Research article

MRC

Received: 12 July 2016 Revised: 13 August 2016 Accepted: 17 August 2016 Published online in Wiley Online Library

(wileyonlinelibrary.com) DOI 10.1002/mrc.4504

Two new 5-deoxyflavan-3,4-diol glucosides from roots of *Albizia chevalieri*

Abdou Tchoukoua,[a,b] Turibio Kuiate Tabopda,[a]* Shota Uesugi,[c] Ken-ichi Kimura,[c] Eunsang Kwon,[d] Hiroyuki Momma,[d] Bonaventure Tchaleu Ngadjui,[a]* Takuya Koseki[b] and Yoshihito Shiono[b]*

ABSTRACT Phytochemical investigation of the roots of *Albizia chevalieri* led to the isolation of two new 5-deoxyflavan-3,4-diol glucosides from roots of *A. chevalieri*, Chevalieriflavanosides A and B. Their structures were established by 2D NMR techniques, UV, IR, CD, and mass spectrometry. Cytotoxicity of the two compounds was evaluated against acute promyelocytic leukemia HL60 cells. The antibacterial activities of 1 and 2 also were evaluated against *Pseudomonas aeruginosa* and *Staphylococcus aureus* using the agar diffusion test. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: NMR; ^{1}H; ^{13}C; Leguminosae; *Albizia chevalieri*; flavan-3,4-diols; cytotoxicity

Introduction

Albizia chevalieri (Mimosaceae) is a tree that grows up to 12 m high or a shrub under harsher conditions of the dry savannah from Senegal, Niger, Nigeria, and Cameroon. The leaf extract of *A. chevalieri* is used for the management of diabetes mellitus by traditional medical practitioners in some parts of Niger Republic and Sokoto, Nigeria.[1] The leaf extract has been reported to have a significant hypoglycemic effect,[1] dysentery,[2,3] hematotoxicity,[4] hypolipidemic,[5] and antioxidant activity.[5] The bark is used in Borno-North eastern Nigeria as purgative, taenicide, and coughs.[6] There are also reports on the local use of the leaves extract for cancer treatment in Zaria city, Kaduna state.[6] In prior studies on the genus *Albizia*, saponins and flavonoids were found as the main constituents.[7–9] A previous phytochemical investigation on *A. chevalieri* stem bark led to the isolation and structure elucidation of three known pentacyclic triterpenoids: friedelin, friedelan-3-ol, and lupeol.[10]

In our continuing search for bioactive compounds from Cameroon medicinal plants, we investigated *A. chevalieri* from a phytopharmacological point of view. Therefore, we report herein the isolation of two previously undescribed flavan-3,4-diol glucosides, chevalieriflavanosides A (**1**) and B (**2**) (Fig. 1) from roots of *A. chevalieri*. Their structures were determined by spectroscopic methods including 1D and 2D NMR experiments, IR, UV, CD, and HR-ESI-MS. Furthermore, they were examined for cytotoxicity against acute promyelocytic leukemia HL60 cells. The antibacterial activity of **1** and **2** was also reported.

