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1 **New glucosyloxybenzyl 2R-benzylmalate derivatives from the**
2 **undergrounds parts of *Arundina graminifolia* (Orchidaceae)**

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20

1 **Abstract**

2 Phytochemical investigation of the underground part of the blossoming tropical orchid
3 *Arundina graminifolia* led to the isolation of six new glucosyloxybenzyl 2*R*-benzylmalate derivatives
4 named arundinosides L-Q (**1-6**) together with 5 known compounds arundinosides D-F, J and K (**7-11**).
5 The structures of the isolated compounds were determined by extensive spectroscopic data analysis.
6 The anti- α -glucosidase and antioxidant activities of the isolated compounds were determined. The
7 result indicated that compounds **4-6** and **9** showed moderate to weak α -glucosidase inhibitory effects
8 as well as moderate antioxidant effect.

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16 **Keywords:** *Arundina graminifolia*, Orchidaceae, glucosyloxybenzyl 2*R*-benzylmalate derivatives,
17 arundinosides L-Q

1 **1. Introduction**

2 The family Orchidaceae is a diverse and widely spread family of flowering plant with
3 approximately 28,000 identified species which is spread across 800 genera [1]. Among these,
4 *Arundina graminifolia* (D. Don) Hochr. popularly known as bamboo is a well-known specie in the
5 family Orchidaceae. It is used in traditional medicine for treating sore throat, snake bites, food
6 poisoning, jaundice, arthritis, dissipating blood stasis and lung infection [2-4]. It is native to the
7 subtropical Asian countries of Thailand, India, Nepal, Malaysia, Singapore, China, Indonesia, Sri
8 Lanka, Vietnam and Philippines [5-10]. To date, a number of secondary metabolites, such as
9 stilbenoids [11, 12], bibenzyls [13, 14], phenanthrenes [15], phenolics [16-18], fluorenones [19] and
10 glucosyloxybenzyl-2-benzylmalate derivatives [20, 21] have been characterized from *A. graminifolia*.
11 Although *A. graminifolia* have been proven to be a reservoir of structurally diverse molecules, only
12 two reports have structurally characterized glucosyloxybenzyl-2-benzylmalate derivatives from this
13 species [20-21]. We previously reported two new stilbenoids and seven new glucosyloxybenzyl-2R-
14 benzylmalate derivatives from the aerial part of the plant [20, 22]. Motivated by a search for additional
15 new metabolites from the plants, we thus investigated the chemical components from the underground
16 parts of *A. graminifolia*. As a result, six new structurally related glucosyloxybenzyl 2R-benzylmalate
17 derivatives named arundinosides L-Q (1–6) along with five known compounds arundinosides D-F, J
18 and K (7-11) were isolated and identified. We herein report the details of isolation and structural
19 elucidation of the compounds.

20 **2. Experimental**

21 *2.1. General experimental procedures*

22 Optical rotations were measured using a Jasco Perkin Elmer 341 polarimeter (Jasco, Lisses,
23 France). UV spectra were recorded on a Shimadzu UV-2401 PC spectrometer (Shimadzu, Kyoto,
24 Japan). IR spectra were recorded on a 380 FT-IR spectrophotometer (Thermo Electron Corporation,
25 Saint Herblain, France). 1D and 2D NMR spectra were obtained using a Bruker 500 MHz Avance III
26 spectrometer equipped with a DCH ¹³C/¹H Cryoprobe (Bruker Biospin, Rheinstetten, Germany). HR-
27 ESI-MS were recorded on a 1200 Agilent Series coupled to an Agilent 6520Accurate Mass Q-TOF

1 spectrometer (Agilent Technologies, Santa Clara, USA). Gas chromatography analysis was conducted
2 on a Thermo Scientific Trace GS Ultra apparatus (Thermo Electron Corporation, Saint Herblain,
3 France) coupled to an EI-MS detector equipped with a capillary TR-5MS SQC column (0.25 μ m, 15 \times
4 0.25 mm, Thermo Fischer Scientific) and a DSQII mass spectrometer (Thermo Electron Corporation,
5 Saint Herblain, France). Semi preparative RP-HPLC was performed on a Gilson LC system using a
6 semi preparative Kinetex Axia C-18 Column (100 mm \times 21.2 mm, 5 μ m; Phenomenex, Torrance, CA,
7 USA). Centrifugal partition chromatography was analyzed on a FCPC200 apparatus (Kromaton
8 Technologies, Angers, France) fitted with a rotor made of 20 circular partition disks (1320 partition
9 cells: 0.130 mL per cell; total column capacity of 1000 mL).

10 2.2. *Plant material*

11 The plant (*A. graminifolia*) was obtained from Joe's orchid farm (Chiang Mai Province,
12 Thailand) in September 2010. The dried roots and rhizomes were imported to France in compliance
13 with the requirements of the Convention on International Trade in Endangered Species (CITES). A
14 reference sample with the number n° 05-563 was deposited at the herbarium of the Faculty of Science,
15 Chiang Mai University, Thailand.

16 2.3. *Extraction and isolation*

17 The air dried undergrounds parts of *A. graminifolia* (350 g) were grinded with the help of a
18 Restch ZM 2000 grinder. The obtained powder was exhaustively extracted with ethanol thrice (ratio of
19 1g powder for 20 mL solvent). The filtrates were combined and evaporated under reduced pressure to
20 afford a crude ethanolic extract (45.63 g). The ethanol extract was then suspended in water and
21 partitioned with CH₂Cl₂ and EtOAc to obtain a CH₂Cl₂-soluble fraction (10.40 g) and an EtOAc-
22 soluble fraction (10.93 g). The EtOAc-soluble fraction was separated by Centrifugal Partition
23 Chromatography (CPC) with the solvent system n-heptane/EtOAc/MeOH/H₂O (0.25:5:1:5). The rotor
24 was filled to capacity with the organic stationary phase mode without rotating. The aqueous (lower)
25 mobile phase was pumped into the column in the head to tail mode at a flow rate of 5 mL/min. Then,
26 the rotation speed was increased from 0 to 1000 rpm until complete equilibrium between the 2 phases,
27 giving a dead volume of 350 mL.

1 The EtOAc-soluble fraction was separated by two consecutive CPC runs with an average of
2 5.0 g injected in each run. For each run, the sample was dissolved in 40 mL of the organic/aqueous
3 phase mixture (1:1 v:v). After the injection, the flow rate was gradually increased from 5 mL/min to
4 11 mL/min in 60 min. The flow rate of 11 mL/min was maintained for 140 minutes. After 200 min on
5 an ascending/head to tail mode, an extrusion step of the organic phase was applied at 70 mL/min and
6 the rotation speed was decreased to 500 rpm. The eluent collected was monitored at 210 and 280 nm
7 and 14 fractions were obtained in total, twelve in the ascending mode/head to tail (Fractions A-L) and
8 two in the extrusion process (Fractions M and N).

9 Fractions B (551 mg), C (863 mg) and D (925 mg) were further fractionated by gel
10 chromatography using Sephadex LH-20 (MeOH). Sub-fraction B-5 (208 mg) was subjected to semi-
11 preparative RP-HPLC. The mobile phase consisted of water (A) and acetonitrile (B) both containing
12 0.05% formic acid. A gradient of 35% B for 2 min, 35% to 38% B in 3 min, 38% to 45% B in 35 min,
13 45% to 50% B in 5 min, 50% to 100% B in 5 min, 100% B for 5 minutes at 14 mL/min was applied to
14 afford compounds **1** (9.3 mg), **2** (5.0 mg), **3** (4.5 mg), **6** (2.6 mg), **9** (2.8 mg) and **10** (15.0 mg).

