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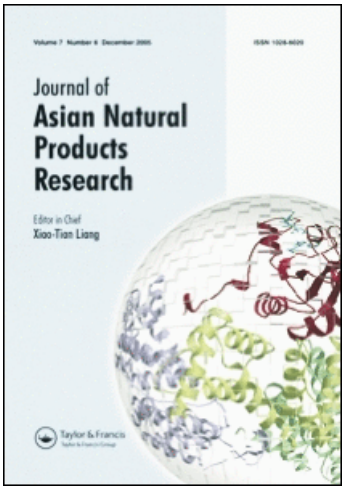

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Dicliptercerebroside, a novel cerebroside from *Dicliptera chinensis*

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A novel cerebroside named dicliptercerebroside (**1**) was isolated from the whole herb of *Dicliptera chinensis*, together with two known compounds asperglaucide (**2**) and amidoalcohol (**3**) for the first time from the title plant. Their structures were elucidated using spectroscopic methods. The structure of dicliptercerebroside was determined as 1-*O*-β-D-glucopyranosyl-2*N*-[(2′*R*)-2′-hydroxy-(9*Z*)-palmitoleoyl]-2*S*,3*S*,4*R*-C_{20}-phytosphingosine.

Keywords: *Dicliptera chinensis*; Dicliptercerebroside; Cerebroside; Phenylamide

1. Introduction

The whole herb of *Dicliptera chinensis* (L.) Juss. (Acanthaceae) is used in folk medicine for several purposes, such as detoxification and diuresis action [1], and anti-tumour activity [2]. A preliminary phytochemical study of the whole herb of *D. chinensis* demonstrated the presence of essential oil [3], flavonoids, organic acids [4,5], α-amino acids, long-chain aliphatic hydrocarbons [6], octasulphur, secoisolariciresinol dimethyl ether diacetate, 5-methoxy-4,4′-di-*O*-methylsecolariciresinol, chinensinaphthol methyl ester, loliolide, daucosterol, and stigmasterol 3-*O*-β-D-glucopyranoside [7]. The present paper is concerned with the isolation of a novel cerebroside, named dicliptercerebroside, and two known compounds, asperglaucide and amidoalcohol, for the first time from the whole herb of *D. chinensis*.

2. Results and discussion

Compound **1** (figure 1) was isolated as white amorphous powder. On TLC it gave an orange colour with Dragendorff's reagent. The ESITOF-MS (positive) showed quasi-molecular ion peaks at *m*/*z* 760 $[M + H]^+$ and 782 $[M + Na]^+$. The HRESI-MS of **1** showed the

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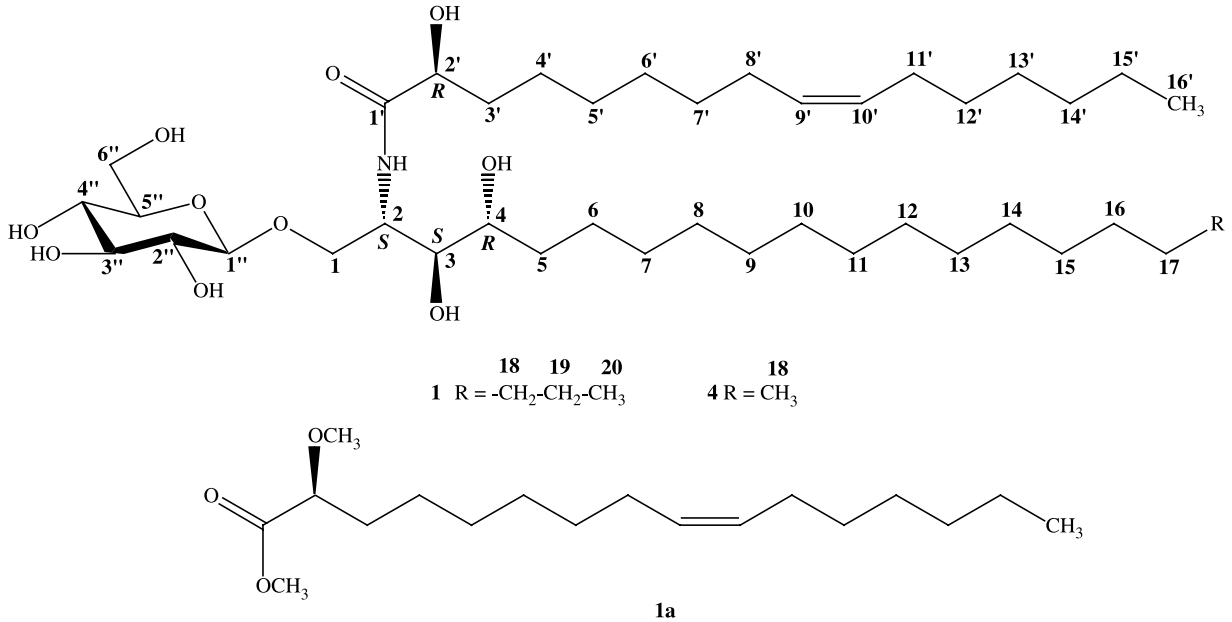

