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LIMONOIDS FROM THE SEEDS OF *AZADIRACHTA INDICA**

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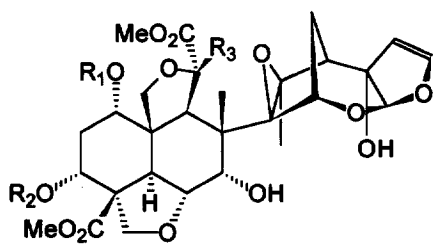
Key Word Index—*Azadirachta indica*; Meliaceae neem seeds; pericarps; 11-hydroxy azadirachtin-B; 1-tigloyl-3-acetylazadirachtinin; 1,2-diacetyl-7-tigloyl-12-hydroxy vilasinin; 23-desmethyllimocin-B.

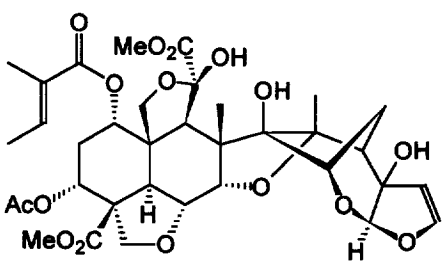
Abstract—Four new compounds, 11-hydroxyazadirachtin-B, 1-tigloyl-3-acetylazadirachtinin, 1,2-diacetyl-7-tigloyl-12-hydroxyvilasinin and 23-desmethyllimocin-B from neem seeds have been isolated and characterized using spectral studies. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The Indian neem tree, *Azadirachta indica*. A. Juss., continues to receive the attention of phytochemists, biochemists and medicinal chemists on account of the extraordinary biological properties of extracts and of several individual compounds [1]. Over 300 compounds have been isolated and characterized from the neem seeds, one-third of these being tetranortriterpenoids (limonoids). One of the limonoids, azadirachtin-A (**1**), isolated from the neem seeds is the most potent, environment friendly, biodegradable pesticide, with antifeedant and growth-inhibiting properties at very low concentration [2]. In addition to azadirachtin-A, several of its analogues, with similar biological activity but present in minor quantities, have also been isolated and named as azadirachtins B to L [3–8]. In continuation of our search for newer compounds, we have isolated four more compounds, namely, 11-hydroxyazadirachtin-B (**3**), 1-tigloyl-3-acetylazadirachtinin (**4**), 1,3-diacetyl-7-tigloyl-12-hydroxyvilasinin (**6**) and 23-desmethyllimocin-B (**8**). These compounds were characterized based on their spectral data.



1 : R_1 = Tigloyl, R_2 = Acetyl, R_3 = OH
2 : R_1 = H, R_2 = Tigloyl, R_3 = H
3 : R_1 = H, R_2 = Tigloyl, R_3 = OH



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RESULTS AND DISCUSSION

Systematic fractionation of an azadirachtin-A rich fraction (see method (I) in Experimental) by preparative HPLC gave eight fractions numbered 1 to 8. Fraction 3 (200 mg), on analytical HPLC, resolved into three peaks; this mixture, on further purification using preparative HPLC and PTLC gave a compound which was characterized as 11-hydroxyazadirachtin-B (**3**) based on spectral data and comparison with that of azadirachtin-A (**1**) and azadirachtin-B (**2**) [9].

The ^{1}H NMR and ^{13}C NMR spectra of compound **3** are similar to that of azadirachtin-B (**2**), except for few minor variations. The signal for proton H-11 (δ 4.45 (*d*, <1 Hz), as in compound **2** is absent, the signal of proton H-9 is shifted downfield (δ 3.34 compared with δ 3.17 in **2** and δ 3.34 in **1**) and H-30 methyl resonates at δ 1.73 (δ 1.45 in **2** and δ 1.74 in **1**). D_2O exchange and HCOH coupling studies in $(CD_3)_2SO$ indicated the presence of four hydroxyls (two secondary and two tertiary): one more tertiary hydroxyl than compound **2**. The molecular mass was found to be 678, as de-

*This paper is dedicated to Prof. N. R. Krishnaswamy on his 60th birthday.