15 Sub-fraction C-3 (130.4 mg) was purified by semi-preparative RP HPLC using the same
16 mobile phase as indicated above to afford compounds **4** (4.1 mg), **5** (8.2 mg), and **6** (1.2 mg). Sub-
17 fraction D-5 (292.5 mg) was further subjected to semi-preparative RP-HPLC (with 40% B for 2 min,
18 40% to 45% B in 31 min, 45% to 100% B in 10 min, 100% B for 5 min at 14 mL/min) to give
19 compounds **8** (19.8 mg) and **11** (32.9 mg).

20 2.3.1. *Arundinoside L (1)*:

21 White amorphous powder (9.3 mg); $[\alpha]_D^{25}$ -56 (*c* 0.4, CH₃OH); UV (CH₃OH) λ_{\max} (log ϵ): 218
22 (3.06), 270 (1.83); IR: 3343, 1720, 1510, 1368, 1233, 1165, 1075, 1034, 826 and 744 cm⁻¹; **H NMR**
23 **see Table 1 and ¹³C NMR see Table 2**; HR-ESI-MS: *m/z* 1169.36070 [M-H]⁻ (calcd. for C₅₆H₆₅O₂₇ for
24 1169.39732).

25 2.3.2. *Arundinoside M (2)*:

26 White amorphous powder (5.0 mg); $[\alpha]_D^{25}$ -64 (*c* 0.2, CH₃OH); UV (CH₃OH) λ_{\max} (log ϵ): 217
27 (3.13), 269 (1.95), 277 (1.82); IR: 3349, 1720, 1522, 1361, 1243, 1165, 1066, 1030, 826 and 755 cm⁻¹;

1 ¹H NMR see Table 1 and ¹³C NMR see Table 2; HR-ESI-MS: *m/z* 1211.37698 [M-H]⁻ (calcd. for
2 C₅₈H₆₇O₂₈ for 1271, 38244).

3 2.3.3. *Arundinoside N* (**3**):

4 White amorphous powder (4.5 mg); [α]_D²⁵ -58 (*c* 0.2, CH₃OH); UV (CH₃OH) λ_{\max} (log ϵ): 219
5 (3.11), 270 (1.95), 277 (1.92); IR: 3364, 1733, 1643, 1529, 1366, 1241, 1164, 1077, 820 and 715 cm⁻¹;

6 ¹H NMR see Table 1 and ¹³C NMR see Table 2; HR-ESI-MS: *m/z* 1211.37566 [M-H]⁻ (calcd. for
7 C₅₈H₆₇O₂₈ for 1271, 38244).

8 2.3.4. *Arundinoside O* (**4**):

9 White amorphous powder (4.1 mg); [α]_D²⁵ -71 (*c* 0.2, CH₃OH); UV (CH₃OH) λ_{\max} (log ϵ): 218
10 (3.04), 277 (1.82); IR 3337, 1762, 1630, 1570, 1571, 1355, 1207, 1143, 1049, 1022, 822 and 704 cm⁻¹;

11 ¹H NMR see Table 1 and ¹³C NMR see Table 2; HR-ESI-MS: *m/z* 1047.32844 [M-H]⁻ (calcd. for
12 C₄₉H₅₉O₂₅ for 1047.33509).

13 2.3.5. *Arundinoside P* (**5**):

14 White amorphous powder (1.2 mg); [α]_D²⁵ -93 (*c* 0.2, CH₃OH); UV (CH₃OH) λ_{\max} (log ϵ): 222
15 (3.06), 270 (2.02), 277 (1.95), 323 (1.84); IR 3345, 1731, 1619, 1515, 1372, 1226, 1160, 1061, 1036,
16 832 and 704 cm⁻¹; ¹H NMR see Table 1 and ¹³C NMR see Table 2; HR-ESI-MS: *m/z* 1112.36172
17 [M+NH₄]⁺ (calcd. for C₅₄H₆₈NO₂₅ for 1130.40749).

18 2.3.6. *Arundinoside Q* (**6**):

19 White amorphous powder (8.2 mg); [α]_D²⁵ -79 (*c* 0.4, CH₃OH); UV (CH₃OH) λ_{\max} (log ϵ): 217
20 (3.07), 269 (2.12), 278 (1.90); IR 3340, 1732, 1625, 1522, 1370, 1229, 1164, 1061, 1044, 830 and 701
21 cm⁻¹ ¹H NMR see Table 1 and ¹³C NMR see Table 2; HR-ESI-MS: *m/z* 737.22886 [M-H]⁻ (calcd. for
22 C₃₄H₄₁O₁₈ for 737.23425).

23 2.4. *Determination of the configuration of the sugar*

24 The configuration of the sugar moiety was determined according to the method of Simmler et
25 al. [23]. The compound (1 mg) was dissolved in 2 M HCl (0.5 mL) and heated for 3 hours under
26 reflux. The solution was cooled and partitioned three times with *n*-butanol. After partitioning, the
27 aqueous phase was dried under reduced pressure and derivatization was performed with pyridine and

1 1-(trimethylsilyl) imidazole (4:1 v/v) at 60°C for 1 hour. The identification of the derivatized sample
2 was conducted on a GC-MS Trace GC Ultra instrument equipped with a TR-5MS SQC column (0.25
3 µm, 15 m x 0.25 mm) and operated using the following set of conditions: 1 min at 40°C; a thermal
4 ramp of 10°C until 250°C (helium flow rate 1 mL/min, injector temperature 250°C, transfer
5 temperature 285°C). The detection was performed on a DSQII Thermo Scientific mass spectrometer,
6 with a detection mass range of m/z 0 to 500. The sugar (D-glucose) was identified based on the
7 comparison of the retention time of the derivative with that of the standard glucose treated in the same
8 manner.

9 **2.6 Determination of α -glucosidase inhibitory activity**

10 The α -glucosidase inhibitory activity was assessed based on previous report [24]. Stock
11 solutions of samples were prepared at 10,000 µg/mL and diluted with 50 mM phosphate buffer (pH
12 6.9) to concentration range of 0.1-5000 µg/ml. The mixture composed of 50 µL of the sample mixed
13 50 µL of α -glucosidase enzyme (0.57 unit/mL) was incubated in a shake-incubator at 37°C for 10
14 mins. Thereafter, 50 µL of the substrate *p*-nitrophenyl α -D- glucopyranoside (5mM) was added to the
15 mixture and further incubated at 37°C for 20 mins. The reaction was halted by adding 50 µL of 1 M
16 Sodium carbonate and the absorbance was determined at 405 nm. Acarbose was used as a standard for
17 comparison. 50 µL of 50 mM phosphate buffer (pH 6.9) was used as the negative control. The
18 concentration which inhibits 50% of α -glucosidase (IC₅₀) was calculated from linear regression.
19 Percentage inhibition was determined according to equation;

$$20 \quad \%inhibition = [A_n - (A_s - A_{bs}) / A_n] \times 100$$

21 Where: A_n = absorbance of negative solution (no sample)

22 A_s = absorbance of sample solution

23 A_{bs} = absorbance of blank sample solution

24 **2.5. DPPH scavenging assay**

25 The DPPH radical scavenging activity was evaluated using the method of Wong et al. [25].
26 Stock solutions of the sample and standard were prepared at 5000 µg/mL and diluted to two-folds
27 (1.22-2500 µg/mL). Then 180 µL of DPPH (80µM) was added to 20 µL of portion of the sample in a
28 96-well plate. The mixture was kept in the dark at 25°C for 30 minutes. The absorbance was read at

1 520 nm. Trolox was used as the positive control. The DPPH radical scavenging activity of the samples
2 and standard was calculated thus;

$$3 \quad \text{Scavenging activity (\%)} = \frac{(\text{OD}_{\text{control}} - \text{OD}_{\text{sample}}) \times 100}{4 \quad \text{OD}_{\text{control}}}$$

