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TETRANORTRITERPENOIDS RELATED TO NIMBIN AND NIMBOLIDE FROM *AZADIRACHTA INDICA* A. JUSS (MELIACEAE)

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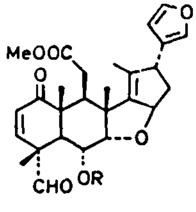
Abstract: *Three new tetranortriterpenoids, 6-deacetylnimbinal (1), nimbinol (3), and 28-deoxonimbolide (6), related to nimbin and nimbolide, have been isolated from Azadirachta indica. (1) and (6) were found in the leaf extracts, (3) in the seeds. The assignment of the structures (1), (3), and (6) was achieved on the basis of ^{1}H and ^{13}C n.m.r. analyses and chemical transformations. The n.m.r. spectra of nimbanal (2), 6-deacetylnimbin (4), nimbin (5), and nimbolide (7) were partially reassigned in this connection.*

INTRODUCTION

Some time ago, we reported on the isolation from *Azadirachta indica* leaves of 6-deacetylnimbinal (1), the first C-4 tetranortriterpenoid aldehyde found in neem.[1] A recent paper on the isolation from neem seeds of nimbanal (2)[2,3] prompts us to report more extensively on our investigations on the isolation and structure determination by n.m.r. of the new compounds 6-deacetylnimbinal (1), nimbinol (3), and 28-deoxonimbolide (6), related to 6-deacetylnimbin (4), nimbin (5), and nimbolide (7), respectively. Assignments of the ^{1}H n.m.r. signals were achieved using homonuclear decoupling, measurements of the nuclear Overhauser effects (n.O.e.) in the FT difference spectra, and spectrum simulation. All ^{13}C signals were assigned unequivocally on the



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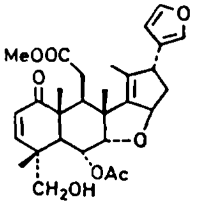
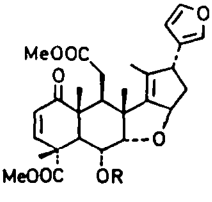
(2) R = Ac



(3)



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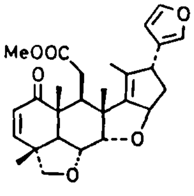
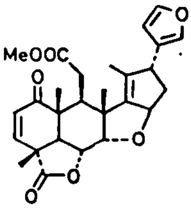
(5) R = Ac



(6)



(7)

Table 1. 250 MHz ^1H n.m.r. data ($CDCl_3$, TMS = 0) of compounds (1) - (5).

