A New Tetranortriterpenoid from *Dysoxylum lenticellatum*

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A new tetranortriterpenoid, named lenticellatumin (**1**), three known terpenoids, dysoxylumin C (**2**), eichlerianic acid (**3**) and dysoxylumin F (**4**), together with three ceramides, 1-*O*-β-*D*-glucopyranosyl-(2*S*,3*S*,4*R*,8*Z*)-2-*N*-(2'-hydroxytetracosanoyl) octadecasphinga-8-ene (**5**), (2*S*,3*S*,4*R*,8*E*)-2-*N*-(2'-hydroxytetracosanoyl) octadecasphinga-8-ene (**6**), (2*S*,3*R*,4*E*)-2-*N*-(2'-hydroxytetracosanoyl) octadecasphinga-4-ene (**7**), were isolated from the twig of *Dysoxylum lenticellatum*. Their structures were determined from spectroscopic analysis. Activity screening showed that compound **5** exhibited strong antifeedant activity against *pieris brassicae* L., while **6**, **7** displayed weak activities.

Key words: Dysoxylum lenticellatum, Tetranortriterpenoid, Antifeeding

Introduction

The genus *Dysoxylum* comprises about 200 species growing naturally in India and Southeast Asia. Fourteen species are distributed in China, among which ten ones including *Dysoxylum lenticellatum* D. L. have been found in Yunnan province [1]. According to the literatures, extracts of some species within this genus have cytotoxic [2, 3], anti-inflammatory and antimalarial [4] activities. Up to now, many sorts of compounds, such as triterpenes [5, 6], triterpene glycosides [7], tetranortriterpenoids [8], diterpenes [9], steroids [10] and alkaloids [11] have been isolated from this genus. As part of a program of seeking new tetranortriterpenoids and antifeeding compounds from Meliaceae plants [12 – 14], we investigated the chemical ingredients of *D. lenticellatum*. A new tetranortriterpenoid, named lenticellatumin (**1**), three known terpenoids, dysoxylumin C (**2**) [15], eichlerianic acid (**3**) [16] and dysoxylumin F (**4**) [17], together with three known ceramides, 1-*O*-β-*D*-glucopyranosyl-(2*S*,3*S*,4*R*,8*Z*)-2-*N*-(2'-hydroxytetracosanoyl) octadecasphinga-8-ene (**5**) [18], (2*S*,3*S*,4*R*,8*E*)-2-*N*-(2'-hydroxytetracosanoyl) octadecasphinga-8-ene (**6**) [19], (2*S*,3*R*,4*E*)-2-*N*-(2'-hydroxytetracosanoyl) octadecasphinga-4-ene (**7**) [20], were isolated from the twig of *D. lenticellatum*. Their structures were determined from spectroscopic analysis. Activity screening showed that compound **5** exhibited strong antifeedant activity against *pieris brassicae* L., while **6**, **7** displayed weak activities.

Results and Discussion

The molecular formula of compound **1** was determined as $C_{28}H_{40}O_6$ by HR-EIMS spectrometry, which was confirmed by the ^{13}C NMR and DEPT spectra. Its IR spectrum showed absorption bands for hydroxyls (3440 cm^{-1}), carbonyl groups (1776, 1731, 1699 cm^{-1}) and double bonds (1651, 1634 cm^{-1}). The ^{1}H NMR spectrum of **1** showed six methyl singlets [δ_H 0.98, 1.00, 1.01, 1.11, 1.16 (tertiary C-methyl groups) and 1.97 (acetate methyl)], a tri-substituted olefinic proton [δ_H 5.30 (d, J = 2.0 Hz, 1 H)] and an oxygenated methine proton [δ_H 5.20 (t, J = 1.9 Hz, 1 H)]. The ^{13}C NMR spectrum of **1** showed 28 signals. DEPT experiments at 135° revealed the presence of five tertiary methyl groups (δ_C 15.1, 21.1, 21.1, 25.8, 27.1), eight methylenes (δ_C 38.7, 34.4, 24.2, 16.4, 33.9, 31.6, 42.2, 78.4), four methines (δ_C 42.2, 74.7, 48.1, 60.3), one of which was oxygenated, five quaternary carbons (δ_C 47.7, 42.1, 36.9, 46.9, 79.2), one double bond [δ_C

