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Short communication

Four new glycosides from the seeds of *Cassia obtusifolia*

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ABSTRACT

Four new glycosides, including one anthraquinone glycoside (**1**), one naphthalene glycoside (**2**), and two naphthopyrone glycosides (**3**–**4**), with 10 known compounds (**5**–**14**) were isolated from the seeds of *Cassia obtusifolia* L. The new structures were determined by spectroscopic analysis and chemical transformations.

1. Introduction

Cassia obtusifolia L. belongs to the *Cassia* genus in the leguminous family, the seeds of which have been widely used as traditional herbal medicine or health tea in many Asian countries for a long time. In traditional Chinese medicine, it has the efficiency to remove "heat", improve eyesight, and relax bowels (Pharmacopoeia of the People's Republic of China, 2005). Modern pharmacological research has revealed that the seed has multiple functions, such as liver protection, bacteriostasis, catharsis, diuresis, neuroprotection, antitumor and anti-oxidation, and it is highly valued for the treatment of hypercholesterolaemia, hypertension and hyperlipidaemia (Patil et al., 2004; Ju et al., 2010; Xu et al., 2014). Previously, we reported the structural determination of six new anthraquinones and one naphthalene (Wang et al., 2007; Tang et al., 2008 Xu et al., 2014). As a continuation of these investigations, a phytochemical screening was conducted with the seeds of *Cassia obtusifolia* L., resulting in the isolation of four new glycosides, assigned as one anthraquinone glycoside (**1**), one naphthalene glycoside (**2**), two naphthopyrone glycosides (**3**–**4**), and ten known compounds (**5**–**14**). The structures of (**1**–**4**) were determined by spectroscopic analysis, including 2D NMR, and chemical transformations.

2. Results and discussion

Compound **1** was obtained as a yellow powder (MeOH), showing positive reaction with Molish and Bornträger reagents. Its methanolic solution had a negative optical rotation ($[\alpha]_D^{20}$ −57.958). Its UV spectrum displayed absorption bands at 221, 257, and 287 nm. Its molecular formula was determined as $C_{39}H_{50}O_{24}$ based on the HRESIMS data at *m*/*z* 901.2574 $[M\text{-}H]^+$ (calcd for 901.2614, $C_{39}H_{49}O_{24}$). The general appearance of its ^1H and ^{13}C NMR spectra (Tables 1 and 2), in addition to the information obtained from its mass spectrum, suggested an anthraquinone skeleton for **1**. By the analysis of the HMBC and HMQC spectrum, the aglycone part was determined to be chrysophanol. The ^{13}C NMR spectrum of **1** showed thirty-nine carbon signals, including one methyl (δ 21.7), fourteen carbon signals ascribed to the aglycone part of anthraquinone, and twenty-four sugar carbon signals (four anomeric carbons at δ 103.9, 102.8, 102.7, and 100.5 and other carbons at δ 88.6–60.5). From the above information, compound **1** was identified as an anthraquinone glycoside with four monosaccharides. After hydrolysis with 5% hydrochloric acid methanol solution and trimethyl silylation, the GC analysis and the NMR data showed that the sugar chain only consisted of D-glucose residues by comparison with the authentic simple. Therefore, the sugar chain was composed of four glucose residues. The four anomeric proton signals were determined at δ 5.17 (1H, d, J = 7.2 Hz), 4.16 (1H, d, J = 7.6 Hz), and 4.31 (2H, d, J = 6.8 Hz). The conformation of D-glucose was determined as β-type by the J value. The DEPT spectrum showed four secondary carbon signals at δ 60.5, 60.9, 68.7, and 68.9, which belonged to the 6 position carbon signals of the four glucose

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Table 1
^{1}H and ^{13}C NMR data of the aglycone for compounds **1–4** (500 and 125 MHz, DMSO, *J* in Hz, δ in ppm).