1a

Figure 1. Structures of compounds **1**, **1a**, and **4**.

Table 1. Fragmentation ions from electronic impact for **1**.

m/z	*Fragments*
327	$[M—C_6H_{11}O_6—CH_3(CH_2)_5CH═CH(CH_2)_6CH(OH)CO]^+$
311	$[M—C_6H_{11}O_6—CH_3(CH_2)_5CH═CH(CH_2)_6CH_2CO]^+$
283	$[M\text{-}C_6H_{11}O_6—CH_3(CH_2)_5CH═CH(CH_2)_6CH_2]^+$
269	$[CH_3(CH_2)_5CH═CH(CH_2)_6CH(OH)CONH_2]^+$
268	$[CH_3(CH_2)_5CH═CH(CH_2)_6CH(OH)CONH]^+$
251	$[CH_3(CH_2)_5CH═CH(CH_2)_6CHCONH]^+$
236	$[CH_3(CH_2)_5CH═CH(CH_2)_6CHCO]^+$
208	$[CH_3(CH_2)_5CH═CH(CH_2)_6CH]^+$

$[M + Na]^+$ ion peak at *m/z* 782.5765 corresponding to molecular formula of $C_{42}H_{81}NO_{10}$. Its IR spectrum revealed strong absorptions for hydroxyl groups (3392 cm^{-1}), amide (1645 and 1535 cm^{-1}), and glycosidic linkage band (1083 cm^{-1}). A β-glucopyranosyl moiety was recognised from signals at δ 105.6, 75.1, 78.3, 71.4, 78.6, and 62.5 in the ^{13}C NMR spectrum and signals at δ 4.95 (1H, d, $J = 7.8$ Hz, glc—H-1), 4.00 (1H, t, $J = 8.4$ Hz, glc—H-2), 4.21 (1H, m, glc—H-3), 4.19 (1H, m, glc—H-4), 3.85 (1H, m, glc—H-5), 4.46 (1H, dd, $J = 11.7$, 5.1 Hz, glc—H_a-6), and 4.34 (1H, dd, $J = 11.7$, 5.1 Hz, glc—H_b-6) in the ^1H NMR spectrum, as well as the ion peaks at *m/z* 597 $[M—C_6H_{10}O_5]^+$ and 579 $[M—C_6H_{12}O_6]^+$ in the EI mass spectrum. The identification of glucose in the aqueous solution after hydrolysis of **1** in 10% HCl supported this confirmation, which was coincident with authentic β-D-glucopyranose on paper chromatography (PC). The ^1H and ^{13}C spectra of **1** (table 3) were consistent with the presence of a secondary amide group [δ_H 8.56 (1H, d, $J = 9.0$ Hz); δ_C 51.7 and 175.7]. ^1H NMR signals at δ 0.85 (6H, t, $J = 7.2$ Hz) were ascribed to two methyl groups and the signals at δ 1.24–2.16, to 26 methylene groups. Therefore, the presence of two aliphatic chains was concluded. One of the two chains (second chain), $CH_3(CH_2)_5CH═CH(CH_2)_6$-CH(OH)CONH—, could be deduced from the significant EI mass spectral peaks as shown in table 1. These results suggested *N*-(2′-hydroxy-palmitoleoyl) group existed in the structure of **1** (figure 1) [8]. Double bond geometry, as shown in figure 1, was the same as cerebroside **4** (figure 1), isolated from rice bran and wheat bran, soybeans, corn, etc. [8], with chemical shift at δ 5.48 (2H, m) for H-9′ and H-10′, and δ 4.57 (1H, dd, $J = 9.6$, 3.9 Hz) for H_α-2′.