	(1)	(2)	(3)	(4)	(5)
2-H	5.97(d,10.0)	6.04(d,10.1)	5.92(d,10.0)	5.85(d,10.1)	5.88(d,10.0)
3-H	6.21(d,10.0)	6.08(d,10.1)	6.40(d,10.0)	6.42(d,10.1	6.34(d,10.0)
5-H	2.92(d,11.0)	3.62(d,12.2)	3.04(d,12.1)	3.40(d,11.6)	3.69(d,11.0)
6-H	3.97(ddd,11.0;9.9;3.6)	5.20(dd,12.2;3.0)	5.40(dd,12.1;3.0)	3.89(ddd,11.6;3.0;10.0)	5.22(dd,11.0;3.0)
7-H	4.05(d,3.6)	4.08(d,3.0)	4.01(d,3.0)	4.03(d,3.0)	4.05(d,3.0)
9-H	2.76(dd,5.4;3.8)	2.86(dd,5,4;3.8)	2.78(dd,5.0;3.0)	2.77(dd,5.4;3.8)	2.87(dd,5.0;3.0)
11-H_a	2.26(dd,3.8;16.3)	2.23(dd,3.8;16.3)	2.23(dd,3.0;16.0)	2.24(dd,3.8;16.3)	2.23(dd,3.0;16.0)
11-H_b	2.92(dd,5.4;16.3)	2.92(dd,5,4;16.3)	2.80(dd,5.0;16.0)	2.90(dd,5.4;16.3)	2.92(dd,5.0;16.0)
15-H	5.54(dddq,8.3;6.2; 1.2;1.7)	5.58(dddq,8.3;6.2; 1.2;1.7)	5.55(dddq,8.3;6.2; 1.2;1.7)	5.55(dddq,8.3;6.2; 1.2;1.7)	5.57(dddq,8.3;6.2; 1.2;1.7)
16-H_a	2.04(ddd,11.8;8.1;8.3)	2.05(ddd,11.8;8.1;8.3)	2.04(ddd,11.8;8.1;8.3)	2.04(ddd,11.8;8.1;8.3)	2.03(ddd,11.8;8.3;8.1)
16-H_b	2.19(dd,11.8;6.2)	2.21(dd,11.8;6.2)	2.19(dd,11.8;6.2)	2.19(dd,11.8;6.2)	2.19(dd,11.8;6.2)
17-H	3.68(dd,8.1;1.2)	3.66(dd,8.1;1.2)	3.63(dd,8.1;1.2)	3.67(dd,8.1;6.2)	3.63(dd,8.1;1.2)
18-H	1.70(d,1.7)	1.68(d,1.7)	1.67(d,1.7)	1.69(d,1.7)	1.67(d,1.7)
19-H	1.25(s)	1.27(s)	1.34(s)	1.21(s)	1.28(s)
21-H	7.34(m)	7.33(m)	7.32(m)	7.33(m)	7.32(m)
22-H	6.33(m)	6.34(m)	6.35(m)	6.34(m)	6.33(m)
23-H	7.25(m)	7.24(m)	7.25(m)	7.25(m)	7.24(m)
28-H	9.36(s)	9.25(s)	28-H_a 3.49(dd,10.8;5.2) 28-H_b 3.82(dd,10.8;7.1)	-	-
29-H	1.54(s)	1.38(s)	1.06(s)	1.59(s)	1.36(s)
30-H	1.31(s)	1.32(s)	1.38(s)	1.29(s)	1.35(s)
$COOCH_3$	3.66(s)	3.64(s)	3.63(s)	3.66(s)	3.66(s)
$COOCH_3$	-	-	-	3.70(s)	3.74(s)
CH_3COO	-	1.99(s)	2.17(s)	-	2.04(s)
6-OH	2.11(d,9.9)	-	-	2.18(d,10.0)	-
28-OH	-	-	1.77(dd,5.2;7.1)	-	-

basis of twodimensional $^1H,^{13}C$ heteroscalar correlated spectra,[4] $^1H,^{13}C$ long range spectra,[4] and DEPT spectra. In this connection, the n.m.r. signals for compounds (2),[2] (4),[5] (5),[5] and (7)[6] were partially reassigned. The relationship between (1), (2), and (3) was shown by conversion of (1) into (2) and (3).

RESULTS

Isolation of Compounds (1), (3), and (6)

6-Deacetylnimbinal (1) and 28-deoxonimbolide (6) along with 6-deacetylnimbin (4), nimbin (5), and nimbolide (7) were isolated by extraction of neem leaves with diethyl ether followed by repeated chromatography. Nimbinol (3) was isolated chromatographically from neem seed methanol extracts.

Structure Determination

The molecular formulas of (1), (3), and (6) were determined from the high resolution mass spectra as $C_{27}H_{32}O_7$ (1), $C_{29}H_{36}O_8$ (3), and $C_{27}H_{32}O_6$ (6). Infrared absorption at 1680 cm^{-1} indicated the presence of a conjugated enone system. The ^1H and ^{13}C n.m.r. data (tables 1, 2, and 3, resp.) indicated that (1), (3) and (6) are closely related to 6-deacetylnimbin (4), nimbin (5), and nimbolide (7). The proton signals at δ 5.97, 6.21 (1), 5.92, 6.40 (3), and 5.85, 7.02 (6) (d, J=10.0 Hz each), and the carbon signals at δ 201.77 (1), 203.1 (3), and 202.52 (6) are consistent with a conjugated enone system as present in ring A of 6-deacetylnimbin (4), nimbin

Table 2. 250 MHz ^1H n.m.r. data ($CDCl_3$, TMS = 0) of compounds (6) and (7).