	1		2		3		4	
Positon	H	C	H	C	H	C	H	C
1		158.3		151.5				165.7
2	7.58 (d, 1.5)	122.9		123.2		169.0		
3		147.5		133.7	6.20 (s)	106.8		152.3
4	7. 71 (d, 1.5)	121.4	7.06 (s)	118.6		183.9	6.15 (s)	104.0
5	7.66 (d, 8.0)	118.3	6.89 (d, 2.0)	101.6		161.9	7.15 (s)	110.5
6	7.74 (dd, 7.2, 8.0)	136.0		158.4		157.6	6.76 (d, 2.0)	100.7
7	7.34 (d, 7.2)	124.1	7.05 (d, 2.0)	103.3	6.80 (d, 2.0)	101.5		160.9
8		161.3		155.3		161.2	6.33 (d, 2.0)	102.3
9		187.6			6.94 (d, 2.0)	99.9		157.7
10		182.0			7.21 (s)	101.1		163.0
4a		134.3		136.9		103.8		132.4
5a						107.8		141.7
8a		116.7		108.8				
9a		118.1				140.4		109.3
10a		132.4				152.5		98.5
3-CH_3	2.48 (s)	21.7	2.22 (s)	19.5			2.22 (s)	18.8
2-CH_3					2.39 (s)	20.3		
8-OH	12.91 (s)							
2-COCH3				204.4				
2-$COCH_3$			2.48 (s)	32.2				
6-OCH_3			3.82 (s)	55.4				
8- OCH_3					3.88 (s)	55.6	3.86 (s)	55.6

residues, and δ 68.7 and 68.9 were at the lower field displacement. This showed that three monosaccharides were connected through two 1 → 6 linkages. Comparing the 13CNMR data of 1 and standard glucose, it can be found that the signal at δ 88.6 was the C-3, which moved to lower field displacement. Therefore, the sugar chain should also have one 1 → 3 linkage. The HMBC spectrum showed an anomeric proton signal at δ 5.17 (1H, d, *J* = 7.2 Hz) with both the C-1 (δ 158.3) of the aglycone part and the sugar carbon signal at δ 74.9, and δ 3.19 with δ 74.9 have cross-peaks. Therefore, the proton signals at δ 5.17 (1H, d, *J* = 7.2 Hz) and δ 3.19 and the carbon signal at δ 74.9 were assigned to H-1', H-5'and C-3'. Then, H-6' (δ 4.12, 3.41), C-6' (δ 68.8) and H-1" [4.16 (1H, d, *J* = 7.6 Hz)] were ascertained by the ^{1}H-^{1}H COSY, HSQC and HMBC experiments, which revealed the presence of a 1 → 6 linkage between the first two glucoses units. The anomeric proton signals of the other two glucoses in the sugar chain were both at δ 4.31 (1H, d, *J* = 6.8 Hz), with an HMBC relationship with δ 68.9 and 88.6. Based on the ^{1}H-^{1}H COSY and HSQC spectrum, H-1", H-2" (δ 2.96), H-3"(δ 3.15) and C-3"(δ 76.0) were confirmed. This result indicated that δ 88.6 was not C-3" and could only be the signal of C-3"'. Therefore, the connection of the second and third glucose was a 1 → 6 linkage, and the last two glucoses were connected by a 1 → 3 linkage. The connections of the

Table 2
^{1}H and ^{13}C NMR data of the sugar for compound **1–4** (500 and 125 MHz, DMSO, J in Hz, δ in ppm).