5 The concentration causing 50% inhibition of DPPH radical (IC₅₀; mg/mL) was determined graphically.
6

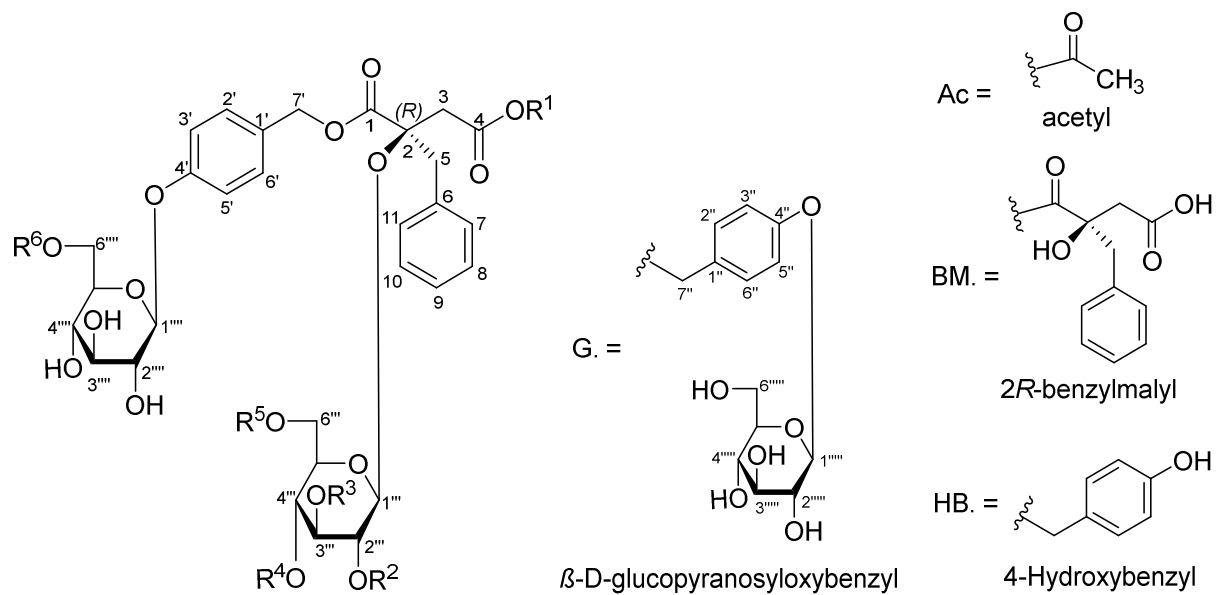
7 **2.6. ABTS scavenging assay**

8 The ABTS radical scavenging ability was performed as previously reported with some
9 modifications [25]. Briefly, 2 mM of ABTS and 2.45 mM of potassium persulfate were mixed in equal
10 proportion and the resulting mixture was incubated in the dark for 16 hours. The mixture was further
11 diluted with phosphate buffer saline until the absorbance value was between 0.68 and 0.72 when
12 measured at 734 nm. The samples were serially diluted to a concentration range of 1.22-2500 µg/mL
13 and 200µL of the ABTS solution was added to 20 µL of the samples in a 96-wells plate. After 6
14 minutes the absorbance was read at 734nm. ABTS radical scavenging ability was calculated from the
15 equation;

$$16 \quad \text{Scavenging activity (\%)} = \frac{(\text{OD}_{\text{control}} - \text{OD}_{\text{sample}}) \times 100}{17 \quad \text{OD}_{\text{control}}}$$

18 **3. Results and discussion**

19 The ethyl acetate extract from the underground parts of *A. graminifolia* was subjected to
20 purification using various chromatographic techniques, namely centrifugal partition chromatography,
21 gel permeation and reverse phase preparative chromatography leading to the isolation of six new
22 compounds: arundinosides L-Q, along with five known compounds arundinosides D-F [20], J and K
23 [21] (Fig. 1).



| | R ¹ | R ² | R ³ | R ⁴ | R ⁵ | R ⁶ |
|---------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Arundinoside L (1) | G | Ac | H | H | BM | H |
| Arundinoside M (2) | G | Ac | H | Ac | BM | H |
| Arundinoside N (3) | G | Ac | Ac | H | BM | H |
| Arundinoside O (4) | G | Ac | Ac | H | H | Ac |
| Arundinoside P (5) | G | Ac | Ac | H | H | HB |
| Arundinoside Q (6) | H | Ac | Ac | H | H | H |
| Arundinoside J (7) | G | Ac | H | H | Ac | Ac |
| Arundinoside K (8) | G | Ac | Ac | Ac | H | Ac |
| Arundinoside D (9) | G | Ac | Ac | Ac | Ac | H |
| Arundinoside E (10) | G | Ac | Ac | H | Ac | H |
| Arundinoside F (11) | G | Ac | H | Ac | H | H |

4

5 **Fig. 1.** The chemical structures of the 11 acylated benzyl ester glucosides isolated from the

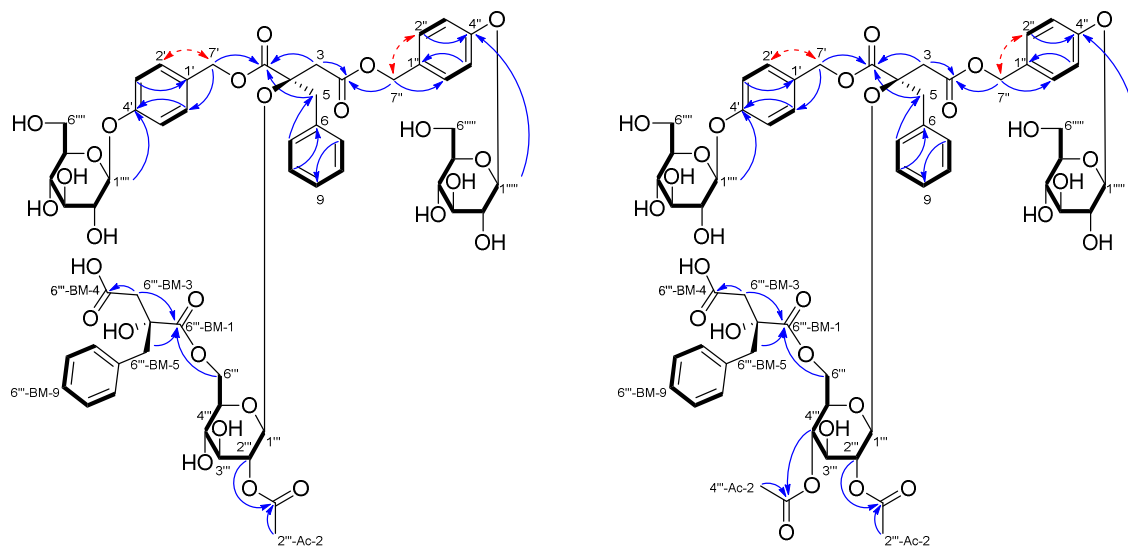
6 underground parts of *A. graminifolia*.