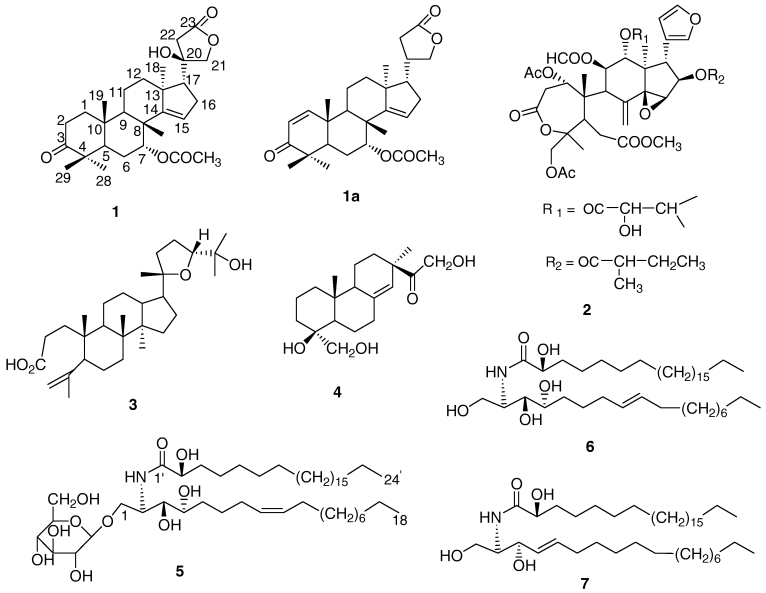

Fig. 1. The structures of compounds **1 – 7**.

158.2 (s), 118.2 (d)], one carbonyl group (δ_C 216.6), one carboxyl group (δ_C 175.6), and an acetate group [δ_C 170.1 (s), 20.3 (q)]. Comparison of these data with those of chisocheton F (**1a**) [21], trichilinin D [22], and other related tetranortriterpenoids [23] suggested that **1** was a $\Delta^{14,15}$ tetranortriterpenoid.

The HMBC correlations of δ_H 1.93 (m, 1 H, 17-H) with δ_C 31.6 (t, C-16), 46.9 (s, C-13), 21.1 (q, C-18), 79.2 (s), 78.4 (t), 42.2 (t), and δ_H 2.75 (s, 1 H, OH) with δ_C 79.2 (s), and δ_H 4.230, 4.235 (d, $J = 10.0$ Hz, each 1 H) showing correlations with δ_C 78.4 (t) in the HMQC spectrum, with δ_C 79.2 (s), 42.2 (t), 175.6 (s) suggested a 20-hydroxy-γ-lactone unit [δ_C 79.2 (s, C-20), 78.4 (t, C-21), 42.2 (t, C-22), 175.6 (s, C-23)] attached to C-17, which was confirmed by comparison of the ^{13}C and ^{1}H NMR spectral data of **1** with that of related compounds in the literature [21, 23]. NOE correlations of OH-20 with H-22β, and H-22α with Me-18 indicated an OH-20β substituent (see Fig. 2). The cross peaks in HMBC experiments between δ_H 5.30 (d, $J = 2.0$ Hz, 1 H, 15-H) and δ_C 60.3 (d, C-17), 31.6 (t, C-16), 46.9 (s, C-13) also indicated a double bond between C-14 and C-15.

Moreover, the HMBC correlations of δ_H 5.20 (t, $J =$ 1.9 Hz, 1 H) with δ_C 42.1 (s, C-8), 42.2 (d, C-5), 24.2 (t, C-6), 48.1 (d, C-9), 27.1 (q, C-30), 170.1 (s), and δ_H 1.97 (s, 3 H) with δ_C 170.1 (s), suggested an acetyl group [δ_C 170.1 (s), 20.3 (q); δ_H 1.97 (s, 3 H)] attached to C-7 [δ_C 74.7 (d)]. According to the NOE interaction

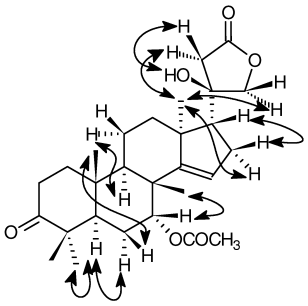

Fig. 2. The key NOE correlations in compound **1**.

between H-7 [δ_H 5.20 (t, $J = 1.9$ Hz, 1 H)] and H-30 [δ_H 1.11 (s, 3 H)] the position of this acetyl group was fixed as 7α. Additionally, the HMBC correlations of δ_H 0.98 (s, 3 H, 29-H), 1.01 (s, 3 H, 28-H) with δ_C 47.7 (s, C-4), 216.6 (s), suggested a carbonyl group at C-3. Based on the above evidence, the structure of **1** was elucidated as shown in Fig. **1**, named lenticellatumin.

