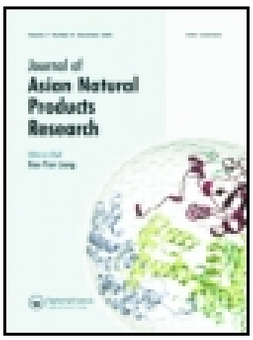

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Chemical constituents from the whole herb of *Hemiphragma heterophyllum*

Jia-Meng Dai[a], Yan-Hong Li[a], Xiao-Yun Pu[a], Cui Yang[a], Jing-Xian Sun[a], Roger Ruan[a], Xiao-Nian Li[b,a], Kai Tian[a] and Xiang-Zhong Huang[a]

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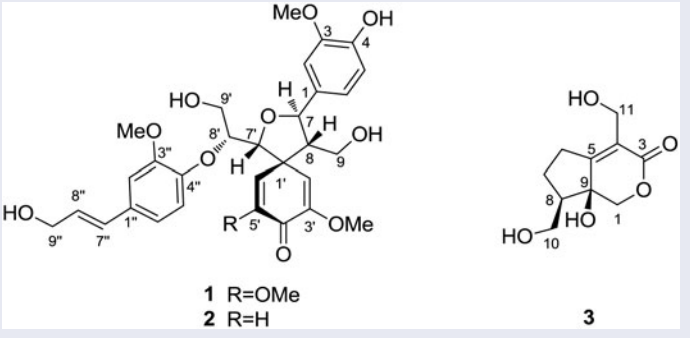
ABSTRACT

Phytochemical investigation on *Hemiphragma heterophyllum* led to the isolation of two new compounds, heterophyllumin A (**1**) and heterophylliol (**3**), along with nine known compounds, (−)-sibiricumin A (**2**), iridolactone (**4**), jatamanin A (**5**), dihydrocatalpolgenin (**6**), 25-hydroperoxycycloart-23-en-3β-ol (**7**), 24-methylenecycloartanol (**8**), (+)-pinoresinol (**9**), hexadec-(4*Z*)-enoic acid (**10**), and 9,12, 15-octadecatrienoic acid (**11**). Their structures were elucidated on the basis of detailed spectroscopic analyses and by comparison with literature data. Further, the structure of compound **3** was unambiguously confirmed by single-crystal X-ray analysis. Some of those compounds showed moderate activity in the α-glucosidase inhibition assay.



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Scrophulariaceae; *Hemiphragma heterophyllum*; sesquineolignans; iridoids; α-glucosidase inhibitory activity

1. Introduction

As a sole species of the genus *Hemiphragma* (Scrophulariaceae), *Hemiphragma heterophyllum* distributes mainly at the rocky mountains of the Yunnan Province in China

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[1]. The herbs are used by Yi people as folk medicine for the treatment of pharyngitis, periodontitis, rheumatism, abnormal menstruation, and traumatic injury by removing blood stasis to stop pain, eliminating wind and dampness, and clearing heat, and detoxifying [2]. Previous chemical investigations on this plant have mainly focused on its monoterpene glycosides and phenylethanoid glycosides [3–5], but have been less concerned on other chemical constituents, especially those with the spirolignan structure. To the best of our knowledge, only four sesquineolignans with a spiro skeleton from the nature plants have been *hitherto* reported [6–8]. Phytochemical investigation on ethyl acetate fraction of ethanolic extract from the dried whole herb of this plant led to the isolation of two new compounds, a new spirodienone sesquineolignan, heterophyllumin A (**1**), and a new iridoid, heterophylliol (**3**), along with nine known compounds (Figure 1). Hereto, this article describes the isolation and structural elucidation of these compounds, and their α-glucosidase inhibitory activities.

