A New Tetranortriterpenoid from *Dysoxylum lenticellatum*

Shu-Hua Qi, Da-Gang Wu, Si Zhang, and Xiao-Dong Luo

* a Guangdong Key Laboratory of Marine Materia Medica, South China Sea Institute of Oceanology, The Chinese Academy of Sciences, 164 West Xingang Road, Guangzhou 510301 Guangdong, People’s Republic of China

* b State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, The Chinese Academy of Sciences, Kunming 650204 Yunnan, People’s Republic of China

Reprint requests to Dr. S.-H. Qi: Tel.: +86-20-89023105. Fax: +86-20-84458964.
E-mail: shuhuaqi2001@yahoo.com

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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-(2S,3S,4R,8Z)-2-N-(2’-hydroxytetraicosanoyl) octadecasphinga-8-ene (5), (2S,3S,4R,8E)-2-N-(2’-hydroxytetraicosanoyl) octadecasphinga-8-ene (6), (2S,3R,4E)-2-N-(2’-hydroxytetraicosanoyl) 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-(2S,3S,4R,8Z)-2-N-(2’-hydroxytetraicosanoyl) octadecasphinga-8-ene (5) [18], (2S,3S,4R,8E)-2-N-(2’-hydroxytetraicosanoyl) octadecasphinga-8-ene (6) [19], (2S,3R,4E)-2-N-(2’-hydroxytetraicosanoyl) 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_{26}H_{40}O_{6} by HR-EIMS spectrometry, which was confirmed by the 13C 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 1H NMR spectrum of 1 showed six methyl singlets [\(\delta_H \ 0.98, 1.00, 1.01, 1.11, 1.16 (\text{tertiary C-methyl groups})\] and 1.97 (acetate methyl), a tri-substituted olefinic proton [\(\delta_H 5.20 (J = 2.0 \ Hz, 1 \ H)\]), an oxygenated methine proton [\(\delta_H 5.20 (t, J = 1.9 \ Hz, 1 \ H)\)]. The 13C NMR spectrum of 1 showed 28 signals. DEPT experiments at 135° revealed the presence of five tertiary methyl groups [\(\delta_C 15.1, 21.1, 21.1, 25.8, 27.1\)], eight methylenes [\(\delta_C 38.7, 34.4, 24.2, 16.4, 33.9, 31.6, 42.2, 78.4\)], four methines [\(\delta_C 42.2, 74.7, 48.1, 60.3\)], one of which was oxygenated, five quaternary carbons [\(\delta_C 47.7, 42.1, 36.9, 46.9, 79.2\)], one double bond [\(\delta_C \)
The structures of compounds 1–7.

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

Moreover, the HMBC correlations of \( \delta_H 5.20 (t, J = 1.9 \text{ Hz}, 1 \text{ H}) \) with \( \delta_C 42.1 (s, C-8), 42.2 (d, C-5), 24.2 (t, C-6), 48.1 (d, C-9), 27.1 (q, C-30), 170.1 (s), \) and \( \delta_H 1.97 (s, 3 \text{ H}) \) with \( \delta_C 170.1 (s) \), suggested an acetyl group \([\delta_C 170.1 (s), 20.3 (q); \delta_H 1.97 (s, 3 \text{ H})]\) attached to C-7 \([\delta_C 74.7 (d)]\). According to the NOE interaction between H-7 \([\delta_H 5.20 (t, J = 1.9 \text{ Hz}, 1 \text{ H})]\) and H-30 \([\delta_H 1.11 (s, 3 \text{ H})]\) the position of this acetyl group was fixed as \( 7\alpha \). Additionally, the HMBC correlations of \( \delta_H 0.98 (s, 3 \text{ H}, 29\text{-H}), 1.01 (s, 3 \text{ H}, 28\text{-H}) \) with \( \delta_C 47.7 (s, C-4), 216.6 (s) \), 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 \textit{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. 1H, 13C 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 measured with a Bruker AM-400 and a DRX-500 MHz NMR spectrometer. 1H, 13C NMR and 2D NMR spectra were recorded on a Bruker AM-400 and a DRX-500 MHz NMR spectrometer. 1H, 13C NMR and 2D NMR spectra were recorded on a Bruker AM-400 and a DRX-500 MHz NMR spectrometer.