The antifeedant activities of compounds **5 – 7** and azadirachtin were tested by the conventional leaf disk method against the larvae of *Pieris brassicae* L, which showed that the antifeedant rates of **5 – 7** and azadirachtin were 62.0%, 3.0%, 0% and 99.5%, and the corresponding mortality ones were 50%, 0%, 0% and 100%, respectively. The above results also suggested that **5** was a significant antifeedant, but its activity was less active than that of the model compound azadirachtin.

Experimental Section

General experimental procedures

All the mps were obtained on an XRC-1 micromelting apparatus and were uncorrected. Optical rotations were measured with a Horiba SEAP-300 spectropolarimeter. UV spectra were measured with a Shimadzu double-beam 210A spectrophotometer in MeOH solution. IR (KBr) spectra were obtained on a Bio-Rad FTS-135 infrared spectrophotometer. ^{1}H, ^{13}C NMR and 2D NMR spectra were recorded on a Bruker AM-400 and a DRX-500 MHz NMR spectrometer with TMS as internal standard. MS spectral data were obtained on a VG Autospec-3000 spectrometer, 70 eV for EI. Silica gel (200 – 300 mesh) for column chromatography and GF_{254} for TLC were obtained from the Qindao Marine Chemical Factory, Qindao, People's Republic of China.

Plant material

The twig of *D. lenticellatum* was collected from Xishuangbanna, Yunnan province, People's Republic of China, in December 2001. It was identified by Prof. J. Y. Cui, Xishuangbanna Botany Garden, *Academia Sinica*. A Voucher specimen (No. 0596375) was deposited in the herbarium of the Department of Taxonomy, Kunming Institute of Botany, *Academia Sinica*, Kunming, People's Republic of China.

Extraction and isolation

The air-dried and powdered twig (12 kg) of *D. lenticellatum* was extracted with 95% EtOH three times at room temperature, and the solvent was evaporated *in vacuo*. The residue was partitioned in H_2O and extracted with $CHCl_3$ three times. The resulting $CHCl_3$ extracts were concentrated *in vacuo* to afford 146 g of residue, which was subjected to column chromatography (CC) on a silica gel, using $CHCl_3$-MeOH system (from 100% $CHCl_3$ to $CHCl_3$-MeOH 1:1) as eluent to yield eight fractions. Fraction 2 (45 g) was further separated on silica gel CC eluted with petrol-Me_2CO system (from 10:1 to 2:1) to give five subfractions (A – F), among which fractions B and C were subjected to silica gel CC, eluted with petrol-EtOAc and petrol-Me_2CO (from 10:1 to 2:1), respectively, to give **1** (6 mg), **2** (31 mg), respectively. Fraction 3 (23 g) was separated on silica gel CC repeatedly, eluted with $CHCl_3$-Me_2CO (from 12:1 to 7:3), to give four subfractions (A – D), among which fraction B (6 g) was subjected to CC on silica gel, eluted with $CHCl_3$-Me_2CO (10:1), to give **3** (650 mg), and fraction C (7 g) eluted with $CHCl_3$-Me_2CO (8:2), to give **4** (25 mg) and **7** (7 mg). Fraction 4 (20 g) was separated on silica gel CC repeatedly, eluted with $CHCl_3$-Me_2CO (from 10:1 to 1:1) to give **6** (9 mg), and fraction 5 (4 g), eluted with $CHCl_3$-MeOH (10:1), to give **5** (12 mg).

Lenticellatumin (**1**): Colorless crystal. $C_{28}H_{40}O_6$. M.p. > 350 °C. – $[\alpha]_D^{18.4}$ $-68.5°$ (*c*, 0.35 in $CHCl_3$). – IR (KBr): $\tilde{\nu} = 3440, 2939, 2363, 2337, 1776, 1731, 1699, 1651, 1634, 1557, 1539, 1456, 1375, 1251, 1033$ cm^{-1}. - ^{1}H NMR (400 MHz, $CDCl_3$) and - ^{13}C NMR (100 MHz, $CDCl_3$) see Table 1. - MS (EI, 70 eV): *m/z* (%) = 472 (30) $[M]^+$, 454 (32), 439 (2), 412 (39), 394 (47), 379 (40), 311 (36), 297 (64), 275 (100), 261 (40), 242 (61), 232 (20), 215 (30), 191 (19), 173 (25), 161 (39), 145 (45), 133 (37), 121 (44), 107 (65), 81 (42), 69 (36). - HREIMS: 472.2836 $[M]^+$ (calcd. for $C_{28}H_{40}O_6$ 472.2824, error: 2.5 ppm).