On the other hand, methanolysis of **1** gave 2-methoxypalmitoleoyl methylate (**1a**), which was supported by its fragmentation ions from electronic impact as shown in table 2.

In the ^{13}C NMR spectrum, the signals at δ 75.8 (C-3), 72.4 (C-4), 70.4 (C-1), and 51.7 (C-2), and ^1H NMR signals at δ 5.29 (1H, *m*, H-2), 4.70 (1H, *dd*, $J = 10.5$, 6.6 Hz, H_a-1), 4.55 (1H, *m*, H_b-1), 4.28 (1H, *d*, $J = 4.8$ Hz, H-3), and 4.21 (1H, *m*, H-4) indicated that β-D-glucopyranosyl

Table 2. Fragmentation ions from electronic impact for **1a**.

m/z	*Fragments*
298	$[CH_3(CH_2)_5CH═CH(CH_2)_6CH(OCH_3)COCH_3]^+$
267	$[CH_3(CH_2)_5CH═CH(CH_2)_6—CH—COCH_3]^+$
239	$[CH_3(CH_2)_5CH═CH(CH_2)_6—CH_2—CH_2]^+$
211	$[CH_3(CH_2)_5CH═CH(CH_2)_6]^+$
127	$[CH_3(CH_2)_5CH═CH]^+$
99	$[CH_3(CH_2)_5CH_2]^+$
85	$[CH_3(CH_2)_5]^+$
71	$[CH_3(CH_2)_4]^+$
57	$[CH_3(CH_2)_3]^+$
43	$[CH_3(CH_2)_2]^+$

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group was connected to the first chain, which bears three hydroxyl groups, as well as the amide [9]. In addition, in the HMBC spectrum (table 3 and figure 2) of **1**, cross peaks at δ_H 4.95/δ_C 78.6 (Glc H-1/Glc C-5), δ_H 4.95/δ_C 70.4 (Glc H-1/C-1) and δ_H 5.29/δ_C 70.4 (H-2/C-1) revealed further that β-D-glucopyranosyl group was connected to C-1. Moreover, cross peaks at δ_H 8.56/δ_C 175.7 (N—H/C-1′) and δ_H 8.56/δ_C 51.7 (N—H/C-2) were observed in the HMBC spectrum of **1**, suggesting that -*N*-(2′-hydroxy-palmitoleoyl) group was connected to C-2 (table 3 and figure 2). From analysis of IR and NMR data, **1** was almost the same as **4**. However, the $[M + H]^+$ of **1** was at *m/z* 760, instead of 731 $[M]^+$ in **4**. Therefore, 1,3,4-eicosanetriol group in **1** replaced 1,3,4-octadecanetriol in **4**. The phytosphingosine group was coincident with C_{20}-phytosphingosine reported in the literature [10]. In the HMBC correlations as shown in figure 2 and table 3, cross peaks at δ_H 8.56/δ_C 51.7 (N—H/C-2), δ_H 5.29/δ_C 70.4 and 75.8 (H-2/C-1 and C-3), δ_H 4.28/δ_C 72.4 (H-3/C-4), δ_H 4.21/δ_C 75.8 (H-4/C-3), δ_H 1.72 and 2.20/δ_C 72.4

Table 3. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) data†, key HMBC correlations of **1** in C_5D_5N.†