Results and Discussion

Compound **1** was obtained as a brownish amorphous powder and gave a dark blue coloration with $FeCl_3$ reagent. Moreover, it showed a positive Shinoda test,[11] suggesting that **1** is a flavonoid. The molecular formula $C_{21}H_{24}O_{11}$ was established from the HR-ESI-MS which showed the pseudo-molecular ion peak at *m/z* 475.12101 ($[M + Na]^+$). The IR spectrum displayed absorption band of hydroxyl groups at ν_{max} 3394 cm^{-1}. The UV spectrum exhibited characteristic absorbance bands of flavan-3,4-diol at λ_{max} 225 and 275 nm.[12] The ^{1}H NMR spectrum of **1** showed an aromatic AB coupled system at δ_H 6.83 (1H, d, $J = 8.3$ Hz, H-5) and 6.89 (1H, d, $J = 8.3$ Hz, H-6), and an AA′BB′ spin system at δ_H 6.81 (2H, d, $J = 8.3$ Hz, H-3′, H-5′) and 7.42 (2H, d, $J = 8.3$ Hz, H-2′, H-6′). This observation suggested a tetrasubstituted A-ring, and hence the AA′BB′ aromatic spin system was located on B-ring. The location of the AB system at H-5 and H-6 was confirmed by the HMBC correlations (Fig. 2) of H-5 with C-6, C-7, C-4, C-4a, and C-8a, and of H-6 with C-4a, C-5, C-7, and C-8. The NMR spectrum of **1** further showed signals of a sugar unit at δ_H/δ_C 4.76 (1H, d, $J = 7.6$ Hz, H-1″) / 104.4 (C-1″), 3.49 (1H, t, $J = 7.6$ Hz, H-2″) / 74.9 (C-2″), 3.45 (1H, dd, $J = 9.0$ Hz, 7.6, H-3″) / 77.6 (C-3″), 3.39 (1H, m, H-4″) / 71.2 (C-4″), 3.42 (1H, m, H-5″) / 78.3 (C-5″), 3.72 (1H, dd, $J = 12.5$, 4.8 Hz, H-6″), and 3.88 (1H, dd, $J = 12.5$, 2.1 Hz, H-6″) / 62.4 (C-6″). Stereochemistry at anomeric position of the sugar moiety

* *Correspondence to: Turibio Kuiate Tabopda and Bonaventure Tchaleu Ngadjui, Département de Chimie Organique, Université de Yaoundé 1, BP 812 Yaoundé, Cameroun. E-mail: ttabopda@yahoo.fr*

** *Correspondence to: Yoshihito Shiono, Department of Food Life, and Environmental Science, Faculty of Agriculture, Yamagata University, Tsuruoka, Yamagata 997-8555, Japan.*

a *Département de Chimie Organique, Université de Yaoundé 1, Yaoundé, Cameroun*

b *Department of Food, Life, and Environmental Science, Faculty of Agriculture, Yamagata University, Tsuruoka, Yamagata, Japan*

c *The United Graduate School of Agricultural Sciences, Iwate University, Morioka, Iwate, Japan*

d *Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University, Sendai, Miyagi, Japan*

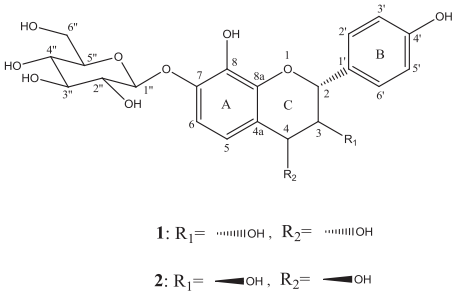

Figure 1. Chemical structures of compounds **1** and **2**.

of **1** was assigned as β on the basis of ^{1}H–^{1}H coupling constants ($J_{1'',2''} = 7.6$ Hz) in the ^{1}H NMR spectrum of **1**. The sugar was identified as D-glucopyranosyl by the measurement of optical rotation and retention time and by the evaluation of spin–spin couplings and chemical shifts.[13] The remaining signals in the ^{1}H and ^{13}C NMR spectra correspond to those of a propan-1,2,3-triol (chroman ring) at δ_H /δ_C 5.11 (1H, br. s, H-2) / 76.4 (C-2), 3.87 (1H, d, $J = 2.7$ Hz, H-3) / 72.5 (C-3), and 4.48 (1H, d, $J = 2.7$ Hz, H-4) / 69.2 (C-4). They were assigned to H-2, H-3, and H-4, respectively as H-2 showed HMBC correlations with C-1′, C-2′, C-3, C-4, and C-8a, and

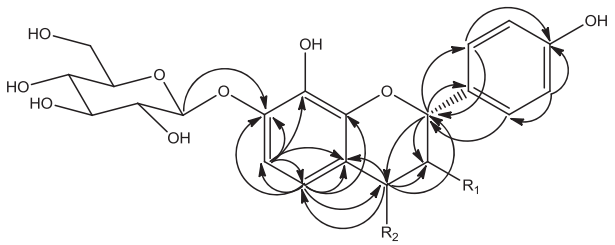

Figure 2. Selected HMBC (H→C) correlations of **1** and **2**.