Dysoxylumin C (**2**): Colorless crystal (Me_2CO). M.p. 188 – 190 °C. – $[\alpha]_D^{27}$ $+60.4°$ (*c*, 0.54 in $CHCl_3$). IR (KBr): $\tilde{\nu} = 3571, 3451, 2964, 2937, 2877, 1747, 1468, 1380, 1279, 1259, 1235, 1168, 1074, 1031, 1006, 979, 931, 877$ cm^{-1}. - ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.54$ (s, 1 H, 1-H), 2.52 (s, 2 H, 2-H), 3.10 (br d, 1 H, $J = 9.2$ Hz, 5-H), 2.20 (m, 2 H, 6-H), 3.10 (br d, 1 H, $J = 9.2$ Hz, 9-H), 5.54 (br s, 1 H, 11-H), 5.83 (br s, 1 H, 12-H), 3.94 (s, 1 H, 15-H), 5.24 (d, $J = 9.2$ Hz, 1 H, 16-H), 3.10 (d, $J = 9.2$ Hz, 1 H, 17-H), 1.08 (s, 3 H, 18-H), 1.48 (s, 3 H, 19-H), 7.29 (s, 1 H, H-21), 6.14 (s, 1 H, H-22), 7.10 (s, 1 H, H-23), 4.22, 4.54 (d, $J = 11.2$ Hz, each 1 H, H-28), 1.48 (s, 3 H, H-29), 5.31, 5.53 (s, each 1 H, H-30), 3.32 (br s, 1 H, H-2'), 1.70 (m, 1 H, 3'-H), 0.88 (d, $J = 6.8$ Hz, 3 H, 4'-H), 0.67 (d, $J = 6.8$ Hz, 3 H, 5'-H), 2.32 (m, 1 H, 2"-H), 1.35, 1.45 (m, 2 H, 3"-H), 0.57 (t, $J = 7.4$ Hz, 3 H, 4"-H), 1.03 (d, $J = 6.8$ Hz, 3 H, 5"-H), 2.02, 2.05 (s, each 3 H, C*H*$_3$COO), 7.95 (s, *H*COO), 3.61 (3H, OC*H*$_3$). - ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 72.0$ (d, C-1), 36.4 (t, C-2), 174.5 (s, C-3), 84.7 (s, C-4), 49.1 (d, C-5), 33.8 (t, C-6), 172.8 (s, C-7), 133.9 (s, C-8), 42.3 (d, C-9), 46.2 (s, C-10), 75.0 (d, C-11), 70.2 (d, C-12), 45.2 (s, C-13), 69.5 (s, C-14), 59.1 (d, C-15), 76.5 (d, C-16), 42.3 (d, C-17), 16.1 (q, C-18), 27.0 (q, C-19), 119.1 (s, C-20), 143.2 (d, C-21), 110.9 (d, C-22), 141.6 (d, C-23), 65.9 (t, C-28), 27.1 (q, C-29), 124.7 (t, C-30), 169.9 (s, C-1'), 75.0 (d, C-2'), 31.8 (d, C-3'), 15.3 (q, C-4'), 18.0 (q, C-5'), 176.7 (s, C-1"), 40.7 (d, C-2"), 26.7 (t, C-3"), 10.8 (q, C-4"), 16.1 (q, C-5"), 21.2, 20.6 (q, $2 \times C$H$_3$COO), 170.3, 169.2 (s, $2 \times$CH$_3$*C*OO), 160.1 (d, HCOO), 52.0 (q, O*C*H$_3$). – Negative ion FABMS: *m/z* 831 $[M\text{-}H]^-$.