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. lenticellat was extracted with 95% EtOH three times at room temperature, and the solvent was evaporated in vacuo. The residue was partitioned in H2O and extracted with CHCl3 in vacuo was extracted with 95% EtOH three times at room

Lenticellatum (1): Colorless crystal. C23H40O6. M.p. > 350 °C. - [α]D27 0.54 (c, 0.35 in CHCl3). - IR (KBr): ʋ = 3440, 2939, 2363, 2337, 1776, 1731, 1699, 1651, 1634, 1557, 1539, 1456, 1375, 1251, 1033 cm-1. - 1H NMR (400 MHz, CDCl3) and - 13C NMR (100 MHz, CDCl3) 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 C23H40O6 472.2824, error: 2.5 ppm).

Eichlerianic acid (3): Colorless crystal (Me2CO). M.p. 188–190 °C. - [α]D27 0.54 (c, 0.35 in CHCl3). - IR (KBr): ʋ = 3571, 3451, 2964, 2937, 2877, 1747, 1468, 1380, 1279, 1259, 1235, 1168, 1074, 1031, 1006, 979, 931, 877 cm-1. - 1H NMR (400 MHz, CDCl3): δ = 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 (each 1 H, H-30), 3.32 (br s, 1 H, H-2'), 1.70 (m, 1 H, H-3'), 0.67 (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, CH3COO), 7.95 (s, HCOO), 3.61 (3H, OCH3). - 13C{1H} NMR (100 MHz, CDCl3): δ = 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), 46.9 (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'), 153.5 (q, C-4'), 18.0 (q, C-5'), 176.7 (s, C-6'), 40.7 (d, C-7'), 26.7 (t, C-7'), 10.8 (q, C-4'), 16.1 (q, C-5'), 21.2, 20.6 (q, 2 x CH3COO), 170.3, 169.2 (s, 2 x CH3COO), 160.1 (d, HCOO), 52.9 (q, OCH3). - Negative ion FABMS: m/z 831 [M-H]-.

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1H, 13C NMR and 2D NMR spectra were recorded on a Bruker AM-400 and a DRX-500 MHz NMR spectrometer.

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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).

Dysoxylum F (4): Colorless crystal (Me$_2$CO). M. p. 121 – 123°C. $[^1]$H NMR (500 MHz, pyridine-d$_5$): $d$ = 5.0, 0.9 Hz, 1 H, 1a-H), 9.45 (t, 23.0 Hz, 2 H, 2-H, 3-H), 4.48 (dd, $J$ = 5.1, 10.4 Hz, 1 H, H-3), 4.30 (dd, $J$ = 5.0, 11.6 Hz, 1 H, H-5), 4.46 (d, $J$ = 11.6 Hz, 1 H, 5'-H), 4.39 (d, $J$ = 4.5, 10.7 Hz, 1 H, 1a-H). 4.54 (m, 1 H, 2-H), 4.48 (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), 8.50 (d, $J$ = 8.1 Hz, 1 H, N-H). – $[^11]$C NMR (125 MHz, pyridine-d$_5$): $d$ = 13.8 (CH$_3$), 22.7 (t, C-17), 27.3 (C-4'), 29.3-29.9 (t, n CH$_3$), 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]$^-$.