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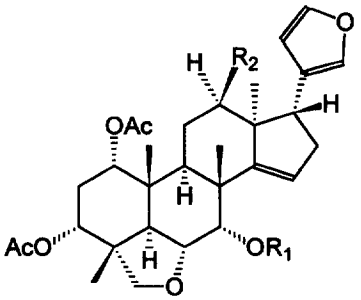
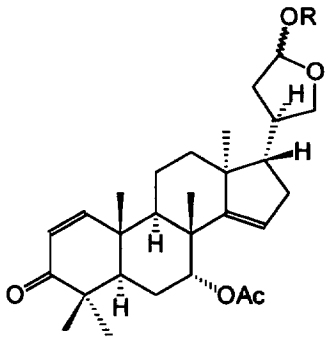


5 : $R_1 = R_2 = H$
6 : R_1 = Tigloyl, R_2 = OH



7 : R = Me
8 : R = H

termined by negative FAB-mass spectrometry. Thus, it has one oxygen atom more than azadirachtin-B (M_r 662) and this could be in the form of a hydroxyl. In the ^{13}C NMR spectra, the signal for C-11 (δ 104.83, *s*) is the same as that in compound **1** (δ 104.10) compared with δ 79.48 in compound **2**, indicating a hemiacetal carbon and thus the extra hydroxyl group can be attached to this carbon. The assignment of a tigloyl group to C-3 is supported by the following facts. The proton H-3 resonated at δ 5.46 (*t*, 3 Hz) as in compound **2** but not as in 3-deacetyl-11-desoxyazadirachtin (δ 3.52, *m*) [10] or as in 3-deacetylazadirachtin-A (δ 3.48, *m*). Also, 3-deacetylazadirachtin-A is different from compound **3**, as shown by the difference in the retention times (5.23 min compared with 6.74 min for **3** on analytical HPLC (RP-8, 60% MeOH–H_2O). All the proton NMR assignments were confirmed by the two-dimensional COSY spectrum and the carbon assignments were based on a DEPT spectrum.

Fraction 6, on maceration with methanol, yielded a pure compound and its structure was determined to be 1-tigloyl-3-acetylazadirachtinin (**4**) on the basis of ^1H NMR, ^{13}C NMR, mass spectra and in comparison with the spectral data of a synthetic compound recently synthesized by Ley *et al.* [11] using a circuitous route starting from 22,23-dihydroazadirachtin-A. 22,23-Dihydroazadirachtin-A is known to rearrange spontaneously under various conditions to the corresponding azadirachtinin derivative. However, similar efforts to rearrange the parent azadirachtin-A to **4** were unsuccessful [11]. This clearly indicated that the compound **4**, which we have isolated, is not an artifact obtained during the isolation process, but a natural compound. This is the first report of its isolation from the neem seeds, although a corresponding 11-OMe analogue of compound **4** was isolated by Kraus *et al.* [12].

Repeated column chromatography of a salannin-rich fraction (see method (II) in Experimental) gave a compound **6** which was slightly more polar than salannin on silica gel TLC (R_f value: 0.465, 10% acetone–chloroform). Its ^1H NMR spectrum showed the presence of a β-substituted furan ring (δ 7.32 (1H, *s*, H-21); δ 7.24 (1H, *s*, H-23) and δ 6.25 (1H, *s*, H-22)), two acetates (δ 2.04 (3H, *s*) and δ 1.90 (3H, *s*)), a tigloyl ester (δ 6.90 (1H, *q*, $J = 7.2$ Hz, H-3′); δ 1.80 (3H, *d*, $J = 7.2$ Hz, H-4′) and δ 1.85 (3H, *s*, H-5′)) in addition to four singlets accounting for four methyl groups at δ 1.14 (H-18), δ 1.16 (H-30), δ 1.0 (H-29) and δ 0.95 (H-19). Protons H-6 at δ 4.20 (*dd*, $J = 12.7$ Hz, $J = 3$ Hz), H-7 at δ 5.66 (*d*, $J = 3$ Hz), H-5 at δ 2.40 (*d*, $J = 12.7$ Hz), H-28a and H-28b at δ 3.50 (*d*, $J = 7.1$ Hz), and δ 3.26 (*d*, $J = 7.1$ Hz) were easily identified. All the proton signals were confirmed by the two-dimensional COSY45 spectrum. Thus, the ^1H NMR spectrum of compound **6** resembled that of 1,3-diacetylvilasinin (**5**) [13] except for the presence of a tigloyl ester, and a minor variation in ring C. The tigloyl group in **6** can be attached to C-7, based on the chemical shift value of H-7 and in comparison with that in **5** [13, 14]. The IR spectrum supported the presence of esters (1732, 1714 cm^{-1}) and the furan ring (875 cm^{-1}).