Eichlerianic acid (**3**): Colorless crystal (Me_2CO). M. p. 124 – 126 °C. – IR (KBr): $\tilde{\nu} = 3550, 2958, 2876, 1715, 1638, 1459, 1418, 1376, 1300, 1205, 1184, 1157, 1124, 1060, 1012, 952, 895$ cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.85, 4.66$ (s, each 1 H, 28-H), 3.74 (t, 1 H, $J = 7.4$ Hz, 24-H), 1.78 (s, 3 H, 29-H), 1.25 (s, 3 H, 27-H), 1.13 (s, 3 H, 26-H), 1.12 (s, 3 H, 21-H), 0.99 (s, 3 H, 30-H), 1.02 (s, 3 H, 18-H), 0.85 (s, 3 H, 19-H). - ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 24.6$ (t, C-1), 34.3 (t, C-2), 179.0 (s, C-3), 147.4 (s, C-4), 41.1 (d, C-5), 31.4 (t, C-6), 33.9 (t, C-7), 40.0 (s, C-8), 49.5 (d, C-9), 39.1 (s, C-10), 22.1 (t, C-11), 25.6 (t, C-12), 42.9 (d, C-13), 50.3 (s, C-14), 31.4 (t, C-15), 27.2 (t, C-16),

Table 1. The 1D and 2D NMR spectral data of compound **1** and ^{13}C NMR data for compound **1a***.

No	**1**					**1a**
	^{13}C NMR	^{1}H (HMQC)	HMBC	^{1}H-^{1}H COSY	NOESY	^{13}C NMR
1	38.7t	1.85, 1.45 (2H, m)	H-2,9,19	H-2		157.8d
2	34.4t	2.41 (2H, m)	H-1	H-1		125.5d
3	216.6s		H-1,2,28,29			204.3s
4	47.7s		H-5,28,29			39.8s
5	42.2d	2.53 (1H, m)	H-6,7,9,19,28,29	H-6α β	H-28	46.5d
6	24.2t	1.66, 1.83 (2H, m)	H-5,7	H-5,7		23.6t
7	74.7d	5.20 (1H, t, 1.9)	H-5,6,30	H-6	H-30	74.2d
8	42.1s		H-7,9,30			42.6s
9	48.1d	1.83 (1H, m)	H-11,12,19,30	H-11	H-5	37.3d
10	36.9s		H-5,6,9,11,19			44.0s
11	16.4t	1.56 (2H, m)	H-9,12	H-9,12		16.3t
12	33.9t	1.96 (2H, m)	H-9,11,18	H-11		33.6t
13	46.9s		H-12,17,15,18			46.0s
14	158.2s		H-12,15,18,30			158.6s
15	118.2d	5.30 (1H, d, 2.0)	H-16,17			118.8d
16	31.6t	2.10, 2.33 (2H, m)	H-15,17	H-17		33.9t
17	60.3d	1.93 (1H, m)	H-15,16,18	H-16		58.0d
18	21.1q	1.16 (3H, s)	H-12,17			21.0q
19	15.1q	1.00 (3H, s)	H-1,5,9		H- 29,30	18.9q
20	79.2s		H-16,17,21,22,OH			37.3d
21	78.4t	4.230, 4.235(each 1H, d, 10.0)	H-17, 22			72.4t
22	42.2t	2.58, 2.67 (2H, m)	H-17,21			34.7t
23	175.6s		H-21,22			176.5s
28	25.8q	1.01 (3H, s)	H-29		H-5	26.9q
29	21.1q	0.98 (3H, s)	H-28		H-19	19.8q
30	27.1	1.11(3H, s)	H-7,9		H-19	27.3q
OH		2.75 (s)				
CH_3COO	170.6s		H-7, CH_3COOCH_3COO			169.9s
	21.2q	1.96 (3H, s)				21.2q

* Chemical shift values δ are in ppm, and coupling constant values J in Hz; in compound **1**, 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, and 500 MHz for 2D NMR in pyridin-d_5 with TMS as internal standard; 75 MHz for ^{13}C NMR spectrum of **1a** in $CDCl_3$ with TMS as internal standard.

50.8 (d, C-17), 15.3 (q, C-18), 20.1 (q, C-19), 86.5 (s, C-20), 23.4 (q, C-21), 35.8 (t, C-22), 26.1 (t, 23), 83.3 (d, C-24), 71.6 (s, C-25), 24.2 (q, C-26), 27.6 (q, C-27), 113.4 (t, C-28), 23.1 (q, C-29), 16.3 (q, C-30). – Negative ion FABMS: *m/z* (%) = 473 $[M-1]^-$ (100), 371 (12), 413 (3), 339 (5).