	1		2		3		4	
Positon	H	C	H	C	H	C	H	C
'1	5.17 (d, 7.2)	100.5	5.09 (d, 6.0)	102.4	5.06 (d, 7.5)	100.9	5.06 (d, 7.5)	100.8
'2	3.44 (m)[a]	73.3	3.35 (m)[a]	73.3	3.43 (m)[a]	73.6	3.40 (m)[a]	73.4
'3	3.46 (m)[a]	74.9	3.47 (m)	75.0	3.46 (m)[a]	75.1	3.45 (m)[a]	75.0
'4	3.06 (m)[b]	70.3	3.07 (m)[b]	70.4	3.08 (m)[b]	70.4	3.06 (m)[b]	70.3
'5*	3.19 (m)[c]	75.9	3.22 (m)[c]	75.9	3.20 (m)[c]	75.9	3.22 (m)[c]	76.0
'6 a	4.12 (m)	68.8	4.15 (m)	68.8	4.13 (m)	68.8	4.14 (m)	68.8
b	3.41 (m)[a]		3.43 (m)[d]		3.46 (m)[a]		3.41 (m)[a]	
"1	4.16 (d, 7.6)	102.7	4.18 (d, 7.5)	102.8	4.18 (d, 7.5)	102.9	4.18 (d, 7.5)	102.8
"2	2.96 (m)	73.7	2.98 (m)	73.8	3.00 (m)	73.9	3.01 (m)	73.8
"3	3.15 (m)[d]	76.0	3.16 (m)[e]	76.0	3.18 (m)[c]	76.1	3.17 (m)[c]	76.0
"4	3.21 (m)[c]	69.9	3.21 (m)[c]	70.0	3.24 (m)[c]	70.0	3.22 (m)[c]	69.9
"5	3.31 (m)	76.3	3.33 (m)[a]	76.1	3.35 (m)[d]	76.4	3.36 (m)	76.2
"6 a	4.01 (m)	68.9	4.03 (m)	68.8	4.00 (m)	68.8	3.98 (m)	68.8
b	3.64 (m)[e]		3.71 (m)		3.71 (m)		3.72 (m)[e]	
"'1	4.31 (d, 6.8)	102.8	4.36 (d, 7.0)	102.6	4.33 (d, 7.5)	102.5	4.33 (d, 7.5)	102.4
"'2	3.17 (m)[d]	71.9	3.26 (m)	71.9	3.22 (m)[c]	72.0	3.24 (m)[c]	71.9
"'3	3.28 (m)	88.6	3.36 (m)[a]	88.8	3.34 (m)[d]	88.8	3.40 (m)[a]	88.6
"4	3.17 (m)[d]	68.6	3.21 (m)[c]	68.6	3.20 (m)[c]	68.7	3.24 (m)[c]	68.6
"'5	3.74 (m)	75.8	3.74 (m)	75.8	3.70 (m)	75.8	3.76 (m)	75.8
"'6 a	3.64 (m)[e]	60.5	3.63 (m)	60.6	3.64 (m)	60.6	3.66 (m)[e]	60.5
b	3.39 (m)		3.40 (m)		3.40 (m)		3.42 (m)[a]	
""1	4.31 (d, 6.8)	103.9	4.35(d, 7.0)	104.0	4.33 (d, 7.5)	104.1	4.33 (d, 7.5)	103.9
""2	3.10 (m)	73.4	3.11 (m)	73.5	3.11 (m)[e]	73.6	3.12 (m)	73.5
""3	3.06 (m)[b]	76.7	3.09 (m)[b]	76.8	3.12 (m)[e]	76.9	3.08 (m)[b]	76.8
""4	3.03 (m)[b]	69.7	3.06 (m)[b]	69.9	3.06 (m)[b]	69.8	3.05 (m)[b]	69.8
""5*	3.19 (m)[c]	75.8	3.17 (m)[e]	75.8	3.24 (m)[c]	75.9	3.26 (m)[c]	75.8
""6 a	3.66 (m)[e]	60.9	3.66 (m)	60.9	3.67 (m)	61.0	3.67 (m)[e]	60.9
b	3.45 (m)[a]		3.43 (m)[d]		3.42 (m)[a]		3.41 (m)[a]	

*^{1}H and ^{13}C NMR signals of this position could be interchanged a, b, c, d, e were overlapped, respectively.

four monosaccharides were also identified by 2D NMR and hydrolysis. Thus, the structure of **1** was characterized as chrysophanol-1-*O*-β-D-glucopyranosyl -(1 → 3)-*O*-β-D-glucopyranosyl-(1 → 6)-*O*-β-D-glucopyranosyl-(1 → 6)- *O*-β-D- glucopyranoside.

Compound **2** was purified as a pale yellow crystal with a negative optical rotation ($[\alpha]_D^{20}$ −49.964) in methanolic solution. The Molish and Bornträger reagent test showed a positive reaction. The UV spectrum displayed absorption bands at 236, 265 and 320 nm, and the compound was assigned the molecular formula $C_{38}H_{54}O_{24}$ from its negative-ion HRESIMS at *m*/*z* 893.2927 $[M-H]^-$ (calcd for $C_{38}H_{53}O_{24}$, 893.2927). The NMR spectroscopic data of the aglycone portion revealed that it was torachrysone (El-Halawany et al., 2007). Comparing the ^1H and ^{13}C NMR spectra of **1** and **2** (Tables 1 and 2), the data of the sugar chain were similar, and the four anomeric carbon signals were at δ 104.0, 102.8, 102.6, and 102.4, with the other sugar carbon signals at δ 88.6-60.5, and the corresponding anomeric proton signals at δ 5.09 (1H, d, *J* = 6.0 Hz), 4.18 (1H, d, *J* = 7.5 Hz), and 4.36 (2H, d, *J* = 7.0 Hz). The key HMBC correlations from δ 5.09 (H-1') to δ 155.3 (C-8 of the aglycone) indicated that the sugar chain was linked to the C-8 of the aglycone, and the connections of the other three monosaccharides were also identified by 2D NMR and hydrolysis. Thus, the structure of **2** was characterized as torachrysone 8-*O*-β-D-glucopyranosyl-(1 → 3)-*O*-β-D-glucopyranosyl-(1 → 6)-*O*-β-D -glucopyranosyl-(1 → 6)-*O*-β-D-glucopyranoside.

