Journal of Natural Products
Vol. 49, No. 6, pp. 1068-1073, Nov-Dec 1986

TWO NEW TETRANORTRITERPENOIDS FROM *AZADIRACHTA INDICA*

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ABSTRACT.—From the fresh, green, spring twigs of *Azadirachta indica*, two new tetranortriterpenoid γ-hydroxybutenolides, desacetylnimbinolide and desacetylisonimbinolide, have been isolated together with desactylnimbin. The structures of these bitter limonoids have been established as **1** and **4**, respectively, through chemical and spectral studies.

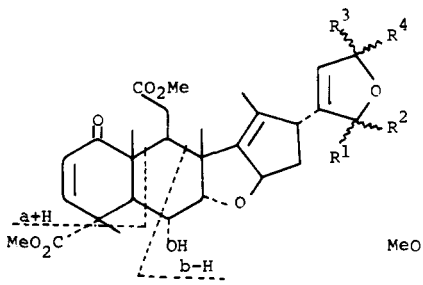
Azadirachta indica A. Juss (Meliaceae), commonly known as "neem," is widely distributed in Asia and Africa, and almost every part of the tree has long been used for the treatment of a variety of human ailments, particularly against diseases of bacterial and fungal origin (1,2). Various parts of the tree have been subjected to chemical and therapeutic studies since about the beginning of the current century. Initially these studies were mainly concerned with the fatty acid components and amorphous bitter substances isolated from the oil (3). In 1942, a reinvestigation of the oil, employing an analytical procedure based on partitioning of the unsaponified oil between petroleum ether and dilute EtOH, resulted in the isolation of the first two crystalline, bitter constituents, nimbin and nimbinin, along with an amorphous bitter principle, nimbidin, from the combined dilute alcoholic extracts (4). Nimbidin is anti-arthritic and anti-inflammatory (5) in its action and possesses significant anti-ulcer potential (6); various other fractions of the tree have been found to have antitumor (7), antipyretic, and anti-inflammatory properties (8). The extracts and certain individual constituents of neem leaves and dried fruits have insect antifeedent activity, and various factors derived from neem possess diverse biological effects such as repellence, phagodeterrence, reduced growth, abnormal development, and reduced oviposition (9,10).

Chemical studies carried out by Siddiqui *et al.* on the terpenoidal constituents of neem led to the isolation and structure elucidation of various triterpenoids from fruits (11-14) and leaves (13, 15-17). The present paper describes the isolation and structure elucidation of two new tetranortriterpenoids, desacetylnimbinolide (**1**) and desacetylisonimbinolide (**4**), along with desacetylnimbin (**3**) (18) from the acidic fraction of the fresh, green, spring twigs. The structures of these compounds have been established through spectral studies and chemical reactions. Compounds **1** and **4** are of potential biological importance as other γ-hydroxybutenolides have been shown to possess insect-growth-regulating (13) and insect-antifeeding (19) properties.

RESULTS AND DISCUSSION

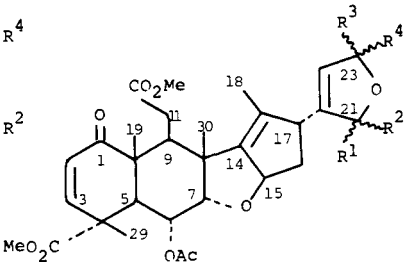
The CH_2Cl_2 extract of the fresh, green, neem twigs was divided into acidic and neutral fractions, and the former after usual work-up was subjected to preparative tlc, ultimately yielding desacetylnimbinolide (**1**), desacetylnimbin (**3**), and desacetylisonimbinolide (**4**).