2. Results and discussion

Compound **1**, obtained as white powder, was determined to possess a molecular formula of $C_{31}H_{36}O_{11}$ with 14 degrees of unsaturation on the basis of HRESIMS ($[M+Na]^+$, *m/z* 607.2160) combined with the ^{13}C and ^{1}H NMR data (Table 1). The IR spectrum indicated the presence of hydroxyl (3438 cm^{-1}), carbonyl (1652 cm^{-1}), and aromatic groups (1630 and 1411 cm^{-1}). Initial analysis of the ^{13}C NMR spectrum of **1** revealed 31 signals. These were sorted, by DEPT experiments, into MeO ×4, OCH_2 ×3, OCH ×3, CH ×1, ═CH ×10, C × 1, ═C × 8, and C═O × 1. The ^{1}H NMR spectrum showed a number of signals indicating two typical ABX spin systems at δ_H 6.15–7.20, two insular protons at δ_H 6.20 and 6.49, one *trans*-substituted olefinic bond at δ_H 6.51 (1H, d, $J = 17.2$ Hz) and 6.26 (1H, dt, $J = 17.2$, 5.6 Hz), and four methoxyl groups at δ_H 3.91, 3.80, 3.72, and 3.54 (each 3H, s) in **1**. The above evidence showed the NMR data of **1** were extremely similar to those of sibiricumin A except for the different chemical shifts at C-5′ (δ_C 153.3) and MeO (δ_C 55.9), which revealed that C-5′ of compound **1** was substituted by the methoxyl group [8]. The HMBC spectrum showed a correlation between the signal at δ_H 3.72 (MeO) and C-5′, indicating the propose. Consequently, the planar structure of compound **1** was shown in Figure 1.

The structure of compound **1** includes four stereogenic carbon atoms (C-7, C-8, C-7′, and C-8′) and their relative configurations were discussed next (Figure 2). The ROESY correlation of H-8/H-7′ indicated that H-8 and H-7′ were on the same side of the tetrahydrofuran ring. Furthermore, the correlations of H-6′/H-7′ and H-6′/H-8 determined that the cyclohexadienone ring was oriented perpendicularly to the tetrahydrofuran ring and that H-6′ was on the same side of the plane as H-7′ and H-8. Conversely, H-2′ was determined to be on the opposite side of the tetrahydrofuran ring based on the ROSEY correlations of H-2′/H-7, and H-2′/H-8′. In addition, the ROSEY correlations of H-7/H-9, H-7/H-2′, and the large coupling constant of $J_{H-7,H-8} = 9.9$ Hz suggested that H-7 is *trans* to H-8. Thus, the relative configurations of C-7, C-8, and C-7′ were established and confirmed to be identical to the configurations of the

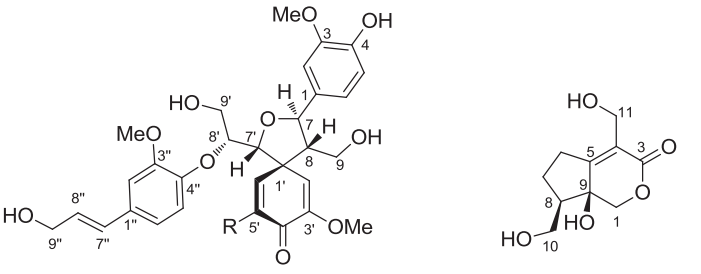

Figure 1. Structures of compounds **1–3**.

Table 1. The ^{1}H and ^{13}C NMR spectral data of compounds **1** and **3** (δ in ppm, J in Hz, CD_3OD).

1							**3**		
No.	δ_H, mult	δ_C, type	No.	δ_H, mult	δ_C, type		No.	δ_H, mult	δ_C, type
1	–	134.9, s	7′	4.88, d (1.4)	86.3, d	–	1	4.65, d (12.0)	77.4, d
2	7.14, s	111.0, d	8′	4.15, brd (4.8)	78.5, d	–	–	4.30, d (12.0)	–
3	–	149.1, s	9′	3.68, dd (12.0, 4.8)	61.2, t	–	3	–	166.6, s
4	–	147.4, s		3.49, dd (12.0, 5.4)		–	4	–	125.2, s
5	6.82, d (7.9)	116.1, d	3′-OMe	3.54, s	55.4, t	–	5	–	165.4, s
6	6.98, d (7.9)	120.2, d	5′-OMe	3.72, s	55.9, q	–	6	2.65–2.82, m	27.6, t
7	5.16, d (9.9)	83.2, d	1″	–	133.0, s	–	–	2.65–2.82, m	–
8	2.88, dt (9.9, 5.5)	62.6, d	2″	7.02, s	111.2, d	–	7	1.88–1.93, m	26.5, t
9	3.45, d (5.5)	60.0, t	3″	–	151.6, s	–	–	1.65–1.76, m	–
3-OMe	3.91, s	56.4, q	4″	–	147.7, s	–	8	1.95–2.02, m	51.2, d
1′	–	54.1, s	5″	6.86, brs	120.6, d	–	9	–	74.6, s
2′	6.49, s	117.3, d	6″	6.86, brs	117.6, d	–	10	3.79, t (10.3)	60.9, t
3′	–	151.7, s	7″	6.51, d (17.2)	131.4, d	–	–	3.64, dd (10.3, 4.8)	–
4′	–	179.2, s	8″	6.26, dt (17.2, 5.6)	128.5, d	–	11	4.22, d (12.1)	57.7, t
5′	–	153.3, s	9″	4.20, d (5.6)	63.7, t	–	–	4.33, d (12.1)	–
6′	6.20, s	120.2, d	3″-OMe	3.80, s	56.3, q	–	–	–	–