	(6)	(7)
2-H	5.85 (d,10.0)	5.89 (d,9.7)
3-H	7.02 (d,10.0)	7.26 (d,9.7)
5-H	2.78 (d,12.5)	3.15 (d,12.8)
6-H	4.09 (dd,12.5;3.4)	4.60 (dd,12.8;3.6)
7-H	4.17 (d,3.4)	4.24 (d,3.6)
9-H	2.61 (dd,5.4;5.4)	2.70 (dd,5.4;5.4)
11-H_a	2.32 (dd,5.4; 16.3)	2.35 (dd,5.4;16.3)
11-H_b	3.23 (dd,5.4;16.3)	3.22 (dd,5.4;16.3)
15-H	5.47 (dddq,8.3;7.0;1.2;1.7)	5.49 (dddq,8.3;7.0;1.2;1.7)
16-H_a	2.08 (ddd,11.8;8.1;8.3)	2.08 (ddd,11.8;8.1;8.3)
16-H_b	2.16 (dd,11.8;7.0)	2.18 (dd,11.8;7.0)
17-H	3.69 (dd,8.1;1.2)	3.64 (dd,8.1;1.2)
18-H	1.65 (d,1.7)	1.67 (d,1.7)
19-H	1.12 (s)	1.19 (s)
21-H	7.26 (m)	7.28 (m)
22-H	6.24 (m)	6.23 (m)
23-H	7.18 (m)	7.19 (m)
28-H_a	3.60 (d,7.2)	-
28-H_b	3.76 (d,7.2)	-
29-H	1.27 (s)	1.44 (s)
30-H	1.30 (s)	1.34 (s)
$COOCH_3$	3.50 (s)	3.50 (s)

(5), and nimbolide (7), respectively. Similar signal patterns are found also for the spin systems 5-H/6-H/7-H, 9-H/11-$H_{a,b}$, and 15-H/16$H_{a,b}$/17-H/18-H of (1), (3), and (6) in comparison to (4), (5), and (7), respectively. In addition spin systems 9-H/11-$H_{a,b}$ and 15-H/16-$H_{a,b}$/17-H/18-H of compounds (1) - (7) were simulated on the basis of chemical shifts and coupling constants to confirm structures (1), (3), and (6), and for partial reassignment of the n.m.r. signals of (2), (4), (5), and (7).

Table 3. 62.89 MHz ^{13}C n.m.r. data ($CDCl_3$ = 77 ppm) of compounds (1) - (7).