Desacetylnimbinolide (**1**) has the molecular formula $C_{28}H_{34}O_{10}$ (hrms). Its uv spectrum showed maxima at 208 nm (ε 8692), while the ir spectrum displayed peaks at 3400 (OH), 1762 (α, β-unsaturated-γ-lactone), 1735 (carbomethoxyl), 1660 (cyclohexenone), 1635 and 820 (trisubstituted double bond), 1150 and 1075 cm^{-1} (ether linkage). The ^{1}H-nmr spectrum of **1** (Table 1) showed that **1** is closely related to nimbin (4, 20). However, in the ^{1}H-nmr spectrum of nimbin, H-6β geminal to the acetoxy group appeared as a double doublet at δ 5.19 while the same proton resonated



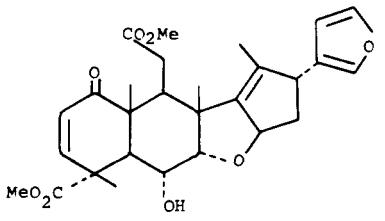
1 $R^1=R^2=O$, $R^3=H$, $R^4=OH$

4 $R^1=H$, $R^2=OH$, $R^3=R^4=O$



2 $R^1=R^2=O$, $R^3=H$, $R^4=OAc$

5 $R^1=H$, $R^2=OAc$, $R^3=R^4=O$



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as a double doublet ($J=11.6$, 3.1 Hz) at δ 3.92 in the case of **1**. This observation led to the placement of a hydroxyl function at C-6, which was supported by the absence of the acetoxy signal in the ^{1}H-nmr spectrum (Table 1), appearance of two hydroxyl protons (δ 3.73 and 2.02), and a carbinylic carbon (δ 65.9) in the ^{1}H- and ^{13}C-nmr spectra, respectively; and shifting of H-6β (δ 3.92) to δ 5.18 in the ^{1}H-nmr spectrum of **2**, obtained on acetylation of **1**. Moreover, the ir, ^{1}H- and ^{13}C-nmr spectra indicated the absence of a furan ring in **1**, and, instead, a γ-hydroxy-α,β-unsaturated-γ-lactone side chain was shown by the ir and nmr spectral data (Tables 1 and 2). Thus, two one-proton multiplets at δ 6.97 and 6.01 have been assigned to H-22 and H-23, respectively, the latter being shifted to δ 7.08 upon acetylation. This was corroborated the presence of a hemiacetal carbon at δ 96.9 (C-23) and an α, β-unsaturated-γ-lactone [δ137.0 (C-20), 171.0 (C-21), and 142.0 (C-22)] in the ^{13}C-nmr spectrum (Table 2), and a diagnostic fragment at *m/z* 430.2010 ($C_{24}H_{30}O_7$) in the mass spectrum of **1**, resulting from the loss of the side chain. These structural features were also supported by two significant ions observed in the mass spectrum at *m/z* 107.0490 (C_7H_7O, fragment a+H) and 263.0911 ($C_{14}H_{15}O_5$, fragment b−H) resulting from the cleavages of ring A and ring B, respectively. The ^{1}H-nmr assignments were finally confirmed through ^{1}H-^{1}H homonuclear decoupling experiments.

The spectral data of desacetylisonimbinolide (**4**) showed that it has an identical carbocyclic nucleus with that of desacetylnimbinolide (**1**) and differs in the side chain only. The nature of the side chain in **4** was shown to be 21-hydroxybut-20(22)-ene-21,23-γ-lactone by the presence of two one-proton signals at δ 5.78 (H-21) and 5.91 (H-22) in the ^{1}H-nmr spectrum (Table 1), the former being shifted to δ 6.87 upon acetylation. This was supported by the resonances at δ 162.0 (C-20), 96.9 (C-21), 120.8 (C-22), and 171.2 (C-23) in the ^{13}C-nmr spectrum of **4** (Table 2). The presence of double signals for the side chain carbons in the ^{13}C-nmr spectrum of **1** and **4** indicated that they are epimeric at C-21 and C-23, respectively, which has also been observed for the other γ-hydroxybutenolides (13, 19).