previously reported sibiricumin A. Moreover, existing spectroscopic data for the derivatives of sesquilignans demonstrate that the coupling constant (J) between H-7′ and H-8′ is $\leq$2.5 Hz for the erythro isomer and $\geq$5.0 Hz for the threo isomer [8–10]. Thus, in compound **1**, the 1.4 Hz coupling constant between H-7′ and H-8′ indicates that compound **1** is the erythro isomer. The relative configuration of compound **1**, at C-7, C-8, C-7′, and C-8′ was assigned as *RSRR/SRSS* upon comparison with the NMR spectroscopic data reported for sesquilignans. The NMR signal assignments of compound **1** were made using a range of multidimensional NMR spectroscopic techniques including COSY, HSQC, HMBC, and ROESY as well as by comparing the ^{1}H and ^{13}C NMR spectra of **1** with those of (−)-sibiricumin A (**2**). Consequently, the structure of compound **1** was established as (7*R*,8*S*,7′*R*,8′*R*/7*S*,8*R*,7′*S*,8′*S*)-(*E*)-7″-en-4,9,9′,9″-tetrahydroxy-3,3′,5′,3″-tetramethoxy-7,7′-epoxy-8′,4″-oxo-8,1′-sesquineolignan-4’-one, named heterophyllum in A.

Compound **3** was obtained as colorless quadrate crystal. HRESIMS gave a molecular ion peak at m/z 237.0738 $[M+Na]^+$, corresponding to the molecular formula $C_{10}H_{14}O_5$ and indicating four degrees of unsaturation. Its IR spectrum showed characteristic bands of OH (3445 cm^{-1}), conjugated C═O (1637 cm^{-1}), and C—O—C (1070 cm^{-1}) functionalities, suggested that **3** had an unsaturated ester carbonyl