the H-4, correlations with C-2, C-3, C-4a, C-5, and C-8a. Acid hydrolysis of **1** afforded a free sugar moiety and (−)-teracacidin.[14] The HMBC correlation between the anomeric proton of the glucose unit and C-7 (δ_C 147.0) suggested that the glucose is fixed at C-7 through an ether linkage. The *R*-configuration of C-2 was deduced from the CD spectra which showed a negative cotton effect within the $^{1}L_b$ transition ($[\theta]_{278} = -4000$).[15] The coupling constants ($J_{2,3}$ = nearly 0 Hz and $J_{3,4} = 2.7$ Hz) between H-2 and H-3, and between H-3 and H-4 of C-ring, confirmed the 2,3-*cis*-3,4-*cis* relative configurations. The trend of small coupling constants compared to their *trans* isomers ($^{3}J = 7.0$ Hz–10.0 Hz) has been well established in closely related 2,3-*cis*-3,4-*cis*-flavan-3,4,7,3′,4′-pentaol ($J_{2,3} = 1.0$ Hz, $J_{3,4} = 4.0$ Hz) and 2,3-*cis*-3,4-*cis*-4-methoxyflavan-3,7,8,3′,4′-pentaol ($J_{2,3} = 1.0$ Hz, $J_{3,4} = 2.8$ Hz).[16,17] Thus, the absolute configuration of the flavan moiety of **1** was elucidated to be 2*R*,3*R*,4*R* as shown in Fig. 1, named chevalieriflavanoside A.

Compound **2**, obtained as a brownish amorphous powder, also gave a dark blue coloration with $FeCl_3$ reagent. It showed a positive Shinoda test suggesting that **2** is a flavonoid. The ^{1}H and ^{13}C NMR spectra of **2** (Table 1) were similar to those of **1** with the differences being the chemicals shifts and coupling patterns of C-2 [δ_H 5.00 (1H, d, $J = 9.0$ Hz); δ_c 78.3], C-3 [δ_H 3.97 (1H, dd, $J = 9.0$, 3.4 Hz); δ_C 72.0], and C-4 [δ_H 4.57 (1H, d, $J = 3.4$ Hz); δ_C $_{6}$7.8] in **2** compared to those of corresponding carbons in **1**. This suggested that **2** has different configurations at the C-ring from those of **1**. The gross structure of **2** was clearly elucidated by analyzing 2D NMR experiments (COSY (Fig. S8), HMQC (Fig. S9), HMBC (Fig. S10)). Furthermore, the absolute configuration of **2** was determined by comparing their coupling constants and CD data. The CD data of **2** ($[\theta]_{270}$ −1000) established its absolute configuration to be 2*R*. By contrast, the large coupling constant between H-2/H-3 in **2** meant that H-3 must be pseudo-equatorial, and so the 4-hydroxy must be β. The small coupling constants between H-3 and H-4 of the C-ring suggested the 3,4-*trans*

Table 1. ^{1}H and ^{13}C NMR data of **1** and **2**

Position	**1**[a]		**2**[a]	
	δ_C	δ_H (m, *J* in Hz)	δ_C	δ_H (m, *J* in Hz)
2	76.4	5.11 (br. s)	78.3	5.00 (d, 9.0)
3	72.5	3.87 (d, 2.7)	72.0	3.97 (dd, 9.0, 3.4)
4	69.2	4.48 (d, 2.7)	67.8	4.57 (d, 3.4)
4a	119.0	—	120.4	—
5	122.6	6.83 (d, 8.3)	119.8	6.70 (d, 8.9)
6	111.3	6.89 (d, 8.3)	111.6	6.82 (d, 8.9)
7	147.0	—	147.7	—
8	136.4	—	138.5	—
8a	145.2	—	145.1	—
1′	130.7	—	130.5	—
2′, 6′	129.5	7.42 (d, 8.3)	130.2	7.29 (d, 8.3)
3′, 5′	115.9	6.81 (d, 8.3)	116.3	6.78 (d, 8.3)
4′	158.2	—	159.3	—
1″	104.4	4.76 (d, 7.6)	104.6	4.74 (d, 7.6)
2″	74.9	3.49 (t, 7.6)	74.9	3.36 (m)
3″	77.6	3.45 (dd, 9.0, 7.6)	77.6	3.42 (m)
4″	71.2	3.39 (m)	71.3	3.44 (m)
5″	78.3	3.42 (m)	78.3	3.36 (m)
6″	62.4	3.72 (dd, 12.5, 4.8)	62.5	3.69 (dd, 12.4, 4.8)
		3.88 (dd, 12.5, 2.1)		3.85 (d, 12.4)