TABLE 1. ^{1}H-nmr Spectral Data (δ_H and J/Hz) of Tetranortriterpenoids

Assignment	Compounds				
	1	**2**	**3**	**4**	**5**
H-2	5.83, d	5.84, d	5.87, d	5.81, d	5.83, d
	$J_{1,2}$ 10.1	$J_{1,2}$ 10.1	$J_{1,2}$ 10.0	$J_{1,2}$ 10.0	$J_{1,2}$ 10.1
H-3	6.41, d	6.40, d	6.42, d	6.39, d	6.40, d
	$J_{2,1}$ 10.1	$J_{2,1}$ 10.1	$J_{2,1}$10.0	$J_{2,1}$ 10.0	$J_{2,1}$ 10.1
H-5	3.31, d	3.36, d	3.46, d	3.30, d	3.36, d
	$J_{5,6}$ 11.6	$J_{5,6}$ 10.6	$J_{5,6}$ 11.6	$J_{5,6}$ 11.5	$J_{5,6}$ 12.8
H-6	3.92, dd	5.18, dd	4.17, dd	3.93, dd	5.20, dd
	$J_{6,5}$ 11.6	$J_{6,5}$ 10.6	$J_{6,5}$ 11.6	$J_{6,5}$ 11.5	$J_{6,5}$ 12.8
	$J_{6,7}$ 3.1	$J_{6,7}$ 2.5	$J_{6,7}$ 2.5	$J_{6,7}$ 3.0	$J_{6,7}$ 2.5
H-7	4.08, d	4.09, d	4.10, d	4.10, d	4.05, d
	$J_{7,6}$ 3.1	$J_{7,6}$ 2.5	$J_{7,6}$ 2.5	$J_{7,6}$ 3.0	$J_{7,6}$ 2.5
H-9	2.56, dd	2.60, m	2.71, m	2.55, dd	2.60, dd
	$J_{9,11\alpha}$ 4.0	—	—	$J_{9,11\alpha}$ 5.0	$J_{9,11\alpha}$ 5.1
	$J_{9,11\beta}$ 4.5	—	—	$J_{9,11\beta}$ 5.5	$J_{9,11\beta}$ 6.6
H-11α	2.89, dd	2.80, m	2.80, m	2.89, dd	2.88, dd
	J_{gem} 16.8	—	—	J_{gem} 16.0	J_{gem} 16.6
	$J_{11\alpha,9}$ 4.0			$J_{11\alpha,9}$ 5.0	$J_{11\alpha,9}$ 5.1
H-11β	2.21, dd	2.17, m	2.25, m	2.21, dd	2.15, dd
	J_{gem} 16.8	—	—	J_{gem} 16.0	J_{gem} 16.6
	$J_{11\beta,9}$ 4.5	—	—	$J_{11\beta,9}$ 5.5	$J_{11\beta,9}$ 6.6
H-15	5.51, m	5.48, m	5.52, m	5.51, m	5.60, m
H-16α	2.31, dd	2.31, dd	2.30, m	2.29, dd	2.30, dd
	J_{gem} 12.0	J_{gem} 11.7	—	J_{gem} 12.0	J_{gem} 12.3
	$J_{16\alpha,15}$ 5.6	$J_{16\alpha,15}$ 4.0	—	$J_{16\alpha,15}$ 5.5	$J_{16\alpha,15}$ 6.1
H-16β	2.09, ddd	2.06, m	2.03, m	2.12, ddd	2.09, m
	J_{gem} 12.0			J_{gem} 12.0	
	$J_{16\beta,15}$ 7.0	—	—	$J_{16\beta,15}$ 7.0	—
	$J_{16\beta,17}$ 7.7	—	—	$J_{16\beta,17}$ 7.5	—
H-17	3.53, d	3.73, d	3.70, d	3.55 d	3.63, d
	$J_{17,16\beta}$ 7.7	$J_{17,16\beta}$ 6.7	$J_{17,16\beta}$ 7.0	$J_{17,16\beta}$ 7.5	$J_{17,16\beta}$ 7.0
H-18	1.84, s	1.75, s	1.69, s	1.80, s	1.60, s
H-19	1.18, s	1.20, s	1.25, s	1.19, s	1.21, s
H-21	—	—	7.40, m	5.78, m	6.87, m
H-22	6.97, m	6.83, m	6.32, m	5.91, m	5.85, m
H-23	6.01, m	7.08, m	7.10, m	—	—
H-29	1.22, s	1.25, s	1.30, s	1.22, s	1.24, s
H-30	1.28, s	1.28, s	1.33, s	1.28, s	1.30, s
OH	3.73, m	—	—	3.73, m	—
	2.02, m	—	—	2.00, m	—
OMe	3.70, s	3.76, s	3.65, s	3.71, s	3.71, s
	3.69, s	3.70, s	3.63, s	3.69, s	3.69, s
OAc	—	2.01, s	—	—	2.02, s
	—	2.03, s	—	—	2.03, s