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
C-1	201.77 s	201.30 s	203.10 s	202.42 s	201.73 s	202.52 s	200.78 s
C-2	128.25 d	129.18 d	125.97 d	126.52 d	125.94 d	130.15 d	130.77 d
C-3	145.81 d	144.82 d	153.85 d	148.22 d	147.61 d	152.07 d	149.43 d
C-4	51.42 s	51.78 s	41.49 s	47.70 s	47.76 s	41.71 s	43.31 s
C-5	44.46 d	40.56 d	38.36 d	43.59 d	41.35 d	48.73 d	47.41 d
C-6	65.92 d	68.53 d	70.30 d	66.17 d	66.52 d	72.28 d	73.16 d
C-7	87.11 d	87.25 d	85.66 d	86.95 d	84.47 d	85.15 d	84.47 d
C-8	47.45 s	47.28 s	48.71 s	47.26 s	46.90 s	50.37 s	49.95 s
C-9	38.74 d	38.32 d	37.90 d	38.99 d	38.39 d	40.97 d	40.73 d
C-10	47.74 s	47.95 s	47.55 s	47.42 s	47.82 s	45.81 s	44.92 s
C-11	34.26 t	34.11 t	34.35 t	34.27 t	34.03 t	32.06 t	31.72 t
C-12	173.56 s	173.85 s	173.83 s	173.84 s	173.72 s	173.38 s	173.72 s
C-13	135.21 s	135.77 s	135.22 s	135.01 s	135.09 s	135.09 s	136.21 s
C-14	146.59 s	145.83 s	146.23 s	146.97 s	146.17 s	145.82 s	144.61 s
C-15	87.11 d	84.34 d	87.08 d	87.45 d	87.38 d	87.63 d	88.10 d
C-16	41.34 t	41.30 t	41.30 t	41.36 t	41.35 t	41.13 t	40.84 t
C-17	49.66 d	49.46 d	49.48 d	49.57 d	49.30 d	49.13 d	49.08 d
C-18	12.81 q	12.74 q	12.72 q	12.71 q	12.58 q	12.52 q	12.44 q
C-19	16.57 q	16.75 q	17.06 q	16.27 q	16.44 q	14.26 q	14.66 q
C-20	126.76 s	126.81 s	126.89 s	126.92 s	126.79 s	126.74 s	126.37 s
C-21	139.05 d	139.15 d	139.17 d	139.13 d	139.01 d	138.75 d	138.71 d
C-22	110.44 d	110.51 d	110.57 d	110.50 d	110.42 d	110.29 d	110.14 d
C-23	143.08 d	144.84 d	143.17 d	143.19 d	143.03 d	142.93 d	142.92 d
C-28	200.80 d	199.68 d	71.22 t	175.74 s	174.68 s	79.08 t	175.00 s
C-29	15.80 q	14.62 q	16.80 q	16.27 q	16.94 q	20.20 q	18.06 q
C-30	17.42 q	16.95 q	17.06 q	17.02 q	16.64 q	16.97 q	16.63 q
$COOCH_3$	51.61 q	51.78 q	51.59 q	51.59 q	51.49 q	51.35 q	51.35 q
$COOCH_3$	-	-	-	52.94 q	52.89 q	-	-
CH_3COO	-	170.43 s	170.38 s	-	170.67 s	-	-
CH_3COO	-	20.71 q	21.62 q	-	20.73 q	-	-

6-Deacetylnimbinal (1). The presence of an aldehyde group was determined from an infrared absorption at 2900 cm^{-1}, and signals at δ 9.36 in the ^1H, and δ 200.80 (d) in the ^{13}C n.m.r. spectra. 6-OH (δ 2.11) which is coupled to 6-H (δ 3.97) was detected by D_2O exchange. The quarternary carbons were assigned from $^1H,^{13}C$ long range coupling C-4/29-H, C-4/5-H, C-8/9-H, C-8/11-H, C-8/30-H, C-10/5-H, and C-10/19-H. The methyl signals were assigned by means of n.O.e. difference experiments (table 4), and $^1H,^{13}C$ COSY long range spectra. This technics allowed also the determination of the position of the aldehyde group attached to C-4. Particularly the enhancement of the 3-H signal on saturation of 29-H demonstrates the nimbin type of the enone system in ring A.

Table 4. Nuclear Overhauser effects in the ^1H n.m.r. spectra (250 MHz, $CDCl_3$) of 6-deacetylnimbinal (1), nimbinol (3), and 28-deoxonimbolide (6).

	(1)	(3) and (6)
irradiated	observed	observed
18-H	17-H, 21-H, 22-H, 23-H, 30-H	17-H, 21-H 22-H, 23-H, 30-H
19-H	6-H, 11-H_b, 30-H	6-H, 11-H_b, 30-H
29-H	3-H, 6-H, 19-H, 28-H	3-H, 6-H, 19-H, 28-$H_{a,b}$

Nimbinol (3): The presence of an OH group attached to C-28 (δ 1.77, coupled to two protons at δ 3.49 and 3.82) was detected by D_2O exchange which converted the signals at δ 3.49 (dd) and δ 3.82 (dd) into doublets (^2J = 10.8 Hz each). N.O.e. experiments (table 4) were used to indentify the methyl groups and 28-$H_{a,b}$.