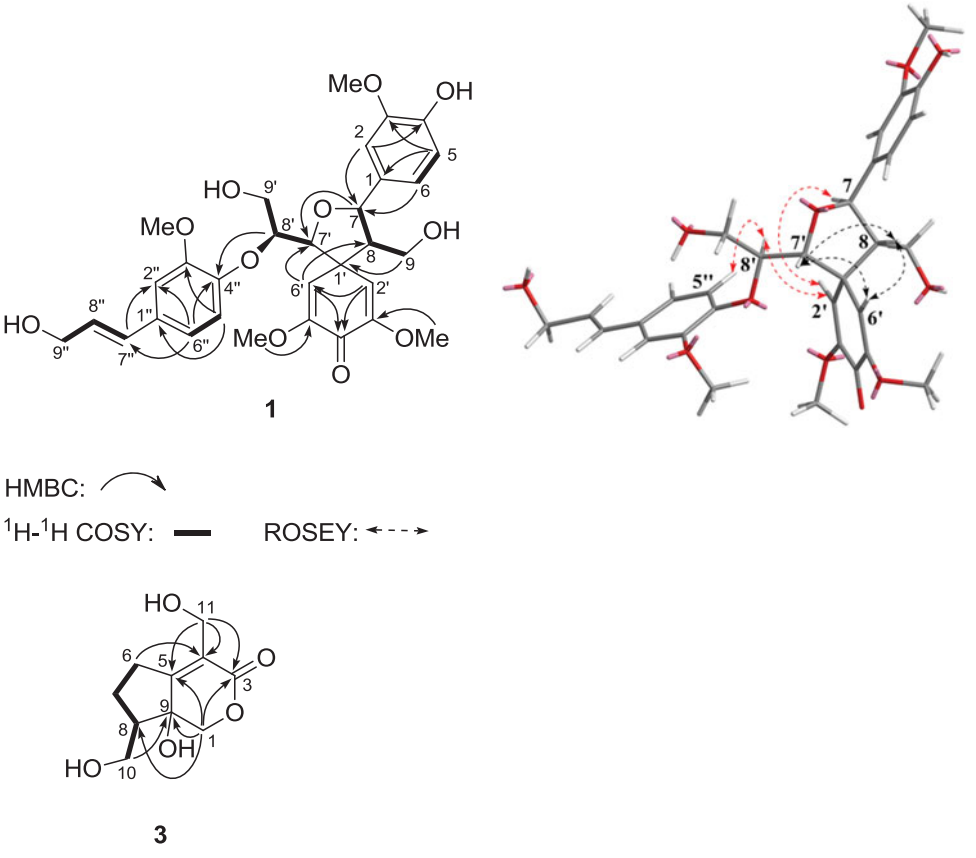

Figure 2. Key HMBC, COSY, and ROESY correlations of compounds **1** and **3**.

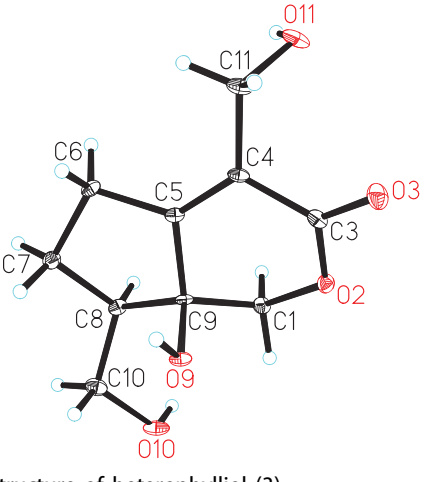

Figure 3. The X-ray crystal structure of heterophylliol (3).

group [11]. The unsaturated carbonyl group in the δ-lactone was also supported by the signal at δ_C 166.6 in the ^{13}C NMR spectrum. The ^{1}H NMR spectrum showed signals of three oxygenated methylenes (Table 1). The ^{13}C NMR and DEPT spectra

exhibited signals for one tetrasubstituted double bond (δ_C 125.2, 165.4), three methylenes bearing oxygen functions (δ_C 77.4, 60.9, 57.7), two methylenes (δ_C 27.6, 26.5), one methine (δ_C 51.2), one oxygenated quaternary carbon (δ_C 74.6), and one carbonyl (δ_C 166.6). Taking into account the molecular formula and 2D NMR spectroscopic analysis, compound **3** was deduced to be an unusual iridolactone bicyclic monoterpene (Figure 1). The HSQC (Figure S16) and ^{1}H-^{1}H COSY (Figure S18) spectra of H_2-6/H_2-7/H-8/H_2-10 suggested the presence of a —CH_2—CH_2—CH—CH_2—O— moiety in **3**. Clear correlations in the HMBC spectrum (Figure S17) were observed between H_2-10 (δ_H 3.64, 3.79) and the carbons at δ_C 26.5 (C-7), 51.2 (C-8), and 74.6 (C-9), and between H_2-11 (δ_H 4.22, 4.33) and the carbons at δ_C 166.6 (C-3), 125.2 (C-4), and 165.4 (C-5), suggesting that two oxymethylenes were located at C-8 and C-4. This spectrum also exhibited cross peaks between H_2-1 (δ_H 4.30, 4.65) and the carbons at δ_C 166.6 (C-3), 165.4 (C-5), 51.2 (C-8), and 74.6 (C-9), and between H_2-6 (δ_H 2.65-2.82) and the carbons at δ_C 125.2 (C-4), 165.4 (C-5), 26.5 (C-7), and 51.2 (C-8). Therefore, the structure of **3** was established as depicted in Figure 1, and its absolute configuration further confirmed as (8*R*,9*S*)-4,8-dihydroxymethyl-9-hydroxy-6,7,8,9-tetrahydrocyclopenta[*c*]pyran-4-ene-3-one by a single-crystal X-ray diffraction study using Cu Kα radiation, named heterophylliol (Figure 3).