The stereochemistry of various centers of desacetylnimbinolide (**1**) has been established through the NOESY spectrum which showed the spatial connectivities of H-15 with H-22 and H-9; H-5 with H-9, H-22, and 28-OMe (δ 3.69); H-22 with H-16α; H-18 with H-11β, H-16β, and H-17; H-19 with H-18, H-30, and H-11β; H-29 with H-6 and H-7; H-30 with H-7, H-11β, H-17, and H-18; and also of H-2 with H-3, H-16β with H-17, and H-22 with H-23. These observations exhibited that ring A and B are transfused, and the spatial proximity of H-15 with H-22 and of H-22 with H-16α showed that the side chain at C-17 has α disposition.

The NOESY spectrum of desacetylisonimbinolide (**4**) showed the spatial connec-

TABLE 2. ^{13}C-nmr Chemical Shifts (δ_c/ppm) of Compounds **1** and **4**

Carbons	Compounds		Carbons	Compounds	
	1	**4**		**1**	**4**
C-1	202.4	202.0	C-17	52.1	52.2
C-2	126.2	126.3	C-18	13.1	13.0
C-3	148.1	148.4	C-19	17.1[c]	17.1[c]
C-4	39.1	39.1	C-20	137.0	162.0
C-5	48.9	50.0		137.2	162.1
C-6	65.9	66.1	C-21	169.9	96.9
C-7	86.4[a]	87.6[a]		171.0	97.1
C-8	47.9[b]	47.9[b]	C-22	142.0	120.8
C-9	39.8	39.8		142.3	120.9
C-10	47.5[b]	47.5[b]	C-23	96.9	171.0
C-11	34.6	34.1		97.0	171.2
C-12	175.4	175.4	C-28	172.0	172.0
C-13	131.1	131.1	C-29	20.5	20.6
C-14	145.0	145.0	C-30	16.1[c]	16.1[c]
C-15	87.8[a]	88.0[a]	-COO*Me*	53.0	52.9
C-16	39.8	39.8		53.1	53.1

[a-c]Assignments may be reversed.

tivities of H-22 with H-9, H-15, and H-16α; H-5 with H-9, H-15, and H-22; H-18 with H-11β, H-16β and H-17; H-19 with H-18, H-30, and H-11β; H-29 with H-6 and H-7; H-30 with H-7, H-11β, H-17, H-18, and H-29; and also of H-2 with H-3 and H-16β with H-17. These interactions revealed that **4** also has the typical *trans* A/B ring junction with the α-oriented side chain at C-17.

The butenolides **1** and **4** as well as desacetylnimbin (**3**) were also detected in the fresh CH_2Cl_2 extract of the twigs, which showed that they are genuine natural constituents and not artifacts. Further, since the hydroxybutenolide side chain has been suggested as the intermediate in the formation of the furan ring of meliacins, **1** and **4** may be regarded as the precursors of nimbin and desacetylnimbin (21).

As experienced in the case of other γ-hydroxybutenolides (13, 17), descetylnimbinolide (**1**) and desacetylisonimbinolide (**4**) were initially obtained together with desacetylnimbin (**3**) as a whitish crystallizate, showing a single spot on tlc (Si gel, C_6H_6-EtOAC, 5:95). Assuming that the crystallizate was an uniform constituent, the structural studies were initiated when the nmr (^{1}H and ^{13}C) spectral data indicated that it was a mixture of more than two compounds. After trying a number of solvent systems on plates coated with silica gel and Al_2O_3, these were ultimately separated into three bands (Al_2O_3, $CHCl_3$-MeOH, 85:15), which were characterized as **1**, **3**, and **4** through chemical and spectral studies.