	HMQC		
Position	δ_H; *J/Hz*	$\delta_{C\ DEPT}$	*HMBC (^{1}H to ^{13}C)*
Ceramide			
NH	8.56 (1H, d, 9.0)	–	C-2, 1′
1	4.70 (1H, dd, 10.5, 6.6)	70.4 t	C-3, 1″
	4.55 (1H, m)		
2	5.29 (1H, m)	51.7 d	C-1, 3, 1′
3	4.28 (1H, *d*, 4.8)	75.8 d	C-4
4	4.21 (1H, m)	72.4 d	C-3
5	2.20 (1H, m)	32.9 t	C-4, 6
	1.72 (1H, m)		
6	1.71 (2H, m)	25.8 t	C-4, 5, 7
7–17	1.23–1.29 (22H, m)	29.5–30.0 t	C-5, 6–C-15, 19
18	1.25 (2H, m)	32.1 t	C-16, 17, 19, 20
19	1.25 (2H, m)	22.9 t	C-17, 18, 20
20	0.85 (3H, t, 7.2)	14.2 q	C-18, 19
1′	–	175.7 s	
2′	4.57 (1H, dd, 9.6, 3.9)	72.4 d	C-1′
3′	2.10 (1H, m)	35.5 t	C-2′, 4′, 5′
	2.00 (1H, m)		
4′	1.97 (2H, m)	26.6 t	C-3′, 5′
5′	1.26 (2H, m)‡	29.8 t	C-3′, 4′, 6′, 7′
6′	1.30 (2H, m)‡	29.8 t	C-5′, 7′, 8′
7′	1.27 (2H, m)‡	29.8 t	C-6′, 8′, 9′
8′	2.20 (2H, m)	27.9 t	C-6′, 7′, 9′, 10′
9′	5.48 (1H, m)	130.8 d	C-8′, 10′
10′	5.48 (1H, m)	130.6 d	C-8′, 9′, 12′
11′	2.20 (2H, m)	27.5 t	C-10′, 12′, 13′
12′	1.26 (2H, m)‡	29.9 t‡	C-10′, 11′, 13′, 14′, 15′
13′	1.30 (2H, m)‡	30.0 t‡	C-11′, 12′, 14′
14′	1.28 (2H, m)‡	29.8 t‡	C-13′, 15′, 16′
15′	1.25 (2H, m)	22.9 t	C-14′, 16′
16′	0.85 (3H, t, 7.2)	14.2 q	C-14′, 15′
Glucosyl			
1″	4.95 (1H, d, 7.8)	105.6 d	C-1, 5″
2″	4.00 (1H, t, 8.4)	75.1 d	
3″	4.21 (1H, m)	78.3 d	C-2″, 4″, 5″
4″	4.19 (1H, m)	71.4 d	C-2″, 3″
5″	3.85 (1H, m)	78.6 d	C-1″, 3″
6″	4.46 (1H, dd, 11.7, 5.1)	62.5 t	–
	4.34 (1H, dd, 11.7, 5.1)		

† All the signals were assigned by 1D and 2D NMR spectra.
‡ Signals interchangeable.

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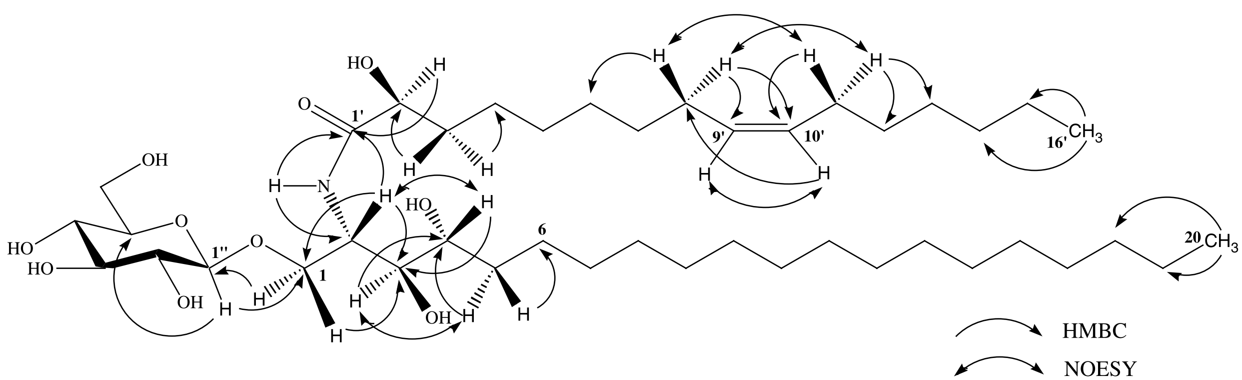

Figure 2. Key NOESY and HMBC correlations of **1**.