1 Compound **1** was isolated as an optically active white amorphous powder ($[\alpha]_D^{25}$ -56 (*c* 0.4,
2 CH₃OH) with a molecular formula of C₅₆H₆₆O₇, based on the HR-ESI-MS (*m/z* 1169.36070, [M-H]⁻).
3 The UV spectrum displayed absorption maxima at 218 and 270 nm. The acid hydrolysis of **1** yielded
4 glucose as the only sugar moiety as confirmed by GC-MS analysis [23]. The ¹H NMR spectrum of **1**
5 (Table 1) displayed signals attributable to one acetyl group at δ_H 1.76 (2''-Ac-2), four methylene
6 groups at δ_H 2.97 (H-3a), 3.07 (H-3b) and 3.02 (H-5a), 3.09 (H-5b), δ_H 2.52, (6'''-BM-3a), 2.97 (6'''-
7 BM-3b), δ_H 2.85 (6'''-BM-5a) and 2.97 (6'''-BM-5b); three anomeric protons at δ_H 4.85 (H-1'''), 4.93
8 (H-1''') and 4.93 (H-1'''''); two A₂B₂ system at δ_H 7.25 (H-2'/6'), 7.09 (H-3'/5')] and δ_H 7.29 (H-2''/6''),
9 7.10 (H-3''/5'') and two mono-substituted aromatic rings at δ_H 7.05 (H-7/11), 7.16 (H-8/10), 7.15 (H-9),
10 7.14 (6'''-BM-H-7/11), 7.21 (6'''-BM-H-8/10) and 7.15 (6'''-BM-H-9). The NMR spectra (¹H and ¹³C)
11 of **1** had a close resemblance to those of arundinoside C [20], possessing two benzylmalic acids, two
12 hydroxybenzyl and three β -D-glucopyranosyl functionalities. The difference between compound **1** and
13 arundinoside C was the absence of two acetyl groups at positions C-3''' and C-4''' in **1**. This 2-
14 benzylmalic derivative obtained exhibited a negative optical rotation of powder ($[\alpha]_D^{25}$ -56 (*c* 0.4,
15 CH₃OH), which is consistent with a *R* absolute configuration and based on the biogenetic relationship
16 as previously reported in the literature [20-21, 26-28]. Therefore we assigned compound **1** as 1,4 bis-
17 (β -D-glucopyranosyloxybenzyl)-2-(β -D-glucopyranosyl-2-acetyl-6->1-2*R*-benzylmalyl)-2*R*-
18 benzylmalic acid which was named arundinoside L.

19 Compound **2** was isolated as a white amorphous powder and had a molecular formula of
20 C₅₈H₆₈O₂₈ based on the analysis of its HR-ESI-MS spectrum which displayed a [M-H]⁻ ion at *m/z*
21 1211.37698. The acid hydrolysis of **2** liberated D-glucose which was identified with GC-MS. The
22 NMR data (¹H and ¹³C; Table 1 and 2) were closely identical to those of **1** with the exception of an
23 additional acetyl group at position C-4''' in **2** (δ_C 172.1, δ_C 21.3, δ_H 2.12). The acetyl group was
24 assigned to C-4''' based on the HMBC correlations between H-4'''/C-4'''-Ac-1 and H-4'''-Ac-2/C-4'''-
25 Ac-1 (Fig. 2). The absolute configuration of **2** was deduced as 2*R* in the same manner as done for
26 compound **1**. Thus, compound **2** was assigned as 1,4 bis-(β -D-glucopyranosyloxybenzyl)-2-(β -D-
27 glucopyranosyl-2,4-diacetyl-6->1-2*R*-benzylmalyl)-2*R*-benzylmalic acid and further named
28 arundinoside M.

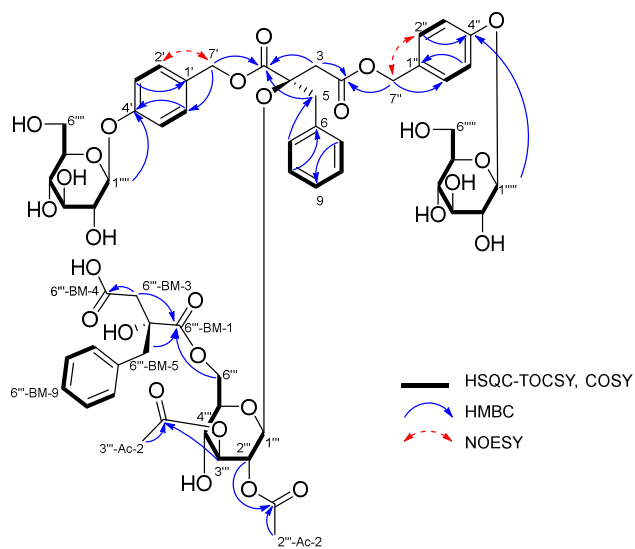
1 The molecular formula of compound **3** was deduced as C₅₈H₆₈O₂₈ according to the molecular
2 ion peak at *m/z* 1211.37566 [M-H]⁻ in the HR-ESI-MS spectrum. The 1D NMR spectra data of **3**
3 (Tables 1 and 2) were very similar to those of compound **2**, with the exception of the acetyl group at
4 C-4''' which was absent in **3** where it was replaced by an acetyl group at C-3''' (δ_C 172.1 ppm, δ_C 20.8
5 ppm, δ_H 2.05 ppm). Correlations from H-3'''/C-3'''-Ac-1 and H-3'''-Ac-2/C-3'''-Ac-1 as evidenced in the
6 HMBC spectrum confirmed the attachment of the acetyl group to C-3''' (Fig. 2). The absolute
7 configuration of **3** was determined by comparison of the negative optical rotation which was similar
8 with a 2*R* absolute configuration with those of previous reports [20-21, 26-28]. Accordingly,
9 compound **3** was assigned as 1,4 bis-(β -D -glucopyranosyloxybenzyl)-2-(β -D-glucopyranosyl-2,3-
10 diacetyl-6- \rightarrow 1-2*R*-benzylmalyl)-2*R*-benzylmalic acid and named arundinoside N.

11



Arundinoside H (1)

Arundinoside I (2)



Arundinoside J (3)

1

2 **Fig. 2.** Key HSQC-TOCSY, COSY, HMBC and NOESY correlations of arundinosides L-N (1-3).

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1 **Table 1.**2 ^1H (500 MHz, methanol- d_4) NMR data of arundinosides L-Q (**1-6**).

| Position | Arundinoside L (1) | Arundinoside M (2) | Arundinoside N (3) | Arundinoside O (4) | Arundinoside P (5) | Arundinoside Q (6) |
|----------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| 1 | | | | | | |
| 2 | | | | | | |
| 3a | 2.97 (d, 17.9) | 2.99 (d, 17.5) | 2.98 (d, 17.5) | 3.12 (d, 18.0) | 3.11 (d, 17.9) | 3.03 (d, 16.8) |
| 3b | 3.07 (d, 17.9) | 3.11 (d, 17.5) | 3.07 (d, 17.5) | 3.16 (d, 18.0) | 3.15 (d, 17.9) | 3.13 (d, 16.8) |
| 4 | | | | | | |
| 5a | 3.02 (d, 13.7) | 3.02 (d, 13.7) | 3.02 (d, 13.7) | 2.96 (d, 13.6) | 2.96 (d, 13.6) | 2.94 (d, 13.6) |
| 5b | 3.09 (d, 13.7) | 3.11 (d, 13.7) | 3.09 (d, 13.7) | 3.02 (d, 13.6) | 3.02 (d, 13.6) | 3.00 (d, 13.6) |
| 6 | | | | | | |
| 7/11 | 7.04 - 7.06 (m) | 7.04 - 7.06 (m) | 7.02 - 7.06 (m) | 7.01 - 7.03 (m) | 7.01 - 7.03 (m) | 7.02 - 7.04 (m) |
| 8/10 | 7.14 - 7.16 (m) | 7.15 - 7.18 (m) | 7.14 - 7.16(m) | 7.13 - 7.17 (m) | 7.13 - 7.18 (m) | 7.14 - 7.18 (m) |
| 9 | 7.14 - 7.16 (m) | 7.15 - 7.18 (m) | 7.14 - 7.16(m)) | 7.13 - 7.17 (m) | 7.15 - 7.18 (m) | 7.15 - 7.17 (m) |
| 1' | | | | | | |
| 2'/6' | 7.24 (d, 8.7) | 7.25 (d, 8.7) | 7.25 (d, 8.5) | 7.24 (d, 8.7) | 7.22 (d, 8.7) | 7.27 (d, 8.7) |
| 3'/5' | 7.09 (d, 8.7) | 7.09 (d, 8.7) | 7.10 (d, 8.5) | 7.06 (d, 8.7) | 7.08 (d, 8.7) | 7.09 (d, 8.7) |