It has been observed in the present studies that γ-hydroxybutenolides are acidic in nature and are isolated from the acidic fraction (pH 9.0-11.0). For instance, five γ-hydroxybutenolides namely isonimbocinolide (17), margosinolide (22), isomargosinolide (22), desacetylnimbinolide (**1**), and desacetylisonimbinolide (**4**) have so far been obtained from the acidic fraction of neem leaves and twigs. On the other hand, if the pH is around 8.0, these form a part of the neutral fraction. For example, nimocinolide (13), isonimocinolide (13), and isonimolicinolide (23), were obtained from the neutral fraction of neem leaves and fruits. It may be noted, however, that in either case traces of these butenolides are detected in the counter fraction.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps were recorded in glass capillary tubes and are un-

corrected. Ir (in $CHCl_3$) and uv (in MeOH) spectra were measured on JASCO IRA-I and Pye-Unicam SP-800 spectrometers, respectively; mass spectra were recorded on Finnigan MAT 112 and 312 double focusing spectrometers. ^{1}H- and ^{13}C-nmr (broad band and gated spin echo) spectra were recorded in $CDCl_3$ on Bruker Aspect AM 300 and Bruker WP-100-SY FT-NMR spectrometers, respectively, and the chemical shifts are reported in ppm relative to TMS=O. ^{13}C-nmr spectral assignments have been made partly through spin echo spectrum and partly through comparison of chemical shifts with published data for similar compounds (13, 24). Optical rotations were measured at 24° in $CHCl_3$ on a Polartronic-D polarimeter. Merck Kieselgel 60 PF_{254} and Al_2O_3 60 PF_{254} coated on glass plates were used for analytical (thin layer) and preparative (thick layer) chromatography.

PLANT MATERIAL.—"Neem" twigs (6 kg) were collected from the Karachi region in the month of April and were identified by Professor S.I. Ali, Department of Botany, University of Karachi. A voucher specimen has been deposited in the Herbarium of the Botany Department, University of Karachi.

EXTRACTION AND ISOLATION.—The fresh, undried, uncrushed, neem twigs were repeatedly percolated with CH_2Cl_2 at room temperature. The CH_2Cl_2 and the aqueous layers were separated from the combined percolates, the former being freed of the solvent under reduced pressure. The dark brownish residue was shaken with EtOAc and H_2O, and the EtOAc layer was repeatedly extracted with 4% Na_2CO_3 to separate the acidic and neutral fractions (pH 9.0-11.0). The combined Na_2CO_3 phase was acidified with dilute HCl and extracted with EtOAc, which was washed, dried (Na_2SO_4 anhydrous), and charcoaled. The charcoal was successively eluted with EtOAc and C_6H_6-MeOH (1:1). The residue obtained from the combined EtOAc filtrate and the former charcoal eluate was subjected to preparative tlc (Si gel, C_6H_6-EtOAc, 5:95) to yield a crystalline product which was ultimately separated into desacetylnimbinolide (**1**), desacetylnimbin (**3**), and desacetylisonimbinolide (**4**) on plates coated with Al_2O_3 ($CHCl_3$-MeOH, 85:15).

DESACETYLNIMBINOLIDE (**1**).—Crystallized from $CHCl_3$ as prismatic rods (10 mg, 0.0003% on the dry wt. basis), mp 195-196°; $[\alpha]_D$ 100° (*c* 0.02 in $CHCl_3$); uv λ max 208 nm (ε 8692); ir ν max 3400, 1765, 1735, 1660, 1635, 1150, 1075, 820 cm^{-1}; hrms *m/z* (%) 530.2196 (M^+, calcd for $C_{28}H_{34}O_{10}$: 530.2150) (8), 498.1858 (M-CH_3OH) (5), 430.2010 (M-side chain) (2), 423.1431 (498-$HCOOCH_3$-CH_3) (6), 263.0911 ($C_{14}H_{15}O_5$, fragment b−H) (45), 245.0811 (263-H_2O) (8), 107.0490 (C_7H_7O, fragment a+H) (10).