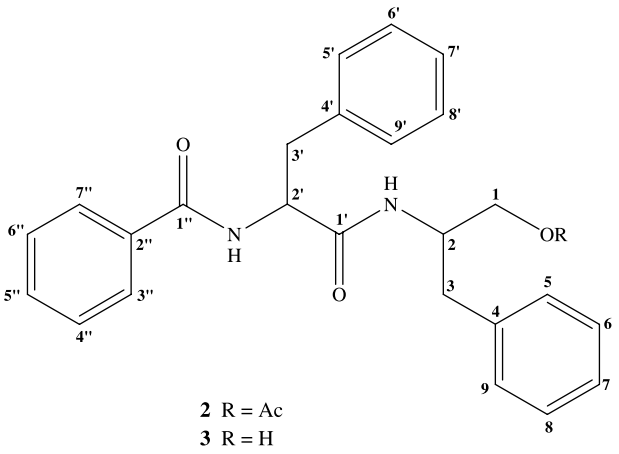

Figure 3. Structures of compounds **2** and **3**.

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(H-5/C-4) and 25.8 (H-5/C-6) indicated connections between -*N*-2′-hydroxy-palmitoleoyl and 1,3,4-eicosanetriol group, and 1,3,4-eicosanetriol and β-D-glucopyranosyl group. Based on the NOESY experiment (the NOE correlation between H_β-2 and H_β-4; H_α-3 and H_α-5; H-8′ and H-11′; H-9′ and H-10′), and compared with NMR data and optical rotation values of halicylindrosides A and B [11], D-*ribo*-[2*S*,3*S*,4*R*], D-*arabino*-[2*S*,3*R*,4*S*], D-*xylo*- [2*S*,3*R*,4*R*], D-*lyxo*-[2*S*,3*S*,4*S*] C_{18}-phytosphingosines [12], **4** [8], and 1-*O*-(β-D-glucopyranosyl)-(2*S*,3*S*,4*R*,8*Z*)-2*N*-[(2′*R*)-2′-hydroxytetracosanoil]-8 (*Z*)-octadecene-1,3,4-triol [13], absolute configuration of **1** was determined as 2*S*,3*R*,4*S*. Thus, the structure of **1** was elucidated as 1-*O*-β-D-glucopyranosyl-2*N*-[(2′*R*)-2′-hydroxy-(9*Z*)-palmitoleoyl]-2*S*,3*S*,4*R*-C_{20}-phytosphingosine (figure 1). It is a new compound and has been named dicliptercerebroside.

Compounds **2** and **3** were identified as asperglaucide and amidoalcohol (figure 3), respectively, by comparison of the NMR and MS spectral data with those previously reported in the literature [14,15], which was isolated from the whole herb of *D. chinensis* for the first time.

3. Experimental

3.1 General experimental procedures

Melting points were determined with an XT4A micromelting point apparatus and are uncorrected. Optical rotations were determined on a Perkin–Elmer 243B polarimeter in pyridine. IR spectra were recorded using a Nicolet Nexus 470 FT-IR spectrometer with KBr disks. ^{1}H NMR, ^{13}C NMR, COSY, NOESY, HMQC, and HMBC experiments were performed on a JEOL JNM- 300 spectrometers operating at 300 MHz. TMS was used as internal standard. EI-MS, ESITOF-MS, and HRESI-MS were measured on Finnigan TRACE 2000 GC-MS, MDS SCIEX API QSTAR and APEX II FT-ICR (Bruker Daltonics) mass spectrometer. Silica gel GF_{254} for TLC and silica gel (100–200 and 200–300 mesh) for column chromatography were obtained from Qingdao Marine Chemical Company, Qingdao, China. Spot of TLC was detected by spraying with Dragendorff's reagent followed by heating. Solvents were analytical grade and purchased from Beijing Chemical Company, Beijing, China.

For preparative HPLC (pump, LC-10ATVP; detector, SPD-M10AV photodiode array; software, CLASS-VP 5.0; Shimadzu LC-10ATVP, Japan) separation, the column used was a Alltima-C_{18} (250 × 10.0 mm, 5 μm), the mobile phase consisted of methanol/water solution (65:35, v/v). The monitored wavelength was 210 nm. The flow rate was 2.0 ml/min.

3.2 Plant material

The whole herb of *D. chinensis* (L.) Juss. (Acanthaceae) was purchased from Guilin Chinese Medicinal Market in August 2004 and identified by Professor Tie-Min Ai. A voucher specimen (No. 0309027) is deposited in the herbarium of the School of Pharmaceutical Sciences, Peking University, China.