[a]Recorded in 600 MHz (for ^{1}H NMR) and 150 MHz (for ^{13}C NMR) in CD_3OD, δ in ppm.

configuration. 2,3-*trans*-3,4-*cis*-orientation was further supported by previously reported compound, 2,3-*trans*-3,4-*cis*-7,4′-dimethoxyflavan-3,4-diol ($J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 3.6 Hz),[18] ($J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 3.5 Hz).[19] On the basis of the evidence, the absolute configuration of the flavan moiety was established as 2*R*,3*S*,4*S* as shown in Fig. 2, named chevalieriflavanoside B.

Compounds **1** and **2** were evaluated for their cytotoxic activities against human cancer. Unfortunately, they exhibited no activities towards HL60 cells at the concentration of 100 μM.

The antibacterial activities of **1** and **2** also were evaluated against *Pseudomonas aeruginosa* and *Staphylococcus aureus* using the agar diffusion test, and the **1** and **2** showed marginal activity at 100 μg/disk.

Catechins having the same skeleton with the chevalieriflavanosides are reported to have antibacterial activity.[20,21] Because of the minimal activity of the chevalieriflavanosides, one might assume that the absence of hydroxyl group at C-5 on A-ring decreases the antibacterial activity, and the occurrence of a glycosidic unit at C-7 also makes them weaker because of their high polarity.[22]

Experimental

General experimental procedure

CD spectra were recorded on a JASCO 302-A spectrophotometer in MeOH. The ESI-MS was measured on a Varian AAT 311A mass spectrometer, and HR-ESI-MS was taken on a JEOL HX110 mass spectrometer. 1D and 2D NMR spectra were run on JEOL JNM-ECZ600R/S1 600-MHz NMR spectrometer. The ^{1}H (600 MHz) and ^{13}C (150 MHz) chemical shifts were referenced to the residual solvent peak of methanol-d_4 at δ_H 3.30 for proton and δ_C 49.0 ppm for carbon. All sample concentrations ranged from 6 to 10 mg/ml with a total volume of 0.5 ml for each sample. The ^{1}H sweep width was set at 11 282 Hz for all experiments with a 45° pulse for ^{1}H and a 30° pulse for ^{13}C. The pulse programs of the COSY, HSQC, and HMBC experiments were taken from the Varian Software Library, and standard pulse sequences were used for 2D spectra. Homonuclear 2D spectra and inverse proton-detected heteronuclear 2D spectra were acquired in the phase-sensitive mode, and HMBC spectra were acquired in the absolute value mode. The COSY was acquired with 200 F1 increments with 32 scans per increment. Sinebell weighting was applied to the F2 dimension before zero filled to 32 K points, and a sinebell was applied to the F1 and zero filled to 2 K points before Fourier transformation. The NMR notebook software was used for 1D and 2D spectra processing. Proton-detected heteronuclear correlations were measured using HSQC (optimized for $^{1}J_{CH}$ = 145 Hz) and HMBC (optimized for J_{CH} = 8 Hz). Sinebell weighting was applied to both ^{1}H and ^{13}C dimensions and zero filled to 4 K and 1 K, respectively. The chemical shifts are given in ppm (δ), relative to TMS as internal standard, and coupling constants are in Hz. Column chromatography (CC) was carried out on silica gel (70–230 mesh, Merck) and vacuum liquid chromatography (VLC) on reversed-phase materials (Lichroprep RP-18, 25–40 μm). TLC was performed on Merck precoated aluminum silica gel 60 F_{254} sheets, and compounds were detected using sulfuric acid spray reagent.

Plant material

A. chevalieri was collected in Maroua, Far North Region of Cameroon and identified by Mr. Tapsou, botanist at the Institute of Agricultural Research for Development in December 2013, and a voucher specimen N° 36696 HNC has been deposited at the Cameroon National Herbarium.