Compound **2** was identified as sibiricumin A by comparison of its NMR spectroscopic data with those in the literature. In addition, the negative optical rotation of **2** ($[\alpha]_D^{28.2}$ − 34.7, c 0.13, MeOH) was in agreement with (−)-sibiricumin A ($[\alpha]_D^{25}$ − 36, c 0.15, MeOH) in the literature, displaying **2** was (−)-sibiricumin A [8]. Known compounds, iridolactone (**4**) [12], jatamanin A (**5**) [13], and dihydrocatalpolgenin (**6**) [14], 25-hydroperoxycycloart-23-en-3β-ol (**7**) [15], 24-methylenecycloartanol (**8**) [16], (+)-pinoresinol (**9**) [17], hexadec-(4*Z*)-enoic acid (**10**) [18], and 9, 12, 15-octadecatrienoic acid (**11**) [19] were established. Among them, compound **6** has been known as an unstable compound presented as a mixture [14].

All isolated compounds were evaluated for their potential to inhibit the α-glucosidase. Among those compounds, compounds **1**, **2**, and **7**–**10** displayed moderate inhibitory activities against α-glucosidase with IC_{50} values of 72.3 ± 0.5, 98.2 ± 0.3, 32.5 ± 0.7, 21.6 ± 0.3, 237.5 ± 0.8, and 40.8 ± 0.1 μM, respectively. The IC_{50} value of acarbose, a positive control, was 620.6 ± 1.3 μM.

3. Experimental

3.1. General experimental procedures

Optical rotations were carried out on a Horiba SEPA-300 high sensitivity polarimeter (HORIBA, Ltd., Kyoto, Japan). IR spectra were measured on a Bio-Rad FTS-135 spectrometer (Bio- Rad Laboratories Inc., Philadelphia, PA) with KBr pellets, ν in cm^{-1}. UV spectra were recorded using a Shimadzu UV-2401A spectrophotometer (Shimadzu Co., Kyoto, Japan). NMR spectra were performed on Bruker AM-400 spectrometers (Bruker, Karlsruhe, Germany) with TMS as an internal standard. HRESIMS were measured using Waters Auto Spec Premier P776 instruments (Waters, Milford, MA). Column chromatography (CC) was performed on silica gel (100–200 mesh, 200–300 mesh; Qingdao Marine Chemical, Inc., Qingdao, China),

MCI gel (75–150 μm, Mitsubishi Chemical Corporation, Tokyo, Japan), and Sephadex LH-20 (Pharmacia Fine Chemical Co. Ltd., Uppsala, Sweden). Acarbose (J&K China Chemical Ltd., Shanghai, China), p-nitrophenyl-α-D-glucopyranoside (pNPG) (Sigma-Aldrich trading Co. Ltd., Shanghai, China), and the α-glucosidase from *Saccharomyces cerevisiae* (Sigma-Aldrich trading Co. Ltd., Shanghai, China), were used for α-glucosidase inhibitory assay.

3.2. Plant material

The plant of *Hemiphragma heterophyllum* was collected at Chuxiong, Yunnan Province in September 2014 and identified by Prof. Qing-Song Yang from School of Ethnomedicine and Ethnopharmacy, Yunnan Minzu University. A voucher specimen (TSY201409) was deposited in the Key Laboratory of Chemistry in Ethnic Medicinal Resources, State Ethnic Affairs Commission and Ministry of Education, Yunnan Minzu University.

3.3. Extraction and isolation

The air-dried plant material (20.0 kg) of *H. Heterophyllum* was powdered and extracted three times with 95% EtOH (60 L) at room temperature for 48 h. The three extracts were combined and concentrated under reduced pressure to give a residue. The residue was suspended in water and then partitioned sequentially with petroleum ether, EtOAc, and n-BuOH. The EtOAc fraction (725.0 g) was fractionated by a silica gel CC (SiO_2: 100–200 mesh) and eluted with a gradient elution of $CHCl_3$/MeOH (1:0 → 0:1) to yield five fractions (I ∼ V).