Positive FAB mass spectral analysis determined its molecular weight to be 610, which was 98 mass units more than that of compound **5**. Thus, compound **6** had, in addition to the tigloyl moiety (82 mass units), an extra oxygen. ^{13}C NMR spectrum showed the presence of 35 distinct carbons, five more than that of compound **5**. The extra carbon atoms were accounted for by the tigloyl moiety. All the carbons were assigned on the basis of DEPT spectra. The extra oxygen was in the form of a free hydroxyl, as supported by the IR spectrum (ν_{max} 3500 cm^{-1}). Thus, the molecular formula of compound **6** was determined to be $C_{35}H_{46}O_9$. In the two-dimensional COSY spectrum, the proton attached to the carbon having the hydroxyl (δ 3.50) coupled only with that of H-11 and no other proton, indicating the presence of the hydroxyl on C-12. Also, in the proton NMR spectrum, H-12 appeared as a doublet with a coupling constant of 7.1 Hz (almost superimposing on that of H-28a). This indicated that H-12 coupled with one of the protons on C-11 to a very large extent. Examination of the dihedral angles in a model showed that this was only possible when the H-12 is α-equatorial and the hydroxyl is β-axial. This was also supported by the fact that the compound did not undergo acetylation under normal conditions because of the

steric hindrance of 12-OH. Based on the evidence, the structure has been proposed to be 1,3-diacetyl-7-tigloyl-12-hydroxyvilasinin (**6**).

The oil obtained from the pericarps of neem seeds (method (III) in Experimental) was fractionated on a silica gel column with increasing percentages of ethyl acetate in hexane. The 50% ethyl acetate–hexane fraction (6 g) on further column chromatography and repeated purification gave a pure compound which was characterized as 23-desmethyllimocin-B (**8**) based on spectral data.

The ^{1}H NMR spectrum closely resembled with that of limocin-B (**7**) [15] except for the absence of a methoxyl signal and was found to be an inseparable 2:1 mixture of diasterioisomers. The A and B rings were easily identified by the presence of two related doublets [δ 7.16 (1H, *d*, $J = 9.7$ Hz, H-1) and δ 5.85 (1H, *d*, $J = 9.7$ Hz, H-2)] owing to an $\alpha\beta$-unsaturated ketone in ring A and an acetyl group at C-7 [δ 5.22 (H-7, *t br*)]. In the place of a furan ring at C-17, a tertrahydrofuran ring substituted with a hydroxyl at C-23 was discernible owing to the signals of H-21 (δ 3.45 (1H, *t*, $J = 8.4$ Hz, H-21a) and δ 4.20 (1H, *t*, $J = 8.4$ Hz, H-21b) and of H-23 (δ 5.48 (1H, *t br*, $J = 2.7$ Hz)). There are five methyl singlets appearing at δ 1.05 (3H, H-18), δ 1.26 (6H, H-19 and H-30), δ 1.05 (6H, H-28 and H-29), also supporting the presence of limocin-B skeleton. The mass spectrum of compound **8** showed its molecular mass as *m/z* 456, which was 14 mass units less than that of compound **7**, clearly supporting the presence of a hydroxyl group in the place of the 23-methoxyl. The other fragments in the mass spectrum, *m/z* 438 $[M - H_2O]^+$, 396 $[M - HOAc]^+$, 381 $[M^+ - CH_3 - HOAc]$, and IR frequencies at 3400 cm^{-1}, 1720 cm^{-1} and 1690 cm^{-1}, were also supportive of the structure assigned. All the carbons were assigned based on DEPT spectra.