Compound **3** was isolated as a pale yellow crystal, showing a positive reaction with Molish and Bornträger reagents. Its UV spectrum displayed absorption bands at 224, 253 and 276 nm, and it had a negative optical rotation ($[\alpha]_D^{20}$ −649.537) in methanolic solution. The molecular formula of **3** was $C_{39}H_{52}O_{25}$, as deduced from the data of its HR-negative-ESI-MS at *m*/*z* 919.2710 $[M-H]^-$ (calcd for $C_{39}H_{51}O_{25}$ 919.2719). The evidence above and the ^1H and ^{13}C NMR spectra (Tables 1 and 2) suggested rubrofusarin (Lee et al., 2006) for **3**. The four anomeric protons at δ 5.06, 4.18, 4.33, and 4.33 (each 1H, d, *J* = 7.5 Hz) and the corresponding carbons at δ 100.9, 102.9, 102.5 and 104.1 revealed the presence of four sugar moieties. Similar to compound **2**, the analysis of the comparison of the ^1H and ^{13}C NMR spectra of **3** with **1** (Tables 1 and 2) showed that the data of the sugar chain were similar. The site of attachment of the four glucose units to the aglycone was assigned to C-6, as indicated from the HMBC correlation between the proton at δ 5.17 (H-1') and the carbon at δ 157.6 (C-6) of the aglycone. The connections of the other three glucoses were also confirmed by 2D NMR and hydrolysis. Therefore, the structure of **3** was rubrofusarin-6-*O*-β-D-glucopyranosyl-(1 → 3)-*O*-β-D-glucopyranosy1-(1 → 6)–*O*-β-D-glucopyranosyl-(1 → 6)-*O*-β-D- glucopyranoside.

Compound **4** was obtained as a pale yellow crystal, and its UV spectrum displayed absorption bands at 207, 225, 269, and 278 nm. Its methanolic solution had a negative optical rotation ($[\alpha]_D^{20}$ −19.985). The molecular formula of **4** was determined as $C_{39}H_{52}O_{25}$ from the $[M-H]^-$ ion peak at m/z 919.2692 in the HRESI mass spectrum (calcd for $C_{39}H_{51}O_{25}$ 919.2719). Comparing the ^1H and ^{13}C NMR data (Table 1 and 2), with the exception of the carbonyl signal, compound **4** was similar to **3**, suggesting that it could be a naphtha-α-pyrone glycoside (Hatano et al., 1999). Furthermore, the aglycone part was identified to be toralactone, and the sugar part was assigned as the same as that of **3** by the 2D NMR and hydrolysis analysis. Thus, the structure of **4** was deduced as toralactone-9-*O*-β-D–glucopyranosyl-(1 → 3)-*O*-β-D-glucopyranosy1-(1 → 6)-*O*-β-D- glucopyranosyl-(1 → 6)-*O*-β-D-glucopyranoside.

By extensive analysis of their ^1H and ^{13}C NMR data, ten known compounds (**5**–**14**) were isolated and identified as chrysophanol-1-*O*-β-D-glucopyranosyl-(1 → 3) -*O*-β-D-glucopyranosyl-(1→6)-*O*-β-D-glucopyranoside (**5**) (Wong and Wong, 1989), aurantio-obtusin (**6**), obtusinfolin (**9**) (Tang et al., 2009a), chryso-obtusin (**7**), emodin (**8**), obtusifolin-2-glucoside (**10**), chrysophanol (**12**), physicon (**13**) (Choi et al., 1996), rubrofusarin gentiobioside (**11**) (Susumu k. Michio, 1988), and aurantio-obtusin-6-*O*-β-D-glucopyranoside (**14**) (Tang et al., 2009b).