| | | | | | | |
|--------------|----------------------|------------------------------|----------------------|----------------------|----------------------|----------------------|
| 4' | | | | | | |
| 7a' | 4.95 – 4.98 (m) | 4.96 (d, 11.8) | 4.96 – 4.98 (m) | 4.93 – 4.95 (m) | 4.96 (d, 11.9) | 4.93 – 4.95 (m) |
| 7b' | 5.02 – 5.05 (m) | 5.04 (d, 11.8) | 5.05 (d, 11.8) | 5.04 (d, 11.9) | 5.03 (d, 11.9) | 5.10 (d, 12.0) |
| 1" | | | | | | |
| 2"/6" | 7.28 (d, 8.7) | 7.29 (d, 8.7) | 7.29 (d, 8.5) | 7.29 (d, 8.7) | 7.27 (d, 8.6) | |
| 3"/5" | 7.09 (d, 8.7) | 7.10 (d, 8.7) | 7.10 (d, 8.5) | 7.09 (d, 8.7) | 7.09 (d, 8.6) | |
| 4" | | | | | | |
| 7a" | 4.91 – 4.93 (m) | 4.87 – 4.90 (m) | 4.91 - 4.93 (m) | 4.90 - 4.92 (m) | 4.89 – 4.92 (m) | |
| 7b" | 5.04 – 5.06 (m) | 5.07 (d, 11.9) | 5.05 (d, 11.8) | 5.07 (d, 12.1) | 5.05 (d, 11.7) | |
| 2-O-glc-1''' | 4.85 (d, 8.0) | 4.92 – 4.94 (m) | 4.98 – 5.01 (m) | 5.10 (d, 8.1) | 5.11 (d, 8.0) | 5.13 (d, 8.1) |
| 2''' | 4.75 (dd, 8.0, 9.3) | 4.81 (dd, 8.0, 9.5) | 4.83 (dd, 8.0, 9.5) | 4.78 (dd, 8.1, 9.6) | 4.78 (dd, 8.0, 9.3) | 4.80 (dd, 8.1, 9.8) |
| 3''' | 3.36 – 3.38 (m) | 3.54 (dd, 9.5, 9.5) | 4.91 – 4.95 (m) | 4.93 – 4.97 (m) | 4.93 - 4.97 (m) | 4.94 – 4.98 (m) |
| 4''' | 3.40 – 3.43 (m) | 4.85 – 4.90 (m) | 3.53 (dd, 9.5, 9.5) | 3.59 (dd, 9.6; 9.6) | 3.58 - 3 .61 (m) | 3.70 (dd, 9.5; 9.5) |
| 5''' | 3.08 - 3.10 (m) | 3.22 (ddd, 2.2, 4.5, 9.5) | 3.07 – 3.11 (m) | 2.94 - 2.98 (m) | 2.95 - 2.98 (m) | 3.07 – 3.11 (m) |
| 6a''' | 4.00 (dd, 4.4, 11.7) | 3.81 (dd, 4.5, 12.1) | 4.00 (dd, 3.8, 11.9) | 3.46 – 3.49 (m) | 3.47 - 3.49 (m) | 3.71 (dd, 5.0; 11.9) |
| 6b''' | 4.12 (d, 11.7) | 4.02 (dd, 2.2, 12.1) | 4.10 (d, 11.9) | 3.55 (dd, 3.7, 12.1) | 3.56 (dd, 3.8, 12.1) | 3.78 (dd, 1.7;11.9) |

| | | | | | | |
|------------------------|-----------------|-----------------|-----------------|----------|----------|----------|
| 2 ^{'''} -Ac-1 | | | | | | |
| 2 ^{'''} -Ac-2 | 1.76 (s) | 1.75 (s) | 1.64 (s) | 1.55 (s) | 1.57 (s) | 1.50 (s) |
| 3 ^{'''} -Ac-1 | | | | | | |
| 3 ^{'''} -Ac-2 | | | 2.04 (s) | 2.03 (s) | 2.02 (s) | 2.03 (s) |
| 4 ^{'''} -Ac-1 | | | | | | |
| 4 ^{'''} -Ac-2 | | 2.12 (s) | | | | |
| 6 ^{'''} -BM-1 | | | | | | |
| 2 | | | | | | |
| 3a | 2.52 (d, 16.0) | 2.50 (d, 16.3) | 2.54 (d, 16.2) | | | |
| 3b | 2.97 (d, 16.0) | 2.97 (d, 16.3) | 2.97 (d, 16.2) | | | |
| 4 | | | | | | |
| 5a | 2.85 (d, 13.5) | 2.88 (d, 13.4) | 2.87 (d, 13.5) | | | |
| 5b | 2.97 (d, 13.5) | 2.97 (13.4) | 2.97 (d, 13.5) | | | |
| 6 | | | | | | |
| 7/11 | 7.13 – 7.16 (m) | 7.15 – 7.18 (m) | 7.14 – 7.16(m) | | | |
| 8/10 | 7.18 - 7.20 (m) | 7.22 (d, 7.2) | 7.21 – 7.23(m) | | | |
| 9 | 7.20 – 7.22 (m) | 7.19 – 7.21 (m) | 7.20 - 7.22 (m) | | | |

| | | | | | | |
|----------------------------|----------------------|----------------------|-----------------|----------------------|-----------------|----------------------|
| 4'- <i>O</i> -glc-1'''' | 4.90 – 4.95 (m) | 4.89 – 4.91 (m) | 4.91 – 4.95 (m) | 4.91 – 4.95 (m) | 4.89 – 4.94 (m) | 4.91 - 4.95 (m) |
| 2'''' | 3.47 – 3.50 (m) | 3.46 – 3.50 (m) | 3.46 - 3.49 (m) | 3.47 – 3.49 (m) | 3.44 – 3.50 (m) | 3.46 – 3.49 (m) |
| 3'''' | 3.47 – 3.50 (m) | 3.46 – 3.50 (m) | 3.46 - 3.49 (m) | 3.46 - 3.50 (m) | 3.58 - 3.61 (m) | 3.45 - 3.50 (m) |
| 4'''' | 3.40 - 3.43 (m) | 3.40 - 3.42 (m) | 3.39 – 3.42 (m) | 3.37 - 3.39 (m) | 3.36 - 3.40 (m) | 3.40 - 3.44 (m) |
| 5'''' | 3.44 – 3.47 (m) | 3.43 – 3.45 (m) | 3.44 – 3.47 (m) | 3.63 - 3.67 (m) | 3.44 – 3.50 (m) | 3.42 - 3.46 (m) |
| 6a'''' | 3.89 (dd, 3.2, 11.7) | 3.88 (dd, 2.0, 12.1) | 3.89 (d, 12.2) | 4.40 (dd, 2.2, 12.1) | 3.59 - 3.63 (m) | 3.72 (dd, 5.0, 11.8) |
| 6b'''' | 3.69 – 3.72 (m) | 3.71 (dd, 5.4, 12.1) | 3.68 – 3.72 (m) | 4.24 (dd, 6.1, 12.1) | 3.82 – 3.84 (m) | 3.90 (dd, 1.9, 11.8) |
| 6''''-Ac-1 | | | | | | |
| 6''''-Ac-2 | | | | 2.04 (s) | | |
| 6''''-G-1 | | | | | | |
| 6''''-G-2/6 | | | | | 7.13 (d, 8.3) | |
| 6''''-G-3/5 | | | | | 6.73 (d, 8.3) | |
| 6''''-G-4 | | | | | | |
| 6''''-G-7a | | | | | 4.42 (d, 11.3) | |
| 6''''-G-7b | | | | | 4.45 (d, 11.3) | |
| 4''- <i>O</i> -glc-1'''''' | 4.90 – 4.95 (m) | 4.91 – 4.93 (m) | 4.91 – 4.95 (m) | 4.91 – 4.95 (m) | 4.89 – 4.94 (m) | |
| 2'''''' | 3.47 – 3.50 (m) | 3.46 – 3.49 (m) | 3.44 – 3.47 (m) | 3.47 – 3.49 (m) | 3.44 – 3.50 (m) | |