EXPERIMENTAL

General experimental procedures. ^{1}H NMR spectra were recorded in $CDCl_3$ at 270 MHz/500 MHz with TMS as an internal reference. ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 MHz/500 MHz with TMS as an internal reference. The 2D-COSY45 experiments were performed at 400 MHz with a sweep width of 4504.5 Hz, 1024 data points in W2 and 512 data points in w1. Positive and negative FAB-MS were recorded in a Finnigan-Mat 312 instrument with data system SS 200-MS. The IR spectra were recorded as KBr discs on a Mattson Galaxy 4020FTIR instrument. $[\alpha]_D$ values were measured on Jasco DIP-370 digital polarimeter. Prep. HPLC studies were carried out on a Buchi 681 system. MPs were determined on an electric hot bench and are uncorr. CC was performed using silica gel (100–200 mesh) and alumina (neutral).

Extraction and isolation.

Method (I). Dried and powdered neem seeds (1 kg) were extracted into MeOH at room temp., filtered and partitioned thoroughly with petrol in order to remove all the fatty materials. The methanolic fr. was evapd under vacuum, dissolved in EtOAc and partitioned with H_2O. The EtOAc fr. was subjected to batch filtration over silica gel, the solvent evapd and the residue was chromatographed over silica gel. On elution with petrol–EtOAc (1:1), an azadirachtin-A-rich fr. was obtained (1.0 g). On prep. HPLC this was divided into three frs A, B, and C. From fr. B, pure azadirachtin-A was obtained. Frs A and C were pooled (0.5 g) and subjected to prep. HPLC (RP-18, 5.4 × 50 cm; CH_3CN–H_2O (2:3); 70 ml min^{-1}; $\lambda = 215$ nm) to obtain eight different fractions: fr. 1 (18 mg), fr. 2 (35 mg), fr. 3 (10 mg), fr. 4 (260 mg), fr. 5 (70 mg), fr. 6 (25 mg), fr. 7 (25 mg) and fr. 8 (45 mg). Fr. 3, on analytical HPLC (RP-8, MeOH–H_2O, 3:2), showed three peaks. A total of 200 mg of fr. 3 (obtained from 10 such prep. HPLC runs) was pooled and further subjected to prep. HPLC (RP-18; 5.4 × 50 cm; MeOH–H_2O, 1:1, 70 ml min^{-1}; $\lambda = 215$ nm) to obtain a fraction rich in compound **3** (25 mg), which was further purified by PTLC (silica gel; Me_2CO–CH_2Cl_2, 1:5) to obtain 10 mg of the pure compound **3**. Maceration of fraction-7 with MeOH gave another pure compound, which was further purified by recrystallization from CH_2Cl_2–MeOH (mp: 180–182°) and characterized as 1-tigloyl-3-acetylazadirachtinin (**4**).

Method (II). Neem seeds (10.0 kg) obtained locally were cleaned, powdered and extracted with $CHCl_3$ (3 × 5 l) at room temp. (3 × 4 hr) and the solvent was removed under vacuum to obtain an oily residue which, on maceration with petrol (40–60°) gave a fine powder (112 g). The powder was filtered and the solvent was evapd under vacuum to obtain 2.0 l of the oil. The oil was filtered through a column of silica gel (700 g, 100–200 mesh). The column was then washed with petrol followed by elution with increasing percentages of EtOAc. EtOAc–petrol (3:7) gave a salannin-containing fr. (50 g), which on fractionation gave 20 g of salannin-rich fr. The salannin-rich fr. on further purification on alumina (neutral) gave 8.0 g of pure salannin and 0.090 g of crude compound **6**. This was further purified by repeated CC and recrystallization from EtOAc–petrol (0.025 g).

Method (III). Neem seed (5.0 kg) pericarps were dried, powdered and extracted with $CHCl_3$ at room temp and proceeded as in method (II) to obtain a fine powder and oil (28 g). The oil, thus obtained, was fractionated on a silica gel column with increasing percentages of EtOAc in petrol. Elution with EtOAc–petrol (1:1) gave a fr. (6 g), which on repeated CC gave pure compound **8** (10 mg).