28-Deoxonimbolide (6). The ^1H and ^{13}C n.m.r. data of (6) (tables 2 and 3) are very similar to that of nimbolide (7), except the following points: the carbon signal of the lactone carbonyl carbon (δ 175.00) is missing. Instead a carbon signal at δ 79.08 (t) of an oxymethylene group appears in the spectrum which was identified to be C-28 by n.O.e and ^1H,^{13}C decoupling experiments. The AB pattern of the 28-H signal in the ^1H n.m.r. spectrum of (6) is very similar to that found for salannin as far as chemical shifts and coupling constants are concerned.[7] The methyl groups and quarternary carbon atoms were assigned by n.O.e. (table 4), and from ^1H,^{13}C long range coupling as described for 6-deacetylnimbinal (1).

Conversion of 6-deacetylnimbinal (1) into (2) and (3). The structural relationship between (1), (2), and (3) was proved by chemical transformation starting from (1). (1) was acetylated to give nimbinal (2) which has recently been described as nimbanal, a constituent of neem seed extracts.[2] A reinvestigation of the n.m.r. spectra of this compound using the technics described above led to partial reassignment of the proton and carbon signals (tables 1 and 3). Since nimbanal is very closely related to nimbin (5) and 6-deacetylnimbinal (1), described earlier,[1] we suggest to rename nimbanal as nimbinal (2). Reduction of (2) with sodium borohydride gave nimbinol (3).

EXPERIMENTAL

Plant Material. - Neem seed kernels were collected and dried in Togo,[8] neem leaves near Poona, India.[9]

N.m.r. Methods. - N.m.r. spectra were run on a BRUKER WM 250 instrument equipped with Aspect 3000 Computer at ambient temperature. *^1H n.m.r.*: 250 MHz, TMS as internal standard. *N.O.e.* experiments were carried out using the standard BRUKER microprogram NOEDIFF.AU with an irradiation time of 2.5 seconds. Two dummy scans were taken before a cycle of 8 scans. *^{13}C n.m.r.*: 62.89 MHz, solvent $CDCl_3$. The center peak of the $CDCl_3$ triplet was used as the standard, and set to 77 ppm. For broad band decoupled spectra the BRUKER microprogram POWGATE.AU, and for the *DEPT spectra* a modified pulse sequence with an additional purging pulse[10] were used. *2D n.m.r. spectra:* $^{1}H,^{13}C$ COSY spectra were accumulated using the standard BRUKER microprogram CHCORR.AU. The sweep width was 10 KHz in F_2 and 473.485 Hz in F_1. 4K data points were used for F_1 giving a digital resolution of 2.44 Hz/data point. 128 experiments were carried out to give, after zerofilling in F_1, a digital resolution of 1.85 Hz per data point in F_1. A Gauß window was applied in both domains with $GB_1 = GB_2 = 0.2$, $LB_1 = -0.8$, and $LB_2 = -4.0$. The delays for the polarization transfer in the $^{1}J_{C,H}$ COSY spectra were optimized to a coupling constant of 130 Hz, for the $^{1}H,^{13}C$ long range spectra to a coupling constant of 20 Hz. ***Spectrum simulation:*** Three-spin system 9-H/11-$H_{a,b}$, and seven-spin system 15-H/16-$H_{a,b}$/17-H/18-H of compounds (1 - 7) were simulated using the BRUKER PANIC program.

Melting points were determined on a Büchi SMR 20 instrument and are not corrected. ***Optical rotations*** were recorded on a Perkin Elmer Polarimeter 241, ***infrared spectra*** on a Zeiss IMR 25, ***mass spectra*** on a Varian MAT 311 A.

*Isolation of **Nimbinol** (3).* - 3-5 kg ground neem seed kernels were stirred three times with 10 liters of methanol at room temperature for 24 hours. Solvent partition between methanol and petrol ether (1:1) of the extract (650 g) followed by partition between water and ethyl acetate (2:1) of the methanol phase gave 180 g crude material. Column chromatography on 1.6 kg Merck silica gel 60 of the ethyl acetate phase with methylene chloride / methanol mixtures (99.5:0.5 ——> 80:20) followed by medium pressure chromatography on Polygosil RP 18 (25-40 µm) with methanol / water (6:4 ——> 7:3, flow 14 ml/min), and repeated HPLC on RP 18 (10 µm) with methanol / water 6:4 and subsequently on Spherisorb Nitrile (5 µm) with petrol ether / methylene chloride / methanol 100:10:8 (flow 6 ml/min.) yielded 3 mg amorphous nimbinol (3). $C_{29}H_{36}O_8$; EI-MS: m/z 512 (M^+), 452, 273, 231, 149; Found 512.2397, $C_{29}H_{36}O_8$, requires 512.2398. ^{1}H and ^{13}C n.m.r. data see tables 1 and 3.