| | | | | | | |
|--------------------|----------------------|----------------------|-----------------|----------------------|----------------------|--|
| 3 ^{''''} | 3.47 – 3.50 (m) | 3.46 – 3.50 (m) | 3.46 - 3.49 (m) | 3.46 - 3.50 (m) | 3.44 – 3.50 (m) | |
| 4 ^{''''} | 3.40 - 3.43 (m) | 3.40 - 3.42 (m) | 3.40 - 3.42 (m) | 3.40 – 3.42(m) | 3.39 - 3.44 (m) | |
| 5 ^{''''} | 3.44 – 3.47 (m) | 3.43 – 3.45 (m) | 3.44 – 3.47 (m) | 3.44 – 3.46 (m) | 3.44 – 3.50 (m) | |
| 6a ^{''''} | 3.89 (dd, 3.2, 11.7) | 3.89 (dd, 2.0, 12.1) | 3.89 (d, 12.0) | 3.70 (dd, 5.4, 12.1) | 3.70 (dd, 5.4, 12.1) | |
| 6b ^{''''} | 3.69 – 3.72 (m) | 3.69 (dd, 5.4, 12.1) | 4.91 – 4.95 (m) | 3.89 (dd, 2.1, 12.1) | 3.89 (dd, 2.0, 12.1) | |

1

2

3 **Table 2.**

4 ¹³C (125 MHz, methanol-*d*₄) NMR data of arundinosides L-Q (**1-6**).

5

6

7

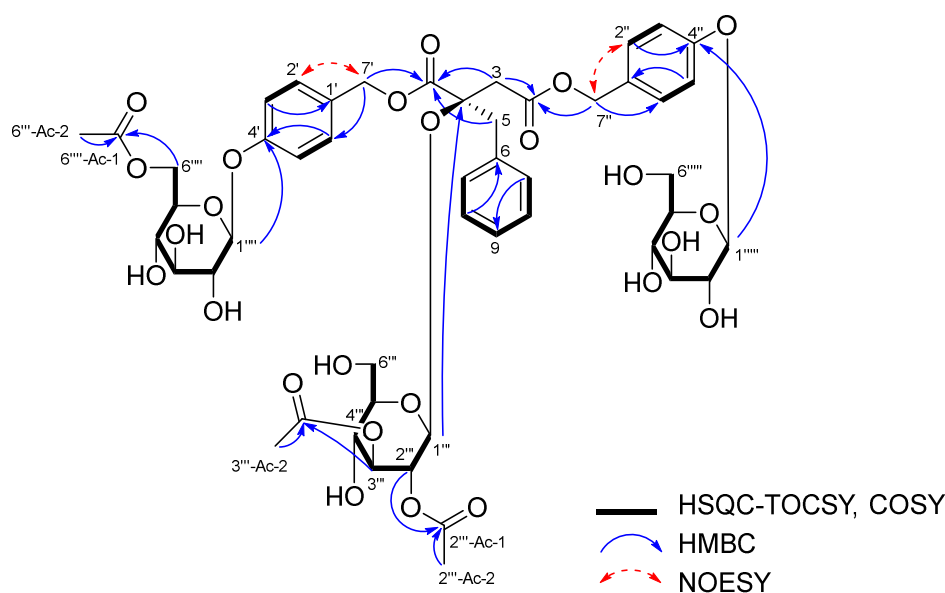
| Position | Arundinoside L (1) | Arundinoside M (2) | Arundinoside N (3) | Arundinoside O (4) | Arundinoside P (5) | Arundinoside Q (6) |
|----------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| 1 | 172.2 | 172.2 | 172.2 | 172.4 | 172.4 | 172.8 |
| 2 | 82.5 | 82.6 | 82.6 | 82.3 | 82.3 | 82.4 |
| 3 | 43.0 | 43.2 | 43.2 | 44.0 | 44.1 | 44.5 |
| 4 | 172.0 | 172.0 | 171.9 | 172.2 | 172.2 | 174.2 |
| 5 | 46.0 | 46.2 | 46.3 | 47.3 | 47.3 | 47.4 |
| 6 | 136.5 | 136.5 | 136.5 | 136.4 | 136.4 | 136.5 |
| 7/11 | 132.0 | 131.8 | 131.8 | 132.0 | 132.0 | 132.0 |
| 8/10 | 129.2 | 129.2 | 129.0 | 129.1 | 129.1 | 129.0 |
| 9 | 128.0 | 128.0 | 127.9 | 127.9 | 128.0 | 127.9 |
| 1' | 130.8 | 130.8 | 130.6 | 130.9 | 131.2 | 130.8 |
| 2'/6' | 131.7 | 131.8 | 131.6 | 131.8 | 131.7 | 131.6 |
| 3'/5' | 118.0 | 118.0 | 117.9 | 117.9 | 118.1 | 117.8 |
| 4' | 159.4 | 159.4 | 159.5 | 159.2 | 159.4 | 159.3 |
| 7' | 68.0 | 68.0 | 68.1 | 68.0 | 68.0 | 68.0 |

| | | | | | | |
|--------------|-------|-------|-------|-------|-------|-------|
| 1" | 131.1 | 131.1 | 130.9 | 131.2 | 131.2 | |
| 2"/6" | 131.7 | 131.8 | 131.6 | 131.5 | 131.5 | |
| 3"/5" | 118.1 | 118.0 | 118.1 | 118.0 | 118.0 | |
| 4" | 159.4 | 159.4 | 159.5 | 159.4 | 159.3 | |
| 7" | 67.5 | 67.5 | 67.6 | 67.5 | 67.5 | |
| 2-O-glc-1''' | 98.6 | 98.5 | 98.4 | 98.5 | 98.5 | 98.6 |
| 2''' | 74.8 | 75.0 | 72.7 | 73.0 | 73.1 | 73.0 |
| 3''' | 75.8 | 73.7 | 76.4 | 77.0 | 77.0 | 77.1 |
| 4''' | 71.0 | 71.8 | 68.9 | 68.9 | 69.0 | 71.4 |
| 5''' | 75.0 | 72.6 | 74.6 | 77.2 | 77.3 | 77.2 |
| 6a''' | 65.0 | 64.4 | 64.7 | 61.6 | 61.6 | 61.3 |
| 2'''-Ac-1 | 172.4 | 172.2 | 171.8 | 172.0 | 172.1 | 172.1 |
| 2'''-Ac-2 | 21.4 | 21.3 | 21.0 | 21.0 | 20.9 | 21.0 |
| 3'''-Ac-1 | | | 172.1 | 172.2 | 172.2 | 172.3 |
| 3'''-Ac-2 | | | 21.0 | 21.0 | 20.8 | 21.0 |

| | | | | | | |
|----------------|-------|-------|-------|-------|-------|-------|
| 4'''-Ac-1 | | 172.1 | | | | |
| 4'''-Ac-2 | | 21.2 | | | | |
| 6'''-BM-1 | 175.5 | 175.6 | 175.6 | | | |
| 2 | 77.6 | 77.3 | 77.4 | | | |
| 3 | 44.5 | 44.3 | 44.4 | | | |
| 4 | 174.6 | 174.8 | 174.5 | | | |
| 5 | 46.4 | 46.1 | 46.3 | | | |
| 6 | 136.8 | 136.9 | 136.8 | | | |
| 7/11 | 132.0 | 131.8 | 131.6 | | | |
| 8/10 | 129.3 | 129.2 | 129.2 | | | |
| 9 | 128.0 | 128.0 | 127.9 | | | |
| 4'-O-glc-1'''' | 102.3 | 102.4 | 102.4 | 102.2 | 102.3 | 102.4 |
| 2'''' | 75.0 | 75.0 | 74.9 | 75.0 | 75.0 | 75.0 |
| 3'''' | 78.0 | 78.0 | 77.8 | 77.8 | 77.2 | 78.0 |
| 4'''' | 71.4 | 71.4 | 71.3 | 71.6 | 71.8 | 71.4 |