11-Hydroxyazadirachtin-B (**3**). Mp 160–162°, negative FAB-MS: 677 $[M - 1]^+$. 660 $[M - H_2O]^+$, 618 $[M - HOAc]^+$, Method ^{1}H NMR ($CDCl_3$): δ 3.96 (1H, *s br*, H-1), 2.22 (1H, *dt*, $J = 16$ Hz, 3 Hz, H-2a), 2.10 (1H, *dt*, $J = 16$ Hz, 3 Hz, H-2b), 5.46 (1H, *t*, $J = 3$ Hz, H-3), 3.26 (1H, *d*, $J = 12$ Hz, H-5), 4.57 (1H, *dd*, $J = 12$ Hz, 3 Hz, H-6), 4.68 (1H, *s br*, H-7), 3.34 (1H, *s br*, H-9), 4.64 (1H, *s br*, H-15), 1.10 (1H, *d*, $J = 13$ Hz, H-16a), 1.88 (1H, *m*, H-16b), 2.38 (1H, *d*, $J = 5$ Hz,

H-17), 2.08 (3H, *s*, H-18), 4.16 (1H, *d*, $J = 10$ Hz, H-19a), 3.44 (1H, *d*, $J = 10$ Hz, H-19b), 5.60 (1H, *s br*, H-21) 5.02 (1H, *d*, $J = 3$ Hz, H-22), 6.42 (1H, *d*, $J = 3$ Hz, H-23), 3.99 (1H, *d*, $J = 9$ Hz, H-28a), 3.82 (1H, *d*, $J = 9$ Hz, H-28b), 1.73 (3H, *s*, H-30), 6.90 (1H, *qq*, $J = 7$ Hz, 1.5 Hz, H-3′), 1.80 (3H, *d*, $J = 7$ Hz, H-4′), 1.82 (3H, *s br*, H-5′), and 3.76 (6H, *s*, –COOMe). ^{13}C NMR ($CDCl_3$): δ 69.60 (*d*, C-1), 32.19 (*t*, C-2), 67.92 (*d*, C-3), 52.19 (*s*, C-4), 35.62 (*d*, C-5), 74.32 (*d*, C-6), 75.18 (*d*, C-7), 45.18 (*s*, C-8), 44.71 (*d*, C-9), 49.23 (*s*, C-10), 104.83 (*s*, C-11), 173.46 (*s*, C-12), 69.00 (*s*, C-13), 71.99 (*s*, C-14), 76.55 (*d*, C-15), 25.16 (*t*, C-16), 52.76 (*d*, C-17), 18.41 (*q*, C-18), 70.36 (*t*, C-19), 83.74 (*s*, C-20), 109.33 (*d*, C-21), 107.81 (*d*, C-22), 146.84 (*d*, C-23), 73.2 (*t*, C-28), 173.82 (*s*, C-29), 21.22 (*q*, C-30), 53.45 and 53.18 (*q*, $-COOCH_3$), 167.06 (*s*, C-1′), 128.73 (*s*, C-2′), 138.75 (*d*, C-3′), 14.57 (*q*, C-4′), and 12.06 (*q*, C-5′).