Dysoxylumin F (**4**): Colorless crystal (Me_2CO). M. p. 121 – 123 °C. – $[\alpha]_D^{19}$ −25.6° (*c*, 0.31 in MeOH). – IR (KBr): $\tilde{\nu}$ = 3524, 3339, 2928, 2870, 1720, 1463, 1446, 1383, 1344, 1310, 1278, 1252, 1103, 1063, 1048 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.38 (s, 1 H, 14-H), 4.28 (d, J = 1.3 Hz, 2 H, 16-H), 3.61 (d, J = 10.8 Hz, 1 H, 18a-H), 3.40 (d, J = 10.8 Hz, 1 H, 18b-H), 1.14 (s, 3 H, 17-H), 0.64 (s, 3 H, 20-H). - ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 38.5 (t, C-1), 18.6 (t, C-2), 35.8 (t, C-3), 73.7 (s, C-4), 55.2 (d, C-5), 21.2 (t, C-6), 36.1 (t, C-7), 140.4 (s, C-8), 49.7 (d, C-9), 39.0 (s, C-10), 19.6 (t, C-11), 31.1 (t, C-12), 46.6 (s, C-13), 123.3 (d, C-14), 214.2 (s, C-15), 64.6 (t, C-16), 23.6 (q, C-17), 62.8 (t, C-18), 15.6 (q, C-20). - MS (EI, 70 eV): *m/z* (%) = 322 (0.4) $[M]^+$, 291 (13), 273 (5), 263 (100), 245 (36), 227 (17), 217 (10), 189 (5), 171 (5), 159 (11), 145 (13), 133 (16), 121 (63), 107 (61), 95 (53), 81 (59), 67 (27), 55 (41).

1-*O*-β-*D*-glucopyranosyl-(2*S*,3*S*,4*R*,8*Z*)-2-*N*-(2'-hydroxytetracosanoyl) octadecasphinga-8-ene (**5**): Colorless powder. M. p. 188 – 190 °C. – IR (KBr): $\tilde{\nu}$ = 3414, 2922, 2853, 1638, 1543, 1466, 1078, 729 cm^{-1}. – ^{1}H NMR (500 MHz, pyri-d_5): δ = 0.83 (t-like, J = 6.8 Hz, 6 H, 2×CH_3), 1.24 – 1.27 (s, 54 H, 27×CH_2), 1.95 (m, 2 H, 5-H), 2.06 (m, 2 H, 10-H), 2.23 (m, 2 H, 7-H), 3.85 (m, 1 H, 5"-H), 3.97 (t, J = 8.0 Hz, 1 H, 2"-H), 4.13 – 4.18 (m, 3 H, 4, 3", 4"-H), 4.26 (dd, J = 5.1, 10.4 Hz, 1 H, 3-H), 4.30 (dd, J = 5.0, 11.6 Hz, 1 H, 6"a -H), 4.46 (d, J = 11.6 Hz, 1 H, 6"b-H), 4.49 (dd, J = 4.5, 10.7 Hz, 1 H, 1a-H), 4.54 (m, 1 H, 2'-H), 4.68 (dd, J = 6.6, 10.7 Hz, 1 H, 1b-H), 4.93 (d, J = 7.8 Hz, 1 H, 1"-H), 5.24 (m, 1 H, 2-H), 5.43 – 5.53 (m, 2 H, olefinic H), 8.51 (d, J = 9.1 Hz, 1 H, N-H). - ^{13}C{^{1}H} NMR (125 MHz, pyridin-d_5): δ = 13.8 (CH_3), 22.7 (t, C-17), 27.3 (C-4'), 29.3-29.9 (t, n×CH_2), 32.0 (t, C-7), 32.9 (t, C-10), 33.2 (t, C-5), 35.2 (t, C-3'), 51.0 (d, C-2), 62.0 (t, C-6"), 70.9 (t, C-1), 72.0 (d, C-4"), 72.4 (d, C-4), 72.5 (d, C-2'), 75.1 (d, C-2"), 75.9 (d, C-3), 77.4 (d, C-5"), 77.6 (d, C-3"), 104.4 (d, C-1"), 130.0 (d, C-8), 130.5 (d, C-9), 175.6 (s, C-1'). Negative ion FABMS: *m/z* = 842 $[M-H]^-$.