3.3 Extraction and isolation

The powdered whole herb (5.0 kg) of *D. chinensis* was extracted with 70% EtOH to give extract (350 g). The 70% ethanolic extract was dissolved with MeOH and defatted with cyclohexane to afford MeOH soluble part (298 g). The latter was redissolved in H_2O and extracted with EtOAc to obtain an EtOAc extract (31.5 g). The EtOAc extract was subjected to silica gel CC eluted with mixture of $CHCl_3$ and MeOH to provide **2** and **3** mixtures (115 mg), and **1** (80 mg; 0.016‰), respectively. A 115 mg amount of **2** and **3** mixtures were separated repeatedly by preparative HPLC to yield **2** (60 mg, 0.012‰) and **3** (5 mg, 0.001‰), respectively.

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3.3.1 1-*O*-β-D-glucopyranosyl-2*N*-[(2′*R*)-2′-hydroxy-(9*Z*)-palmitoleoyl]-2*S*,3*S*,4*R*-C_{20}-phytosphingosine (1). White amorphous powder (CH_3Cl/MeOH); $[\alpha]_D^{25}$ −25 (*c* 0.1, pyridine); IR (KBr) ν_{max} (cm^{-1}): 3392, 2921, 2852, 1645, 1627, 1535, 1466, 1374, 1083, 1037; ^1H NMR (C_5D_5N, 300 MHz), ^{13}C NMR (C_5D_5N, 75 MHz), and 2D NMR spectra data are shown in table 3. Positive ESITOF-MS *m/z* 760 $[M + H]^+$, 782 $[M + Na]^+$; HRESI-MS *m/z* 782.5765 $[M + Na]^+$ (calcd for $C_{42}H_{81}NO_{10}Na$, 782.5752); EI-MS *m/z* 742 $[M—OH]^+$, 580 $[M—C_6H_{11}O_6]^+$, 294 $[M—C_6H_{11}O_6—CH_3(CH_2)_5CH{=}CH(CH_2)_6CH(OH)CONH—H_2O]^+$; other fragments are shown in table 1.

3.3.2 Methanolysis of 1. To a solution of **1** (10 mg) in methanol (6 ml) was added NaOMe (1 mg), then the mixture was stirred at room temperature for 4 h. The reaction mixture was acidified and extracted with ether to afford 2-methoxypalmitoleoyl methylate (**1a**). The fragment peaks of **1a** from electronic impact are shown in table 3.

3.3.3 Asperglaucide (2). Colourless needles (CH_3COCH_3); mp 185–187°C; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.03 (3H, s, CO—CH_3), 2.75 (2H, m, C_3—H), 3.16 (2H, m, $C_{3'}$—H), 3.86 (2H, m, C_1—H), 4.35 (1H, m, C_2—H), 4.75 (1H, m, $C_{2'}$—H), 5.90 (1H, d, $J = 8.4$ Hz, N—H), 6.72 (1H, d, $J = 7.5$ Hz, N—H), 7.00–8.00 (15H, m, Ar—H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 64.5 (C-1), 49.4 (C-2), 37.4 (C-3), 136.6 (C-4), 129.1 (C-5), 128.6 (C-6), 127.1 (C-7), 128.6 (C-8), 129.1 (C-9), 170.2 (C-1′), 54.9 (C-2′), 38.4 (C-3′), 136.6 (C-4′), 129.3 (C-5′), 128.8 (C-6′), 126.7 (C-7′), 128.8 (C-8′), 129.3 (C-9′), 167.1 (C-1′), 133.6 (C-2′), 127.0

(C-3′), 128.6 (C-4′), 131.9 (C-5′), 128.6 (C-6′), 127.0 (C-7′), 170.8 (—C═O), 20.8 (—CH_3); EI-MS *m*/*z* 444 $[M]^+$(1), 252 (32), 224 (28), 105 (100).

3.3.4 Amidoalcohol (3). Colourless needles (CH_3COCH_3); mp 189–191°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.74 (2H, m, C_3—H), 2.96 (2H, m, $C_{3'}$—H), 3.32 (2H, m, C_1—H), 4.08 (1H, m, C_2—H), 4.75 (1H, m, $C_{2'}$—H), 5.76 (1H, d, $J = 8.4$ Hz, N—H), 6.77 (1H, d, $J = 7.5$ Hz, N—H), 7.00–8.00 (15H, m, Ar—H); EI-MS *m*/*z* 402 $[M]^+$(1), 252 (46), 224 (35), 105 (100).

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