeletons [1–5]. ^{13}C NMR spectral assignments of **1** and **2** have been made partly through BB, DEPT and heteroCOSY spectra and partly through a comparison of chemical shifts with those reported for similar constituents [1–5]. Assignments of various protons are based on double resonance experiments COSY-45 and heteroCOSY. Purity of compounds was checked on silica gel GF-254 coated plates.

Extraction and isolation

The ethanolic extract of the fresh undried, uncrushed, ripe fruit coats of *A. indica* (neem) was divided into acidic and neutral fractions [1, 2]. The neutral fraction was partitioned between petrol and 90% aq. MeOH. The 90% aq. MeOH phase was extracted with EtOAc after addition of saline. The EtOAc phase was washed, dried (Na_2SO_4) and freed of the solvent affording 200 g of neutral gummy residue, 180 g of which was subjected to VLC [6, 7]. (petrol, petrol–EtOAc in order of increasing polarity). The petrol–EtOAc (1:4, 1:9). EtOAc and EtOAc–MeOH (9:1, 4:1, 7:3 and 2:3) eluates were combined together on the basis of TLC to give fraction E (30 g) which was again subjected to VLC ($CHCl_3$, $CHCl_3$–MeOH in order of increasing polarity). The $CHCl_3$–MeOH (99:1) eluates furnished various fractions of which fractions 5 and 6 (5.2 g), 7 and 8 (3.39 g) and, 9 and 10 (2.5 g) were combined on the basis of TLC. The combined fractions (7 and 8) were subjected to prep. thick layer chromatography ($CHCl_3$–MeOH: 9.65:0.35) affording five bands. The band designated as 8a (1.50 g) was further subjected to prep. TLC ($CHCl_3$–MeOH, 9.75:0.25) affording salimuzzalin (amorphous powder, 30.4 mg), as a chromatographically pure component. The combined fractions 9 and 10 (2 g) were subjected to flash CC (silica gel E. Merck 9385; $CHCl_3$, $CHCl_3$-MeOH in order of increasing polarity). The $CHCl_3$ and $CHCl_3$–MeOH (19:1) eluates furnished azadirolic acid (amorphous powder, 56 mg) and azadiradionol (amorphous powder, 32.6 mg) respectively. The combined fractions 5 and 6 (2.6 g) were also subjected to flash CC (silica gel E. Merck 9385; petrol–EtOAc in order of increasing polarity). The petrol–EtOAc (4:1) eluate furnished azadironol (amorphous powder 20.4 mg).

Salimuzzalin (**1**). UV λ_{max} (MeOH) nm: 230.4; IR ν_{max} ($CHCl_3$) cm^{-1}: 3545 (OH), 2800–2850 (CH), 1725 (CO), 1660 (cyclohexenone), 1600, 820 (trisubstituted double bonds), 1375 (geminal methyls); FDMS m/z 512; HRMS m/z (rel. int.): 512.2816 [M^+; calc. for $C_{30}H_{40}O_7$, 512.2773] (87), 497.2553 [$C_{29}H_{37}O_7$] (23), 482.2662 [$C_{29}H_{38}O_6$] (21), 453.2668 [M^+ – AcO; $C_{28}H_{37}O_5$] (15), 452.2602 [M^+ – HOAc; $C_{28}H_{36}O_5$] (20), 328.2368 [$C_{22}H_{32}O_2$; fragment **c**] (100), 310.2304 [$C_{22}H_{30}O$] (24), 295.2020 [$C_{21}H_{27}O$] (8), 243.1440 [$C_{16}H_{19}O_2$] (6), 201.1282 [$C_{14}H_{17}O$] (6), 149.1019 [$C_{10}H_{13}O$; fragment **b**] (7), and 137.0973 [$C_9H_{13}O$; fragment **a**] (10); ^{1}H NMR: Table 1; ^{13}C NMR: Table 2.

Azadirolic acid (**2**). UV λ_{max} (MeOH) nm: 230; IR ν_{max} ($CHCl_3$) cm^{-1}: 3450 (OH), 2910 (CH), 1720, 1700 (CO), 1660 (cyclohexenone), 1600, 860 (C=C), 1375 (geminal methyls); EIMS m/z 498 [M^+]; HRMS m/z

(rel. int.): 498.2953 [M^+; calc. for $C_{30}H_{42}O_6$, 498.2980] (13), 483.2251 [$C_{29}H_{39}O_6$] (12), 469.2950 [$C_{29}H_{41}O_5$] (25), 454.2679 [$C_{28}H_{38}O_5$] (19), 438.2811 [$C_{28}H_{38}O_4$; fragment **c**] (11), 426.2802 [$C_{27}H_{38}O_4$; fragment **d**] (27), 414.2827 [$C_{26}H_{38}O_4$] (13), 325.2163 [$C_{22}H_{29}O_2$, fragment **a**] (15), 150.1003 [$C_{10}H_{14}O$] (13), 137.0855 [$C_9H_{13}O$] (27), 126.0689 [$C_7H_{10}O_2$; fragment **e**] (11), 121.0864 [C_8H_9O; fragment **b**] (26); ^{1}H NMR: Table 1; ^{13}C NMR: Table 2.

Azadiradionol (**3**). UV λ_{max} (MeOH) nm: 228.8; IR ν_{max} ($CHCl_3$) cm^{-1}: 3450 (OH), 2900 (CH), 1720 (CO), 1710 (cyclopentenone), 1665 (cyclohexenone), 1610, 820 (trisubstituted double bond), 1375 (geminal methyls); EIMS *m/z*: 484 [M^+]; HRMS *m/z* (rel. int.) 484.3183 [M^+; calc. for $C_{30}H_{44}O_5$, 484.3188] (31), 426.2772 [$C_{27}H_{38}O_4$; fragment **b**] (49), 413.2709 [$C_{26}H_{37}O_4$; fragment **c**] (20), 380.2692 [$C_{26}H_{36}O_2$; fragment **d**] (22), 326.2275 [$C_{22}H_{30}O_2$; fragment **a**] (100), 231.1707 [$C_{16}H_{23}O$; fragment **e**] (39); ^{1}H NMR: Table 1.

Azadironol (**4**). UV λ_{max} (MeOH) nm: 284.5, 229.8; IR ν_{max} ($CHCl_3$) cm^{-1}: 3450 (OH), 2910 (CH), 1720–1700 (CO), 1660 (cyclohexenone), 1600, 850 (C=C), 1380 (geminal methyls); FDMS *m/z* 522; HRMS *m/z* (rel. int.) 522.2976; [M^+; calc. for $C_{32}H_{42}O_6$; 522.2980] (6), 504 (12), 328 [$C_{22}H_{32}O_2$, fragment **a**] (6), 309 (4), 194.0578 [$C_{10}H_{10}O_4$; fragment **b**] (20), 177.0551 [$C_{10}H_9O_3$; fragment **c**] (80), 149.0602 [$C_9H_9O_2$; fragment **d**] (21), 83.0496 [C_5H_7O; fragment **e**] (100); ^{1}H NMR: Table 1.

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