| | | | | | | |
|--|-------|-------|-------|-------|-------|------|
| 5 ^{'''} | 78.2 | 78.2 | 78.0 | 75.4 | 78.1 | 78.2 |
| 6 ^{'''} | 62.6 | 62.6 | 62.6 | 64.8 | 70.5 | 62.5 |
| 6 ^{'''} -Ac-1 | | | | 172.9 | | |
| 6 ^{'''} -Ac-2 | | | | 21.0 | | |
| 6 ^{'''} -G-1 | | | | | 130.5 | |
| 6 ^{'''} -G-2/6 | | | | | 130.8 | |
| 6 ^{'''} -G-3/5 | | | | | 116.2 | |
| 6 ^{'''} -G-4 | | | | | 158.3 | |
| 6 ^{'''} -G-7 | | | | | 74.5 | |
| 4 ^{''} -O-glc-1 ^{''''} | 102.2 | 102.3 | 102.4 | 102.3 | 102.3 | |
| 2 ^{''''} | 75.0 | 75.0 | 74.9 | 75.0 | 75.0 | |
| 3 ^{''''} | 78.0 | 78.0 | 77.8 | 78.0 | 78.1 | |
| 4 ^{''''} | 71.5 | 71.4 | 71.3 | 71.4 | 71.5 | |
| 5 ^{''''} | 78.2 | 78.2 | 78.0 | 78.2 | 78.2 | |
| 6 ^{''''} | 62.6 | 62.6 | 62.6 | 62.6 | 62.6 | |

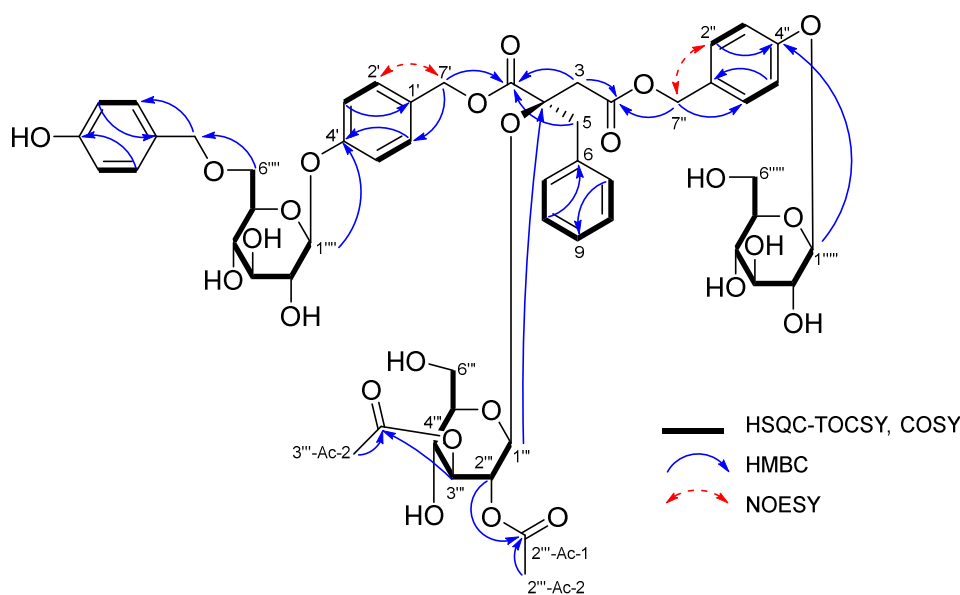
2 The molecular formula of compound **4** was assigned to be C₄₉H₆₀O₂₅ based on the [M-H]⁻ ion peak at
 3 *m/z* 1047.32844. The molecular formula of **4** was observed to be the same with compound **7**, a
 4 previously reported compound name arundinoside J [21]. The 1D NMR spectroscopic data of **4** (Table
 5 1 and 2) were similar with those of arundinoside J (compound **7** [21]), which implied the presence of a
 6 glucosyloxybenzyl 2*R*-benzylmalate derivative with three acetyl groups. The detailed analysis of the
 7 NMR spectra indicated that the acetoxy moiety at C-6''' in arundinoside J was replaced by a hydroxyl
 8 in **4**, while the acetoxy moiety was at position C-3'''. This substitution pattern was affirmed by HMBC
 9 cross-peak of H-3''' to C-3'''-Ac-1, which confirmed that the acetoxy group was attached to C-3'''
 10 (Figure 3). The absolute configuration of **4** was also deduced as 2*R* by comparison of the optical
 11 rotation which was similar with a 2*R* absolute configuration as previous reports [20-21, 26-28].
 12 Compound **4** was therefore assigned as 1-(β-D-glucopyranosyloxybenzyl)-2-(β-D-glucopyranosyl-2,3-
 13 biacetyl)-4-(β-D-glucopyranosyloxybenzyl-6-acetyl)-2*R*-benzylmalate and named arundinoside O.



14
 15 **Fig. 3.** Key HSQC-TOCSY, COSY, HMBC and NOESY correlations of arundinosides **O** (**4**).
 16

17 Compound **5** was obtained as a white amorphous powder. It showed a molecular ion peak at
 18 *m/z* 1130.40617 [M+NH₄]⁺ in the HR-ESI-MS, suggesting a molecular formula of C₅₄H₆₄O₂₅. Detailed
 19 analysis of the NMR data of **5**, indicated structural similarities between **5** and compounds **4**,
 20 suggesting the presence of the 2-benzylmalic acid, benzyl-β-D-glucopyranoside, β-D-glucopyranoside
 21 and acetyl moieties. The major difference in **5** was the presence of an hydroxybenzyl moiety in C-6''''

22 [δ_{H} 7.13, H-6'''-G-2/6 and 6.73, H-6'''-G-3/5)]; [δ_{C} 130.5, 130.8, 116.2 and 158.3]. HMBC correlations
 23 of H₂-6'''b with C-6'''-G-7 as well as H₂-6'''-G-7 with C- 6'''-G-2/6 confirmed the presence and
 24 position of the hydroxybenzyl unit (Fig. 4). The absolute configuration of **5** was also deduced as 2*R* by
 25 comparing the optical rotation which was similar with a 2*R* absolute configuration with previous
 26 reports [20-21, 26-28] .Therefore, compound **5** was deduced as 1-(β -D-glucopyranosyloxybenzyl)-2-
 27 (β -D-glucopyranosyl-2,3-diacetyl)-4-(β -D-glucopyranosyloxybenzyl)-6-hydroxybenzyl)-2*R*-
 28 benzylmalate and named arundinoside P.



29
 30 **Fig. 4.** Key HSQC-TOCSY, COSY, HMBC and NOESY correlations of arundinoside P (**5**).

31
 32 Compound **6** was obtained as a white amorphous powder with a molecular formula of
 33 C₃₄H₄₂O₁₈ as deduced on the basis of the positive HR-ESI-MS (*m/z* 737.22886 [M-H]⁻). The ¹H NMR
 34 (Table 1) of **6** remarkably similar to those of the known arundinoside E (compound **10**) [20],
 35 displaying signals of the 2-benzylmalic acid [δ_{H} 7.03 (H-7/11), 7.16 (8/10), 7.27 (H-2'/6'), 7.09 (H-
 36 2'/6'), 5.10 (H-7b'), 4.95 (H-7a'), 3.13 (H-3b), 3.03 (H-3a)], the β -D-glucopyranosyl moieties
 37 connected to C-2 of the benzylmalic acid [δ_{H} 5.13 (H-1'''), 4.80 (H-2'''), 4.96 (H-3'''), 3.70 (H-4'''), 3.09
 38 (H-5'''), 3.71 (H-6a'''), 3.78 (H-6b''')], one gluosyloxybenzyl moiety connected to C-2 [4.93 (H-1'''),
 39 3.48 (H-2'''), 3.47 (H-3'''), 3.42 (H-4'''), 3.45 (H-5'''), 3.72 (H-6a'''), 3.90 (H-6b''')], and two acetyl
 40 groups at δ_{H} 1.50 (2'''-Ac-2) and δ_{H} 2.03 (3'''-Ac-2). The acetyl groups were positioned with the help of
 41 the HMBC cross peaks between cross-peak of H-2''' to C-2'''-Ac-1 and H-3''' to C-3'''-Ac-1. The

42 glucosyloxybenzyl moiety connected to C-4 in arundinoside E was replaced by a hydroxyl group
 43 in **6** (Fig. 5). The absolute configuration of **6** was determined as 2*R* by comparing its negative optical
 44 rotation which was similar with a 2*R* absolute configuration with previous reports [20-21, 26-28].
 45 Therefore, the structure of compound **6** was identified as 1-(β -D-glucopyranosyloxybenzyl)-2-(β -D-
 46 glucopyranosyl-2,3-diacetyl-2*R*-benzylmalate and named arundinoside Q.