1-*Tigloyl*-3-*acetylazadirachtinin* (**4**). Positive FAB-MS: 721 $[MH]^+$, 703 $[MH^+ - H_2O]$, 685, 563 etc., ^{1}H NMR ($CDCl_3$): δ 4.70 (1H, *t br*, H-1), 2.27 (1H, *dt*, $J = 16$ Hz, 3 Hz, H-2a), 2.15 (1H, *dt*, $J = 16$ Hz, 3 Hz, H-2b), 5.45 (1H, *t*, $J = 3$ Hz, H-3), 3.25 (1H, *d*, $J = 12$ Hz, H-5), 4.50 (1H, *dd*, $J = 12$ Hz, 3 Hz, H-6), 4.60 (1H, *s br*, H-7), 3.40 (1H, *s br*, H-9), 4.20 (1H, *s br*, H-15), 1.50 (1H, *d*, $J = 13$ Hz, H-16a), 1.98 (1H, *m*, H-16b), 2.18 (1H, *d*, $J = 5$ Hz, H-17), 1.50 (3H, *s*, H-18), 4.21 (1H, *d*, $J = 10$ Hz, H-19a), 3.64 (1H, *d*, $J = 10$ Hz, H-19b), 5.60 (1H, *s br*, H-21), 4.90 (1H, *d*, $J = 3$ Hz, H-22), 6.40 (1H, *d*, $J = 3$ Hz, H-23), 4.03 (1H, *d*, $J = 9$ Hz, H-28a), 3.68 (1H, *d*, $J = 9$ Hz, H-28b), 1.67 (3H, *s*, H-30), 6.90 (1H, *qq*, $J = 7$ Hz, 1.5 Hz, H-3′), 1.80 (3H, *d*, $J = 7$ Hz, H-4′), 1.82 (3H, *s br*, H-5′), 3.71 (3H, *s*, –COOMe), 3.76 (3H, *s*, –COOMe) and 2.00 (3H, *s*, –OCOMe). ^{13}C NMR ($CDCl_3$): δ 69.96 (*d*, C-1), 30.19 (*t*, C-2), 67.92 (*d*, C-3), 52.19 (*s*, C-4), 35.52 (*d*, C-5), 73.32 (*d*, C-6), 81.90 (*d*, C-7), 50.90 (*s*, C-8), 47.71 (*d*, C-9), 49.23 (*s*, C-10), 104.83 (*s*, C-11), 172.46 (*s*, C-12), 94.00 (*s*, C-13), 92.90 (*s*, C-14), 81.55 (*d*, C-15), 30.16 (*t*, C-16), 50.76 (*d*, C-17), 27.41 (*q*, C-18), 70.36 (*t*, C-19), 85.74 (*s*, C-20), 109.33 (*d*, C-21), 108.81 (*d*, C-22), 146.84 (*d*, C-23), 73.2 (*t*, C-28), 173.82 (*s*, C-29), 18.00 (*q*, C-30), 53.45 and 53.18 (*q*, $-COOCH_3$), 169.90 (*s*, –OCOMe), 166.06 (*s*, C-1′), 128.70 (*s*, C-2′), 138.17 (*d*, C-3′), 14.17 (*q*, C-4′), and 12.06 (*q*, C-5′).

1,3 - *Diacetyl* - 7 - *tigloyl* - 12 - *hydroxyvilasinin* (**6**). $[\alpha]_D^{30} = +10.8°$ ($CHCl_3$, $c = 1$), mp: 248–250°, IR ν_{max}^{KBr} cm^{-1}: 3500, 3000, 2928, 1732, 1714, 1375, 1250, 1125, 1053, 1026, 875. Positive FAB-MS: 611 $[MH]^+$, 551 $[MH - HOAc]^+$, 451 $[MH - HOTig - HOAc]^+$, 391, etc. ^{1}H NMR ($CDCl_3$): δ 5.08 (1H, *s br*, H-1), 2.00 (1H, *dt*, $J = 16$ Hz, H-2a), 2.25 (1H, *dt*, $J = 16$ Hz, 3 Hz, H-2b), 5.61 (1H, *s br*, H-3), 2.40 (1H, *d*, $J = 12.7$ Hz, H-5), 4.20 (1H, *dd*, $J = 12.7$ Hz, 3 Hz, H-6), 5.66 (1H, *d*, $J = 3$ Hz, H-7), 2.97 (1H, *m*, H-9), 2.45 (1H, *dd*, $J = 16$ Hz, 7.1 Hz, H-11a), 2.25 (1H, *d*, $J = 16$ Hz, H-11b), 3.50 (1H, *d*, $J = 7.1$ Hz, H-12), 5.08 (1H, *m*, H-15), 2.30 (1H, *m*, H-16a), 1.50 (1H, *m*, H-16b), 2.97 (1H, *dd*, $J = 11.4$ Hz, 7.1 Hz, H-17), 1.14 (3H, *s*, H-18), 0.95 (3H, *s*, H-19), 7.32 (1H, *s*, H-21), 6.25 (1H, *s*, H-22), 7.24 (1H, *s*, H-23), 3.50 (1H, *d*, $J = 7.1$ Hz, H-28a), 3.26 (1H, *d*, $J = 7.1$ Hz, H-28b), 1.0 (3H, *s*, H-29), 1.16 (3H, *s*, H-30), 6.90 (1H, *q*, $J = 7.2$ Hz, H-3′), 1.80 (3H, *d*, $J = 7.2$ Hz, H-4′), 1.85 (3H, *s*, H-5′), 2.04 (3H, *s*, $-OCOCH_3$), and 1.90 (3H, *s*, $-OCOCH_3$). ^{13}C NMR ($CDCl_3$): δ 72.80 (*d*, C-1), 27.22 (*t*, C-2), 72.00 (*d*, C-3), 42.40 (*s*, C-4), 40.40 (*d*, C-5), 72.60 (*d*, C-6), 72.80 (*d*, C-7), 44.30 (*s*, C-8), 36.80 (*d*, C-9), 40.20 (*s*, C-10), 30.00 (*t*, C-11), 78.00 (*d*, C-12), 51.80 (*s*, C-13), 155.75 (*s*, C-14), 122.80 (*d*, C-15), 36.26 (*t*, C-16), 50.60 (*d*, C-17), 19.00 (*q*, C-18), 24.40 (*q*, C-19), 125.00 (*s*, C-20), 140.30 (*d*, C-21), 112.00 (*d*, C-22), 142.00 (*d*, C-23), 78.00 (*t*, C-28), 15.60 (*q*, C-29), 15.80 (*q*, C-30), 166.80 (*s*, C-1′), 124.00 (*s*, C-2′), 137.00 (*d*, C-3′), 12.40 (*q*, C-4′), 14.75 (*q*, C-5′), 171.00 and 169.00 (*s*, $-OCOCH_3$), 21.40 and 21.00 (*q*, $-OCOCH_3$).