3. Experimental

3.1. General experimental procedure

Optical rotations were measured on an Autopol V polarimeter with MeOH as solvent at 20 °C. Melting points were measured on a Sgwx-4 melting point apparatus (China). UV spectra were recorded on an Agilent UV-8453 spectrophotometer (USA). 1D and 2D NMR data were obtained on a BrukerAV-500 instrument (Germany) in DMSO, using TMS as the internal standard. The chemical shifts are given in δ (ppm), and the coupling constants (*J*) are reported in Hz. HRESIMS were recorded on an Agilent G-6540 Q-TOF MS (USA). Silica gel GF254 prepared for TLC and silica gel (100–200 mesh) for column chromatography were obtained from Qingdao Marine Chemical Company, Qingdao, China. Macroporous adsorption resin AB-8 was produced by the Chemical Plant of Nankai University, Tianjin, China. The compounds were purified by preparative HPLC on a Gilson 306 pump, 800C dynamic mixer, 506C system interface, and 118UV detector instrument (USA) equipped with a YMC-Pack ODS-A column (250 × 20 mm, Japan). The GC data were recorded on an Agilent GC 7890A GC system using an HP-5 (30 m × 0.32 mm × 0.25 μm) column, FID detection, N_2 carrier gas, 250 °C injection temperature, 280 °C detection temperature, and 280 °C column temperature.

3.2. Plant material

The seeds of *Cassia obtusifolia* L. were collected in Anguo, Hebei province, China and were identified by Professor Chen Sui Qing (Henan University of Traditional Chinese Medicine). A voucher specimen was deposited in our laboratory (voucher No. COL-2009-05).

3.3. Extraction and isolation

The dried and powdered seeds of *Cassia obtusifolia* L. (15 kg) were extracted with hot 70% EtOH (45 L × 2). After the solvent was concentrated under reduced pressure, the extracted EtOH (1500 g) was suspended in water (10 L) and extracted with petroleum ether (5 L × 4) and chloroform (5 L × 4) to afford a petroleum ether soluble fraction (200 g) and a chloroform soluble fraction (150 g). The remaining water extracts were passed through a macroporous adsorption resin AB-8 column eluted with H_2O–EtOH (9:1) (5 L), H_2O–EtOH (7:3) (5 L), H_2O–EtOH (1:1) (5 L), H_2O–EtOH (3:7) (5 L), and EtOH (5 L). The 30% EtOH eluate portion (320 g) was subjected to silica gel column chromatography eluted with $CHCl_3$–MeOH (9:1, 4:1, 2:1, 1:1) and MeOH alone to give 8 fractions (A–H). Fraction A was applied to a silica gel column eluted with petroleum ether–acetone (5:1) to give **12** (15.3 mg) and **13** (20.9 mg). Fractions B and C were separated by silica gel column chromatography eluted with petroleum ether–EtOAC (4:1) and (3:1) to give **7** (25.3 mg), **8** (18.0 mg) and **9** (12.3 mg). Fractions D and G were purified by silica gel column chromatography eluted with petroleum ether–EtOAC (3:1) and sephadex LH-20 eluted with MeOH–H_2O (8:2) to give **6** (30.0 mg) and **10** (16.8 mg). Fraction F was separated by polyamide column chromatography eluted with MeOH–H_2O (8:2) and purified by sephadex LH-20 eluted with MeOH–H_2O (1:1) to give **11** (200.0 mg) and **14** (21.3 mg). Fraction H