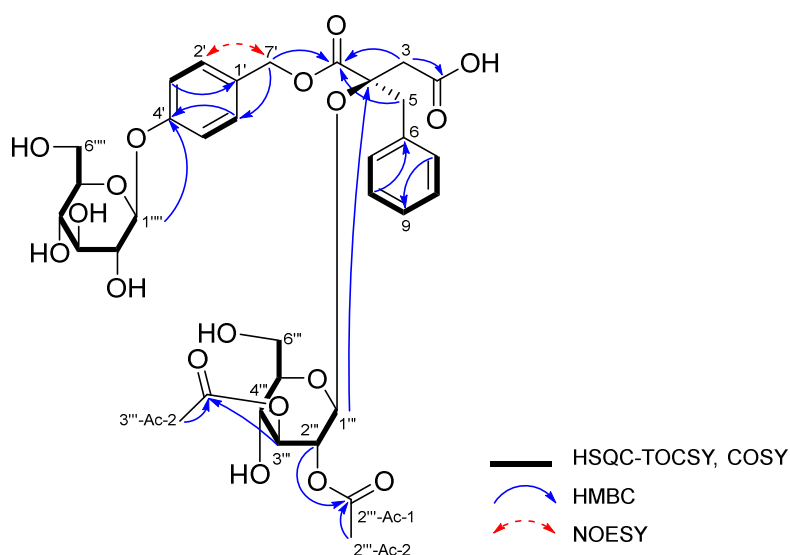


Fig. 5. Key HSQC-TOCSY, COSY, HMBC and NOESY correlations of arundinoside Q (**6**).

49 α -Alkylmalate ester derivatives are rather uncommon secondary metabolites which have been
 50 reported in the family Cephalotaxaceae as alkylmalate alkaloids [29] and Orchidaceae as benzylmalate
 51 alkaloids derivatives [30, 31], hydroxybenzyl [23], benzyl [32,33], or isobutylmalates ester glucosides
 52 derivatives [34, 35]. Till date, glucosyloxybenzyl 2*R*-benzylmalate derivatives have only been
 53 exclusively found in the Orchidaceae family, especially in terrestrial orchids from the genus
 54 *Coeloglossum* [33], *Cremastra* [36], *Cymbidium* [37-38], *Grammatophyllum* [26], and recently in
 55 *Arundina* [20-21]. These compounds are structurally arranged in a very specific manner, with at least
 56 one benzylmalic acid, which will serve as a central pillar to which the other biosynthetic parts are
 57 attached. One to two hydroxybenzyl moieties (gastrodigenin) esterified to the acidic function of the
 58 benzylmalic acid and a D-glucose in its pyranose form, is the only sugar reported till date in the
 59 structures of these glycosides. Glucosylation occurs on the free hydroxyl groups of gastrodigenin and
 60 the benzylmalic acid at position C-2 on the structure. Furthermore, cinnamoyl, acetyl and

61 benzylmaloyl moieties can be added to the basic functions described above by esterification on the
62 hydroxyl group of the sugar.

63 The isolated compounds were subjected to α -glucosidase inhibitory activity as well as DPPH
64 and ABTS radical scavenging activities. Arundinosides D, O, P and Q exhibited moderate α -
65 glucosidase inhibitory (IC₅₀ values of 159.74, 22.06, 18.24 and 90.22 μ g/mL, respectively), ABTS
66 radical scavenging (IC₅₀ values of 4.98, 4.40, 2.96, and 6.75 μ L/mL, respectively) activities.

67 In conclusion, six new glucosyloxybenzyl 2*R*-benzylmalate derivatives, arundinosides L-Q (**1-**
68 **6**) along with 5 known glucosides arundinosides D-F, J and K (**7-11**) were isolated for the first time
69 from the underground part of *A. graminifolia*. Their structures were elucidated based on extensive
70 spectroscopic data analysis. The structural novelty of arundinoside P, carrying a hydroxybenzyl
71 moiety attached to the hydroxybenzylglucose moiety is a new kind of acylation, which has never been
72 reported for this kind of compound. Furthermore, arundinoside Q is the first bidesmosidic derivative
73 reported in *A. graminifolia*.

74

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79 Strasbourg University) for the NMR experiments.

80 **Conflict of interest**

81 No competing interest declared

82 **A. Supplementary data**

83 Supplementary data associated with this article can be found on online at

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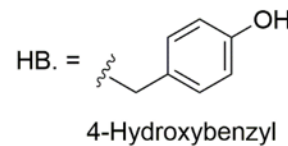
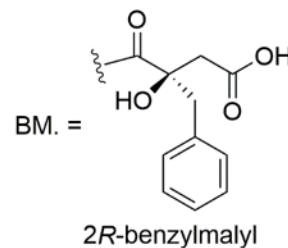
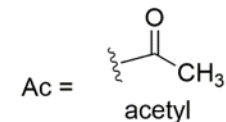
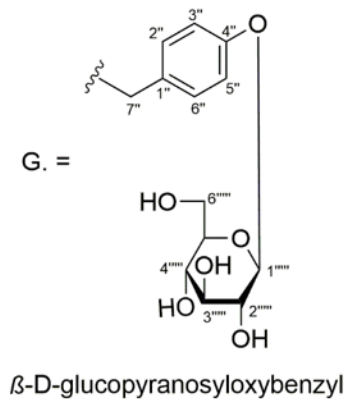
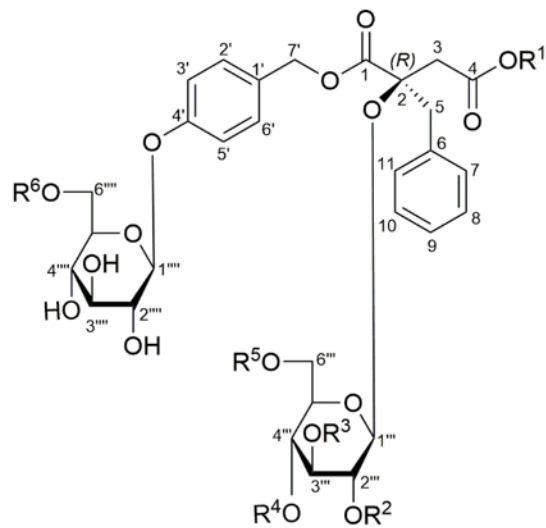
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Arundinosides L-Q



**Dried Underground Parts of the tropical orchid
Arundina graminifolia (D. Don) Hochr.**



| | R ¹ | R ² | R ³ | R ⁴ | R ⁵ | R ⁶ |
|--------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Arundinoside L (1) | G | Ac | H | H | BM. | H |
| Arundinoside M (2) | G | Ac | H | Ac | BM. | H |
| Arundinoside N (3) | G | Ac | Ac | H | BM. | H |
| Arundinoside O (4) | G | Ac | Ac | H | H | Ac |
| Arundinoside P (5) | G | Ac | Ac | H | H | HB |
| Arundinoside Q (6) | H | Ac | Ac | H | H | H |