Fraction II (145.0 g) was subjected to silica gel CC and eluted with petroleum ether/acetone (50:1 → 0:1) to provide subfractions $II_1 \sim II_7$. Subfraction II_3 (47.0 g) was subjected to silica gel CC, and eluted with petroleum ether/EtOAc (50:1) and petroleum ether/acetone (30:1) to yield compound **10** (10.0 mg). Compounds **7** (20.5 mg) and **8** (8.1 mg) were furnished from the residual of subfraction II_3 by further Sephadex LH-20 CC ($CHCl_3$/MeOH, 1:1). Subfraction II_6 (23.0 g) was subjected to MCI gel CC (30% → 90% MeOH/H_2O) to yield compound **11** (9.3 mg). Fraction III (134.0 g) was fractionated by silica gel CC and eluted with $CHCl_3$/acetone (50:1 → 0:1) to provide subfractions $III_1 \sim III_5$. Subfraction III_3 (2.2 g) was purified on a silica gel CC (SiO_2: 200–300 mesh; EtOAc/MeOH, 80:1) and further Sephadex LH-20 CC (100% MeOH) to furnish compounds **1** (4.0 mg) and **2** (5.8 mg). Fraction IV (205.0 g) was subjected to silica gel CC and eluted with $CHCl_3$/acetone (20:1 → 0:1) to provide subfractions $IV_1 \sim IV_5$. Subfraction IV_2 (26.0 g) was performed on a MCI gel CC (50% → 100% MeOH/H_2O) to afford eight subfractions $IV_{2.1} \sim IV_{2.8}$. Subfraction $IV_{2.1}$ (6.0 g) was chromatographed on a silica gel CC with an eluent of $CHCl_3$/MeOH (50:1 → 0:1) to yield eight subfractions $IV_{2.1.1} \sim IV_{2.1.8}$. Subfraction $IV_{2.1.2}$ (0.2 g) was purified on a Sephadex LH-20 CC (100% MeOH), and further semi-preparative HPLC (67% MeOH/H_2O, 3 ml/min, 203 nm) to furnish compound **6** (t_R 13.67 min, 17.0 mg). Subfraction $IV_{2.3}$ (0.5 g) was further purified on a Sephadex LH-20 CC (100% MeOH), and further semi-preparative HPLC (54% MeOH/H_2O,

3 ml/min, 254 nm) to furnish compounds **3** (t_R 11.85 min, 27.0 mg), **4** (t_R 15.23 min, 9.0 mg), and **5** (t_R 23.52 min, 30.0 mg). Subfraction $IV_{2.4}$ (1.0 g) was chromatographed on a silica gel CC (SiO_2: 200–300 mesh) with an eluent of $CHCl_3$/acetone (10:1) to yield compound **9** (6.2 mg).

3.3.1. Heterophyllumin A (1)

White powder; $[\alpha]_D^{28.3} \approx 0$ (c 0.12, MeOH); UV (MeOH) λ_{max}: 204, 269 nm; IR (KBr) υ_{max}: 3438, 2984, 1652, 1630, 1411, 1070, and 545 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD) spectral data, see Table 1; HRESIMS *m/z*: 607.2160 $[M + Na]^+$ (calcd for $C_{31}H_{36}O_{11}Na$, 607.2155).

3.3.2. Heterophylliol (3)

Colorless quadrate crystal; M.p. 149.8 ~ 150.6°. $[\alpha]_D^{27.9}$ +45.1 (*c* 0.74, MeOH); UV (MeOH) λ_{max}: 218, 226 nm; IR (KBr) υ_{max}: 3445, 2320, 2026, 1637, 1418, 1070, 1015, 860, 543 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD) spectral data, see Table 1; HRESIMS *m/z*: 237.0738 $[M + Na]^+$ (calcd for $C_{10}H_{14}O_5Na$, 237.0733). Crystal data are provided in the supporting information.

3.4. The α-glucosidase inhibitory assay

The inhibitory effects of all compounds on the α-glucosidase were evaluated using a modification of a technique previously described [20]. Acarbose was administrated as a positive control.

Supporting information

Detailed experimental procedures, 1D and 2D NMR, HRMS, IR, UV spectra, and X-ray crystal data are provided.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

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