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Constituents of *Carapa guianensis* Aubl. (Meliaceae)

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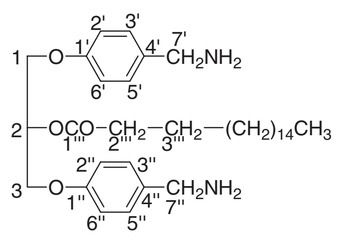
Nine compounds were isolated from the EtOH extraction of the twig of *Carapa guianensis* Aubl. On the basis of spectroscopic methods, their structures were elucidated as 1,3-di-benzene carbon amine-2-octadecylic acid-glyceride (**1**), hexacosanoic acid-2,3-dihydroxy-glyceride (**2**), ursolic acid (**3**), naringenin (**4**), scopoletin (**5**), 3,4-dihydroxymethylbenzoate (**6**), 2,6-dihydroxymethylbenzoate (**7**), tetratriacontanoic acid (**8**), triacontanoic acid (**9**) respectively. Among them **1** was new, **2** was firstly isolated from nature, and **3**–**9** were obtained from this plant for the first time.

1. Introduction

The tree *Carapa guianensis* Aubl., of the Meliaceae family, is naturally distributed in South America, West India, and South Africa. The wood of this plant is extensively used as commercial timber. The seeds have also been used as a source of vegetable oils, but this is limited due to the occurrence of bitter principles in the seeds; probably this is associated with the use of the seeds in indigenous medicine. Several tetranortriterpenoids had been isolated from this plant (Marcelle et al. 1975). As part of a program of searching chemical constituents of Meliaceae plants (Luo et al. 2000; Luo et al. 2002; Qi et al. 2003), we undertook the investigation of *C. guianensis* which is a introduced variety in Yunnan province, China. Nine compounds were obtained. On the basis of spectroscopic methods, their structures were elucidated as 1,3-di-benzene carbon amine-2-octadecylic acid-glyceride (**1**), hexacosanoic acid-2,3-dihydroxy-glyceride (**2**) (Porter et al. 1982), ursolic acid (**3**) (Kojima et al. 1986), naringenin (**4**) (Shen et al. 1993), scopoletin (**5**) (Jiang et al. 1995), 3,4-dihydroxymethylbenzoate (**6**) (Katherine 1972), 2,6-dihydroxymethylbenzoate (**7**) (Watanabe 1988), tetratriacontanoic acid (**8**), triacontanoic acid (**9**), respectively. Among them **1** was new, **2** was firstly isolated from nature, and **3**–**9** were obtained from this plant for the first time.



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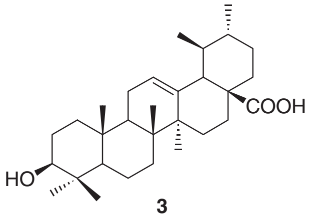

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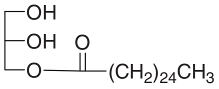

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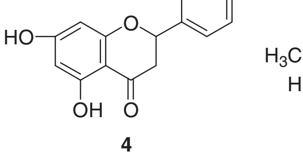

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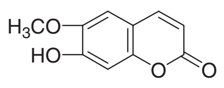

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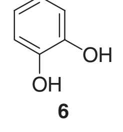

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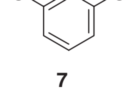

7

$CH_3(CH_2)_{32}COOH$

8

$CH_3(CH_2)_{28}COOH$

9

2. Investigations, results and discussion

Compound **1** was obtained as white powder, showing the molecular formula of $C_{35}H_{56}N_2O_4$ as determined by EIMS and NMR spectra. Its IR spectrum showed absorption bands for -NH_2 (3435 cm^{-1}) and aromatic ring (1564, 1510 cm^{-1}). While the UV spectrum exhibited maximum absorption at 208, 229, 256, 277, 284 nm (aromatic ring). The ^{13}C (DEPT) and ^1H NMR spectra of **1** showed the following signals: two same and symmetrical 1,4-di-substituted aromatic ring {δ_C 157.1 (s), 143.3 (s), 127.6 (d), 114.5 (d); δ_H 6.88 (4H, d, J = 8.8 Hz), 7.07 (4 H, d, J = 8.8 Hz)}, a long chain fatty acid {δ_C 13.9 (q), 22.5 (t), 25.3 (t), 29.2–30.1 (t), 31.8 (t), 34.6 (t), 175.8 (s); δ_H 0.84 (3H, t, J = 5.2 Hz), 1.24–1.29 (m, n × CH_2), 1.64 (2H, m), 2.48–2.52 (2 H, overlap)}, two symmetrical oxymethylene [δ_C 69.1 (t), δ_H 4.47 (4 H, m)] and one oxymethine [δ_C 68.4 (d), δ_H 4.84 (1 H, m)], which were the typical signals for glyceride (Kong et al. 1996; Yang et al. 2000).