23-*Desmethyllimocin-B* (**8**). MS: *m/z* 456 $[M]^+$, 438 $[M - H_2O]^+$, 396 $[M - HOAc]^+$, 381 $[M - CH_3 - HOAc]^+$, 362, 335, 310, etc., IR ν_{max}^{KBr} cm^{-1}: 3400, 2900, 1720, 1690, 1480, 1390, 1285, etc. ^{1}H NMR ($CDCl_3$): δ 7.16 (1H, *d*, $J = 9.7$ Hz, H-1), 5.85 (1H, *d*, $J = 9.7$ Hz, H-2), 2.15 (1H, *m*, H-5), 1.95 (1H, *m*, H-6a), 1.75 (1H, *m*, H-6b), 5.22 (1H, *t br*, H-7), 2.20 (1H, *m*, H-9), 1.70 (1H, *m*, H-11a), 1.80 (1H, *m*, H-11b), 1.90 (1H, *m*, H-12a), 1.50 (1H, *m*, H-12b), 5.28 (1H, *s br*, H-15), 2.15 (1H, *m*, H-16a), 2.05 (1H, *m*, H-16b), 1.60 (1H, *m*, H-17), 1.05 (3H, *s*, H-18), 1.26 (6H, *s*, H-19 and H-30), 1.50 (1H, *m*, H-20), 3.45 (1H, *t*, $J = 8.4$ Hz, H-21a), 4.20 (1H, *t*, $J = 8.4$ Hz, H-21b), 3.60 (*t*, $J = 8.4$ Hz, H-21′a), 3.97 (*t*, $J = 8.4$ Hz, H-21′b), 2.24 (1H, *m*, H-22a), 1.45 (1H, *m*, H-22b), 5.48 (1H, *t br*, $J = 2.7$ Hz, H-23), 5.53 (1H, *t br*, H-23′) and 1.05 (6H, *s*, H-28 and H-29). ^{13}C NMR ($CDCl_3$): δ 158.09 (*d*, C-1), 125.57 (*d*, C-2), 204.00 (*s*, C-3), 44.19 (*s*, C-4), 46.23 (*d*, C-5), 23.82 (*t*, C-6), 74.53 (*d*, C-7), 42.75 (*s*, C-8), 37.48 (*d*, C-9), 39.91 (*s*, C-10), 16.48 (*t*, C-11), 33.56 (*t*, C-12), 46.78 (*s*, C-13), 158.81 (*s*, C-14), 119.09 (*d*, C-15), 35.34 (*t*, C-16), 58.98 (*d*, C-17), 58.28 (*d*, C-17′), 21.16 (*q*, C-18), 19.05 (*q*, C-19), 38.39 (*d*, C-20), 40.67 (*d*, C-20′), 72.23 (*t*, C-21), 70.55 (*t*, C-21′), 35.34 (*t*, C-22), 97.81 (*d*, C-23), 98.47 (*d*, C-23′), 21.34 (*q*, C-28), 22.09 (*q*, C-29), 27.39 (*q*, C-30), 170.13 (*s*, $-OCOCH_3$), 20.14 (*q*, $-OCOCH_3$).

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