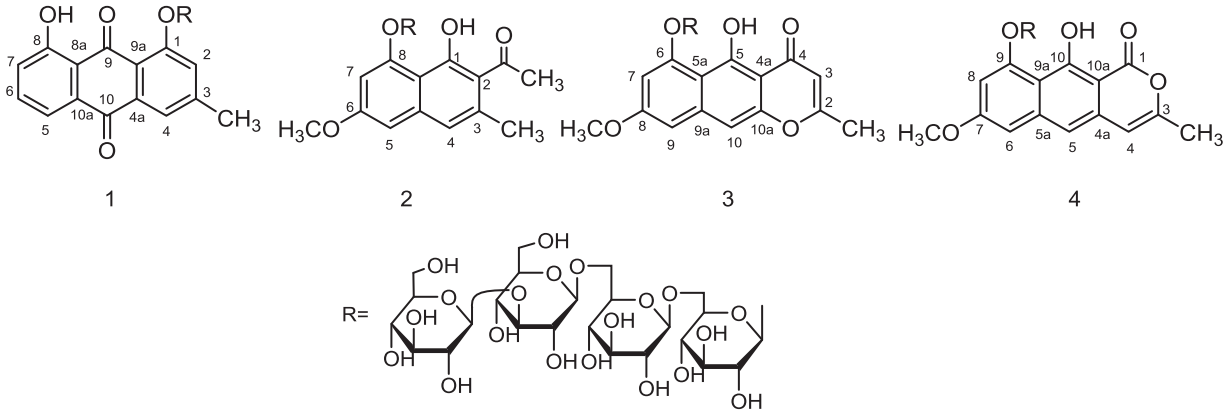

Fig. 1. Structures of compounds **1-4**.

was applied to an ODS silica gel column eluted with MeOH–H_2O (1:1) to yield **1** (20.2 mg) and **5** (10.5 mg), and the other portion was separated by preparative HPLC, eluting with CH_3OH-H_2O (45:55) to give compounds **2** (14.7 mg), **3** (12.0 mg) and **4** (11.5 mg) Fig. 1.

*3.3.1. Compound **1***

Yellow powder, mp 205–206 °C; $[\alpha]_D^{20}$ −57.958 (*c* = 0.10, MeOH); UV λmax (MeOH) nm (log ε): 221, 257, 287; ^{1}H NMR and ^{13}C NMR data, see Table 1 and 2; HRESI-MS *m/z* 901.2574 [M-H]$^-$ (calcd for $C_{39}H_{49}O_{24}$, 901.2614).

*3.3.2. Compound **2***

Pale yellow crystal, mp 187–188 °C; $[\alpha]_D^{20}$ −49.964 (*c* = 0.10, MeOH); UV λmax (MeOH) nm (log ε): 236, 265, 320; ^{1}H NMR and ^{13}C NMR data, see Table 1 and 2; HRESI-MS *m/z* 893.2927[M-H]$^-$ (calcd for $C_{38}H_{53}O_{24}$, 893.2927).

*3.3.3. Compound **3***

Pale yellow crystal, mp 210–211 °C; $[\alpha]_D^{20}$ −649.537 (*c* = 0.10, MeOH); UV λmax (MeOH) nm (log ε): 224, 253, 276; ^{1}H NMR and ^{13}C NMR data, see Table 1 and 2; HRESIMS *m/z* 919.2710 [M-H]$^-$ (calcd for $C_{39}H_{51}O_{25}$ 919.2719).

*3.3.4. Compound **4***

Pale yellow crystal, mp 216–217 °C; $[\alpha]_D^{20}$ −19.985 (*c* = 0.10, MeOH); UV λmax (MeOH) nm (log ε): 207, 225, 269, 278; ^{1}H NMR and ^{13}C NMR data, see Table 1 and 2; HRESIMS *m/z* 919.2692 [M-H]$^-$ (calcd for $C_{39}H_{51}O_{25}$ 919.2719).

3.4. Acid hydrolysis of the glycosides

Compounds **1**,**2**, **3** and **4** (each 2 mg) were heated in 2 M HCl (5 ml) at 90 °C for 4 h. (Xu et al., 2014) The reaction mixture was extracted with $CHCl_3$ (5 ml × 3). Each remaining aqueous layer was concentrated to dryness to give a residue and was dissolved in pyridine (0.3 ml), and then L-cysteine methyl ester hydrochloride (3.0 mg) was added to the solution. The mixture was heated at 60 °C for 1 h, and trimethyl chlorosilane (0.5 ml) was added, followed by heating at 60 °C for 30 min. Then, the solution was concentrated to dryness and dissolved in water (1 ml × 3), followed by extraction with *n*-hexane (1 ml × 3). The hexane extract was subjected to GC analysis. The absolute configurations of the monosaccharide were confirmed to be D-glucose by comparison of the retention times of the monosaccharide derivatives of **1** (25.040 min), **2** (25.041 min), **3** (25.039 min), and **4** (25.045 min) with those of a standard sample of D-glucose (25.047 min).

Conflict of interest

The authors declare no conflicts of interest.

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