The HMBC correlations of δ_H 4.84 (1 H, m, H-2), 2.49 (2 H, overlap, H-2‴), 1.64 (2 H, m, H-3‴) with δ_C 175.8 (s, C-1‴), δ_H 4.47 (4 H, m, H-1 and H-3) with δ_C 68.4 (d, C-2), and δ_H 4.84 (1 H, m, H-2) with δ_C 69.1 (t, C-1 and C-3), indicated a long chain fatty acid attached to the C-2 of glycerine. Moreover, the HMBC spectrum showing the cross peaks between δ_H 4.47 (4 H, m, H-1 and H-3), 6.88 (4 H, d, J = 8.8 Hz, H-2′, 6′ and H-2″, 6″), 7.07 (4 H, d, J = 8.8 Hz, H-3′, 5′ and H-3″, 5″) with δ_C 157.1 (s, C-1′ and C-1″), and δ_H 7.07 (4 H, d, J = 8.8 Hz, H-3′, 5′ and H-3″, 5″) with δ_C143.3 (s, C-4′ and C-4″), respectively, and the ^1H–^1H COSY spectrum showing the correlations of δ_H 6.88 (4 H, d, J = 8.8 Hz, H-2′, 6′, 2″, 6″) with δ_H 7.07 (4 H, d, J = 8.8 Hz, H-3′, 5′, 3″, 5″), respectively, suggested two same and symmetrical 1,4-di-substituted aromatic rings placed at the C-1 and C-3 of glycerine, respectively.

Furthermore, in the HMBC spectrum, the correlations of δ_H1.57 (4 H, t, J = 4.0 Hz) with δ_C 41.2 (t, C-7′ and C-7″), 143.3 (s, C-4′and C-4″), and δ_H 7.07 (4H, d, J = 8.8 Hz, H-3′, 5′ and C-3″, 5″) with δ_C 41.2 (t, C-7′ and C-7″), respectively, and the correlations of δ_H1.57 (4 H, t, J = 4.0 Hz) with δ_H 2.48–2.52 (4 H, overlap, H-7′, 7″) in the ^1H–^1H COSY spectrum, respectively, suggested two –CH_2NH_2 units attached to the two aromatic rings, respectively. According to its molecular weight and the mass fragments at m/z 267 $[M-301]^+$ and 239 $[M-301-28]^+$ in the EIMS (Fig. 2), the long chain fatty acid should be octadecanoic acid. Based on these data, the structure of **1** was elucidated to be 1,3-dibenzene carbon amine-2-octadecylic acid-glyceride (Fig. 2).

3. Experimental

3.1. General procedures

All the m.p.'s 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 IR spectrophotometer. ^1H NMR, ^{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 Qindao Haiyang Chemical Co. Ltd, Qindao, China.

3.2. Plant material

The twig of *Carapa guianensis* Aubl. was collected from Xishuangbanna, Yunnan province, China, in December 2001. It was identified by Prof. J. Y. Cui, Xishuangbanna Botany Garden, *Academia Sinica*. A Voucher specimen (No. 2001–13) was deposited in the herbarium of the Department of Taxonomy, Kunming Institute of Botany, Academia Sinica, Kunming, China.