(2S,3S,4R,8E)-2-N-(2'-hydroxyoctacosanoyl)octadecaphinga-8-ene (6): White powder. – IR (KBr): $\tilde{\nu}$ = 3335, 2918, 2849, 1621, 1544, 1468, 1068, 1023, 722 cm$^{-1}$.
\[ ^1H\text{ NMR (400 MHz, pyridine-d}_5\text{): } \delta = 5.56 (dd, J = 5.6, 15.3\text{ Hz, 1 H, 9-H}), 5.46 (dd, J = 15.3, 5.7\text{ Hz, 1 H, 8-H}), 5.13 (m, 1 H, 2-H), 4.62 (dd, J = 3.8, 7.6\text{ Hz, 1 H, 2''-H}), 4.52 (dd, J = 10.8, 4.5\text{ Hz, 1 H, 1a-H}), 4.42 (dd, J = 10.8, 8.4\text{ Hz, 1 H, 1b-H}), 4.35 (m, 1 H, 3-H), 4.28 (m, 1 H, 4-H), 2.26, 2.00 (m, 2 H, 3'-H), 2.03 (m, 2 H, 10-H), 2.20, 2.02 (m, 2 H, 7-H), 1.96 (m, 2 H, 5-H), 1.76 (m, 2 H, 4'-H), 0.85 (t, J = 6.8\text{ Hz, } 6\text{ H, } 2\times\text{CH}_3), 1.87, 1.57 (m, 2 H, 3'-H), 1.52 (m, 2 H, 4'-H), 1.25 – 1.16 (m, 62 H, 31\times\text{CH}_2), 0.78 (t, J = 6.8\text{ Hz, } 6\text{ H, } 2\times\text{CH}_3)\]

\[ {^13C\text{ NMR (100 MHz, pyridine-d}_5\text{): } \delta = 13.8 (q, 2\times\text{CH}_3), 22.4 (t, C-17), 26.2 (t, C-4'), 29.0 – 29.8 (t, n\times\text{CH}_2), 32.5 (t, C-7), 32.8 (t, C-10), 33.3 (t, C-5), 35.2 (t, C-3'), 52.4 (d, C-2), 61.4 (t, C-1), 72.5 (d, C-4), 72.5 (d, C-2'), 76.3 (d, C-3), 130.2 (d, C-8), 130.3 (d, C-9), 174.7 (s, C-1'). Negative ion FABMS: m/z = 660 [M-H]^- \]

\[ (25,3R,4E)-2-N-(2'-hydroxytetradecanoyl) octadecasphinga-4-ene (7): \text{White powder. – } ^1H\text{ NMR (400 MHz, CDCl}_3+\text{CD}_3\text{OH}: } \delta = 5.30 (m, 1 H, 5-H), 3.97 (m, 1 H, 4-H), 3.71 (dd, J = 3.8, 11.5\text{ Hz, 1 H, 1a-H}), 3.58 (dd, J = 5.3, 11.5\text{ Hz, 1 H, 1b-H}), 3.45 – 3.31 (m, 3 H, 2-H, 3-H, 2''-H), 2.12, 1.90 (m, 2 H, 3'-H), 1.87, 1.57 (m, 2 H, 3-H, 6-H), 1.52 (m, 2 H, 4'-H), 1.25 – 1.16 (m, 62 H, 31\times\text{CH}_2), 0.78 (t, J = 6.8\text{ Hz, } 6\text{ H, } 2\times\text{CH}_3). – ^13C\text{ NMR (100 MHz, CDCl}_3+\text{CD}_3\text{OH}: } \delta = 60.9 (t, C-1), 51.7 (d, C-2), 75.6 (d, C-3), 174.5 (s, C-1'), 72.2 (d, C-2'), 130.6, 129.6 (d, C-4 and C-5), 36.4 (t, C-3'), 32.6 (t, C-6), 25.6 (t, C-4''), 22.5 (t, C-17), 13.9 (q, 2\times\text{CH}_3). – MS (EL, 70\text{ eV}): m/z (\%) = 666 (25) [M+1]^+\text{, 652 (12), 468 (6), 454 (16), 440 (40), 426 (20), 410 (35), 396 (35), 382 (36), 368 (65), 60 (100)]. \]

**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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