Extraction and isolation

The powdered roots (1.5 kg) of *A. chevalieri* were extracted with *n*-hexane (2 × 5 l), then with MeOH (3 × 6 l) at room temperature. After filtration and evaporation procedures, *n*-hexane (4 g) and MeOH (94 g) extracts were obtained, respectively. The MeOH extract was dissolved in H_2O (400 ml) and successively partitioned with EtOAc (3 × 200 ml) and *n*-BuOH (3 × 200 ml) saturated with H_2O. The *n*-BuOH extract (33 g) was subjected to VLC using reversed-phase material (RP-18) employing H_2O (1750 ml), H_2O–MeOH (8:2, 2750 ml; 6:4, 2250 ml; 4:6, 8000 ml; 2:8, 2500 ml), and MeOH (750 ml) to give 18 main fractions (Fr. 1-1–1-18). Fractions were combined based on their thin layer chromatography profiles (TLC). Fr. 1-3–1-5 (2.12 g) were combined and submitted to silica gel (350 g) CC with the solvent system CH_2Cl_2–MeOH–H_2O (80: 20: 2, 2000 ml; 70: 30: 3, 2500 ml) to give 685 fractions (Fr. 2-1–2-685). Fr. 2-284–2-393 (89.8 mg) was subjected to MPLC (RP-18) using H_2O–MeOH (9:1) to provide 63 fractions (Fr. 3-1–3-63). Fr. 3-19–3-35 (20.9 mg) was subjected to open CC using RP-18 (20 g) eluted with H_2O–MeOH (9:1) to give **1** (14 mg). Fr. 2-196–2-276 (190.4 mg) was subjected to MPLC (RP-18) using H_2O–MeOH (9:1 and 8:2) to provide 168 fractions (Fr. 4-1–4-168). Fr. 4-149–4-162 (25.2 mg) was subjected to open CC using RP-18 (25 g) eluted with H_2O–MeOH (9: 1, 8: 2) to give **2** (10 mg).

Cell culture and cytotoxicity

HL60 cell (RCB0041, RIKEN BioResource Center, Tsukuba, Japan) was grown in RPMI 1640 medium supplemented with 10% heat-inactivated FBS (Sigma Aldrich Corp. St. Louis, USA) and penicillin (50 units/ml)–streptomycin (50 μg/ml) (Gibco Corp., Carlsbad, USA) in a humidified atmosphere at 37 °C under 5% CO_2. The cytotoxicity of the compounds was examined by MTT assay, as described previously.[23]

Assay for antimicrobial activity

Antimicrobial activities were determined using the agar diffusion test using paper disks (8 mm in diameter, thin, ADVANTEC) against *S. aureus* NBRC 13276, *P. aeruginosa* ATCC 15442. An antibiotic paper disk was loaded with a sample soln. and then dried for 2 h *in vacuo* to remove the solvent. Each test sample-loaded disk was placed on the agar plates inoculated with tester strains, which were incubated at 25 °C. Antimicrobial activities were estimated by measuring the diameter of inhibition zone formed on the agar.[24]

Acid hydrolysis

Each solution of **1** (5 mg) and **2** (5 mg) in 0.2 M HCl (dioxane-H_2O 1:1, 3 ml) was heated at 95 °C for 30 min under argon. After cooling, the mixture was neutralized by passage through an Amberlite-IRA-93ZU (Organo, Tokyo, Japan) column and chromatographed (Diaion HP-20, 40% MeOH followed by Me_2CO–EtOH 1:1) to give aglycone fractions (2.5 mg) and a sugar fraction (1.7 mg). After the sugar fraction was passed through a Sep-Pak-C_{18} cartridge (Waters, Milford, MA, USA; with 40% MeOH) and Toyopak-IC-SP-M-cartridge (Tosoh; with 40% MeOH), it was analyzed by HPLC (MeCN–H_2O 17: 3, flow rate, 0.9 ml.min^{-1}; detection, refractive index (RI), and optical retention (OR): D-glucose (t_R 15.84, $[\alpha]_D^{25}$ +53.3 ° in **1** and **2** (lit.[25] +52.7 °).