3.3. Extraction and isolation

The air-dried and powdered twig (13.5 kg) of *C. guianensis* was extracted with EtOH three times under reflux, and the solvent was evaporated *in vacuo*. The residue was partitioned in H_2O and extracted with $CHCl_3$, EtOAc and *n*-BuOH three times, respectively. The $CHCl_3$ and EtOAc extracts were concentrated *in vacuo* to afford 88 g and 50 g of residue, respectively. The $CHCl_3$ portion was subjected to column chromatography (CC) on silica gel, using petroleum ether – Me_2CO gradients (from petroleum ether – Me_2CO 20 : 1 to Me_2CO) as eluents. Combined the fractions with TLC (GF_{254}) monitoring, eight fractions were obtained. Then, Fr. 2 (16 g) was subjected to CC on silica gel, eluted with petroleum ether – EtOAc gradient to give **8** (18 mg) and **9** (14 g). Fr. 3 (7 g) was subjected to CC on silica gel, eluted with $CHCl_3$–Me_2CO gradients (from 10 : 0 to 9 : 1) to give **3** (10 mg). Fr. 5 (23 g) was subjected to CC on silica gel, eluted with $CHCl_3$–Me_2CO (from 10 : 1 to 10 : 3) to give **4** (8 mg) and **5** (9 mg). Fr. 6 (7 g) was subjected to CC on silica gel, eluted with $CHCl_3$–Me_2CO gradients (from 8 : 2 to 7 : 3) to give **1** (9 mg), **2** (11 mg), **7** (7 mg) and **6** (8 mg).

3.4. 1,3-Di-benzene carbon amine-2-octadecylic acid-glyceride (1)

White powder; $C_{35}H_{56}N_2O_4$; mp 115–116 °C, UV (MeOH) λ_{max}: 209, 229, 256, 277, 284 nm; IR (KBr) ν_{max}: 3435, 3000, 2923, 2850, 1730, 1630, 1510, 1104, 826, 802 cm^{-1}; ^1H NMR (400 MHz, pyridine-d_5) δ_H: 0.84 (6H, t, J = 5.2 Hz, Me-18‴), 1.24–1.29 (m, H-4‴ to H-17‴), 1.57 (4 H, t, J = 4.0 Hz, 2 NH_2), 1.64 (2 H, m, H-3‴), 2.48–2.52 (6 H, overlap, H-7′, 7″, 2‴), 4.47 (4 H, m, H-1, 3), 4.84 (1 H, m, H-2), 6.88 (4 H, d, J = 8.8 Hz, H-2′, 6′, 2″, 6″), 7.07 (4H, d, J = 8.8 Hz, H-3′, 5′, 3″, 5″); ^{13}C NMR (100 MHz, pyri-d_5) δ_C: 13.9 (q, Me-18‴), 22.5 (t, C-16‴), 25.3 (t, C-3‴), 29.2–30.1 (t, C-4‴ to 15‴), 34.6 (t, C-2‴), 41.2 (t, C-7′, 7″), 68.4 (d, C-2), 69.6 (t, C-1, 3), 114.5 (d, C-2′, 2″, 6′, 6″), 127.6 (d, C-3′, 3″, 5′, 5″), 143.3 (s, C-4′, 4″), 157.1 (s, C-1′, 1″), 175.8 (s, C-1‴); EIMS m/z: 568 $[M]^+$ (2), 566 (13), 551 (26), 534 (1), 506 (6), 492 (4), 478 (29), 464 (10), 450 (53), 436 (25), 422 (41), 408 (16), 394 (31), 380 (21), 366 (18), 271 (2), 267 (8), 239 (3), 211 (11), 184 (8), 128 (32), 110 (17), 96 (34), 84 (41), 72 (60), 56 (100).

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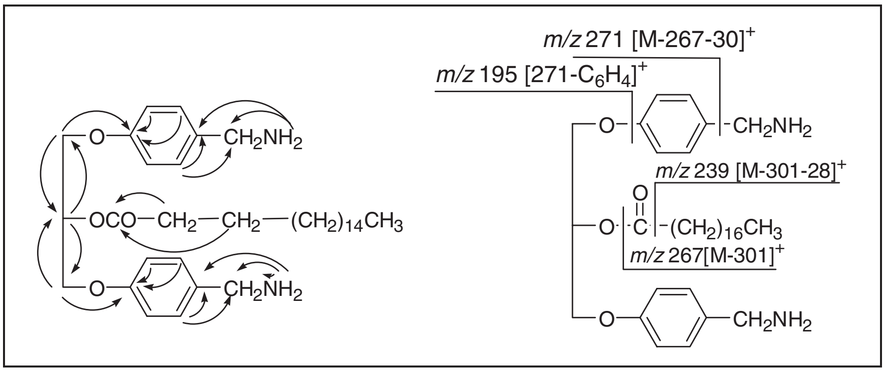

Fig:
Structure, selective HMBC correlations and EIMS mass fragments of **1**

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