(2*S*,3S,4*R*,8*E*)-2-*N*-(2'-hydroxytetracosanoyl)octadecasphinga-8-ene (**6**): White powder. – IR (KBr): $\tilde{\nu}$ = 3335, 2918, 2849, 1621, 1544, 1468, 1068, 1023, 722 cm^{-1}. –

^{1}H NMR (400 MHz, pyridine-d_5): $\delta = 5.56$ (dd, $J = 5.6$, 15.3 Hz, 1 H, 9-H), 5.46 (dd, $J = 15.3$, 5.7 Hz, 1 H, 8-H), 5.13 (m, 1 H, 2-H), 4.62 (dd, $J = 3.8$, 7.6 Hz, 1 H, 2'-H), 4.52 (dd, $J = 10.8$, 4.5 Hz, 1 H, 1a-H), 4.42 (dd, $J = 10.8$, 4.8 Hz, 1 H, 1b-H), 4.35 (m, 1 H, 3-H), 4.28 (m, 1 H, 4-H), 2.26, 2.00 (m, 2 H, 3'-H), 2.03 (m, 2 H, 10-H), 2.20, 2.02 (m, 2 H, 7-H), 1.96 (m, 2 H, 5-H), 1.76 (m, 2 H, 4'-H), 0.85 (t, $J = 6.8$ Hz, 6 H, 2×CH_3), 1.25 – 1.29 (m, 54 H, 27×CH_2). - ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): $\delta = 13.8$ (q, 2×CH_3), 22.4 (t, C-17), 26.2 (t, C-4'), 29.0 – 29.8 (t, n×CH_2), 32.5 (t, C-7), 32.8 (t, C-10), 33.3 (t, C-5), 35.2 (t, C-3'), 52.4 (d, C-2), 61.4 (t, C-1), 72.5 (d, C-4), 72.5 (d, C-2'), 76.3 (d, C-3), 130.2 (d, C-8), 130.3 (d, C-9), 174.7 (s, C-1'). Negative ion FABMS: *m/z* = 680 $[M-H]^-$.

(2*S*,3*R*,4*E*)-2-*N*-(2'-hydroxytetracosanoyl) octadecasphinga-4-ene (**7**): White powder. – ^{1}H NMR (400 MHz, $CDCl_3$+CD_3OH,): $\delta = 5.30$ (m, 1 H, 5-H), 3.97 (m, 1 H, 4-H), 3.71 (dd, $J = 3.8$, 11.5 Hz, 1 H, 1a-H), 3.58 (dd, $J = 5.3$, 11.5 Hz, 1 H, 1b-H), 3.45 – 3.31 (m, 3 H, 2-H, 3-H, 2'-H), 2.12, 1.90 (m, 2 H, 3'-H), 1.87, 1.57 (m, 2 H, 6-H), 1.52 (m, 2 H, 4'-H), 1.25 – 1.16 (m, 62 H, 31×CH_2), 0.78 (t, $J = 6.8$ Hz, 6 H, 2×CH_3). - ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$+CD_3OH): $\delta = 60.9$ (t, C-1), 51.7 (d, C-2), 75.6 (d, C-3), 174.5 (s, C-1'), 72.2 (d, C-2'), 130.6, 129.6 (d, C-4 and C-5), 36.4 (t, C-3'), 32.6 (t, C-6), 25.6 (t, C-4'), 22.5 (t, C-17), 13.9 (q, 2×CH_3). – MS (EI, 70 eV): *m/z* (%) = 666 (25) $[M+1]^+$, 652 (12), 468 (6), 454 (16), 440 (40), 426 (20), 410 (35), 396 (35), 382 (36), 368 (65), 60 (100).

Bioassay

The test compounds were dissolved in acetone (including five drops of DMSO) at concentrations of 1000 ppm, respectively. Leaf disks of *Brassica oleracea* L. (1.5 cm diameter) were dipped in the test solutions and the control discs were in acetone (including five drops DMSO) for one second. All the leaf disks were dried before being presented to the insect. The test insects were third instar larvae of *pieris brassicae* L., which had been deprived of food for 6 h prior to being individually placed in the Petri dish. Five Petri dishes, each containing two larvae and three leaf discs were used for each sample. After 48 h, the areas eaten were measured using a LI-3000 area-measurement apparatus. The antifeedant rate was calculated from [(*C*-*T*)/*C*]100, where *C* and *T* are control discs areas eaten and treated discs areas eaten, respectively. After six days, the mortality of the test insects was calculated, respectively.

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