$$[\alpha]^{\lambda}_{20^\circ C} = \frac{589}{+172}\;\frac{578}{+185}\;\frac{546}{+206}\;\frac{436}{+323}\;\frac{405}{+344}\;\frac{365}{-13} \qquad (CHCl_3,\ c = 0.1)$$

Isolation of (1) and (6). - Soxhlet extraction of 10 kg finely powdered air dried neem leaves with diethyl ether followed by chromatography on 4.5 kg silica gel of the crude extract (283 g) with petrol ether / ethyl acetate (90:10 ——> 0:100) gave a mixture (6 g) of nimbolide (7) and 28-deoxonimbolide (6) (fraction 1), 2.8 g nimbin (5) (fraction 2), and a mixture (2.5 g) consisting of 6-deacetylnimbinal (1) and 6-deacetylnimbin (4) (fraction 3).

28-Deoxonimbolide (6). - 4 g Nimbolide (7) crystallized from a methanolic solution of fraction 1. Reversed phase chromatography on Nucleosil C 18 (25-40 µm) of the mother liquor with methanol / water 3:1 gave 0.6 g 28-deoxonimbolide (6), m.p. 170°C (from methanol). IR (KBr): 1730 (C=O), 1685 (C=C), 1170, 1140, 1030 cm^{-1} (C-O). EI-MS: m/z 452 (M^+), 335, 259, 185, 133; Found 452.2179, $C_{27}H_{32}O_6$ requires 452.2181. ^{1}H and ^{13}C n.m.r. data see tables 2 and 3.

$$[\alpha]^{\lambda}_{20^\circ C} = \frac{589}{+203}\;\frac{578}{+213}\;\frac{546}{+248}\;\frac{436}{+480}\;\frac{405}{+643} \qquad (CHCl_3,\ c = 0.1)$$

6-Deacetylnimbinal (1). - Reversed phase chromatography on LiChroprep RP 18 (25-40 µm) of fraction 3 with methanol / water 4:1 gave 1.2 g amorphous (1). IR (KBr): 3420 (OH), 2900 (CHO), 1740, 1720 (C=O), 1680 (C=C), 1270, 1260, 1170, 1050, 1020 cm^{-1} (C-O). EI-MS: m/z 468 (M^+), 439, 375, 231, 147; Found 468.2144 $C_{27}H_{32}O_7$ requires 468.2143. ^1H and ^{13}C n.m.r. data see tables 1 and 3.

$$[\alpha]^{\lambda}_{20^\circ C} = \begin{array}{cccccc} 589 & 578 & 546 & 436 & 405 & 365 \\ \hline +18 & +20 & +24 & -56 & -158 & -664 \end{array} \qquad (CHCl_3,\ c = 0.1)$$

Conversion of 6-deacetylnimbinal (1) to nimbinol (3). - 50 mg 6-deacetylnimbinal (1) were dissolved in 0.5 ml pyridine. One drop acetyl chloride and a catalytic amount of dimethylaminopyridine were added. After 18 hours stirring the mixture was filtered through a short silica column. Removal of the solvent *in vacuo* gave 52 mg nimbinal (2). 40 mg (2) in 4 mg ethanol were stirred with 1 mg $NaBH_4$ for 1.5 hours at -20°C. During this time the reaction mixture warmed up to room temperature. After acidification with 2 ml 2 N HCl, extraction with methylene chloride followed by drying over magnesium sulfate and removal of the solvent, the product (35 mg) was further purified by flash chromatography on silica gel with petrol ether / ether / ethyl acetate / acetone = 15:10:10:5 to give 17 mg (3). The ^1H n.m.r. spectrum was identical with that of the product isolated from neem leaf extracts.

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REFERENCES AND NOTES

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