ACETYLATION OF DESACETYLNIMBINOLIDE (**1**).—Ac_2O (2 ml) was added to a solution of **1** (4 mg) in pyridine (1 ml), and the reaction mixture was kept overnight at room temperature. Usual work-up of the reaction mixture afforded the acetyl derivative **2** as a crystalline residue which on recrystallization from $CHCl_3$ formed rods, mp 130-132°; uv λ max 210 nm (ε 4620); ir ν max 1760 (α, β-unsaturated-γ-lactone), 1735 (carbomethoxyl), 1720 (ester carbonyl), 1662 (cyclohexenone), 1640 and 825 (trisubstituted double bond), 1150 and 1075 cm^{-1} (ether linkage); hrms *m/z* (%) 614.2361 (M^+, calcd for $C_{32}H_{38}O_{12}$: 614.2361) (3), 554.2167 (M-$C_2H_4O_2$) (5), 494.1940 (M-2x$C_2H_4O_2$) (7).

DESACETYLISONIMBINOLIDE (**4**).—It crystallized from MeOH as bunches of rods (15 mg, 0.0004% on the dry wt. basis), mp 178-180°; $[\alpha]_D$ 50° (*c* 0.06 in $CHCl_3$); uv λ max 210 (ε 9752), 285 (ε 1484) nm; ir ν max 3400 (OH), 1760 (α, β-unsaturated-γ-lactone), 1740 (carbomethoxyl), 1665 (cyclohexenone), 1630 and 820 (trisubstituted double bond), 1145 and 1070 cm^{-1} (ether linkage); hrms *m/z* (%) 530.2170 (M^+, calcd for $C_{28}H_{34}O_{10}$: 530.2150) (4), 498.1858 (M-CH_3OH) (6), 430.1990 (M-side chain) (4), 423.1440 (498-$HCOOCH_3$-CH_3) (8), 263.0920 ($C_{14}H_{15}O_5$, fragment b−H) (30), 245.0818(263-H_2O) (10), 107.0475 (C_7H_7O, fragment a+H) (12).

ACETYLATION OF DESACETYLISONIMBINOLIDE (**4**).—Compound **4** was acetylated in the same manner as desacetylnimbinolide (**1**) to yield **5** which crystallized from $CHCl_3$ as needles, mp 112-114°; uv λ max 210 nm (ε 5110); ir ν max 1765 (α, β-unsaturated-γ-lactone), 1740 (carbomethoxyl), 1725 (ester carbonyl), 1665 (cyclohexenone), 1645 and 820 (trisubstituted double bond), 1150 and 1070 (ether linkage); hrms *m/z* (%) 614.2393 (M^+, calcd for $C_{32}H_{38}O_{12}$:614.2361) (5), 554.2167 (M-$C_2H_4O_2$) (3), 494.1940 (M-2x$C_2H_4O_2$) (6).

DESACETYLNIMBIN (**3**).—It crystallized from MeOH as rods, mp 210-212°; $[\alpha]_D$ +110°; uv λ max 225 nm (ε 9163); ir ν max 3500 (OH), 1735 (carbomethoxyl), 1660 (cyclohexenone), 1625 and 815 (trisubstituted double bond), 1145 and 1065 cm^{-1} (ether linkage); eims *m/z* (%) 498.2248 (M^+, calcd for $C_{28}H_{34}O_8$: 498.2252) (2), 436 (M-32-30) (8), 423 (M-60-15) (85), 408 (M-60-30) (100).

ACKNOWLEDGMENTS

One of us (TM) wishes to express his grateful thanks to Hamdard Foundation Pakistan for providing a research fellowship during the course of this work.

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Received 12 June 1986