Chevalieriflavanoside A (1)

Brownish amorphous powder; $[\alpha]_D^{22}$ −190° (*c* 0.08, MeOH); UV (MeOH) λ_{max} (logε) nm 225 (5.57), 275 (4.83); IR ν_{max} (KBr) 3394, 2946, 2834, 1654, 1469, 1025 cm^{-1}; CD (*c* 0.1, MeOH) [θ] (nm) −4000 (278) (neg. max.), +7000 (235) (pos. max.); ^1H and ^{13}C NMR data, see Table 1; HR-ESI-MS (positive-ion mode) *m/z* 475.1210 ($[M + Na]^+$ calcd for $C_{21}H_{24}O_{11}Na$ 475.1215).

Chevalieriflavanoside B (2)

Brownish amorphous powder; $[\alpha]_D^{22}$ −106° (*c* 0.15, MeOH); UV (MeOH) λ_{max} (logε) nm 228 (6.58), 275.5 (5.90); IR ν_{max} (KBr) 3367, 2946, 2834, 1654, 1469, 1025 cm^{-1}; CD (*c* 0.1, MeOH) [θ] (nm) −1000 (270) (neg. max.), −10 000 (224) (neg. max.); ^1H and ^{13}C NMR data, see Table 1; HR-ESI-MS (positive-ion mode) *m/z* 475.1210 ($[M + Na]^+$ calcd for $C_{21}H_{24}O_{11}Na$ 475.1215).

Acknowledgements

Abdou T. is grateful to JSPS for financial support through JSPS RONPAKU Program, (Dissertation PhD, ID: R11516).

References

[1] Y. Saidu, M. Lawal, S. A. Isezuo, R. A. Shehu, D. M. A. Sahabi, L. S. Bilbis. *J. Pharmacol. Toxicol.* **2007**, *2*, 513–523.
[2] H. M. Burkill. *Royal Botanic. Gardens, Kew.* **1995**, *3*, 207–208.
[3] H. Le Houèrou, website. http://www.fao.org/ag/AGP/AGPC/doc/GBASE/Data/pf000366. htmaccessed [21-03-**2009**].
[4] Y. Saidu, L. S. Bilbis, N. Lawal, S. A. Isezua, S. W. Hassan, A. Y. Abbas. *Asian J. Biochem.* **2007**, *2*, 224–236.
[5] Y. Saidu, L. S. Bilbis, S. A. Isezuo, S. A. Habibullah, M. J. Ladan, M. Lawal. *Cameroon J. Exp. Biol.* **2009**, *5*, 37–43.
[6] A. B. Aliyu, A. M. Musa, M. A. Ibrahim, H. Ibrahim, A. O. Oyewale. *Bajopas.* **2009**, *2*, 149–153.
[7] J. Kamga, L. P. Sandjo, N. Böke-Sarikahya, S. Kirmizigül, V. Kuete, B. T. Ngadjui. *Nat. Prod. Res.* **2014**, *28*, 1574–1578.
[8] M. J. Jung, S. S. Kang, H. A. Jung, G. J. Kim, J. S. Choi. *Arch. Pharm. Res.* **2004**, *27*, 593–599.
[9] Y. Koteswararao, M. V. Bhaskar Reddy, C. Venkatarao, D. Gunasekar, A. Blond, C. Caux, B. Bodo. *Chem. Pharm. Bull.* **2002**, *50*, 1271–1272.
[10] S. N. Mathias, M. S. Abubakar, N. October. *Int. J. Pharm. Pharm. Sci.* **2016**, *8*, 261–265.
[11] V. K. Sahu, R. Irchhaiya, A. Shashi, H. Gurjar. *Int. J. Pharm. Sci. Res.* **2010**, *1*, 39–45.
[12] H. Takahashi, Y. Kubota, H. Miyazaki, M. Onda. *Chem. Pharm. Bull.* **1984**, *32*, 4852–4857.
[13] J. Polonsky, Z. Baskevitch, N. Cagnoli-Bellavita, P. Ceccherelli, B. L. Buckwalter, E. Wenkert. *J. Am. Chem. Soc.* **1972**, *94*, 4369–4370.
[14] J. W. Clark-Lewis, G. F. Katekar, P. I. Mortimer. *J. Chem. Soc.* **1961**, 499–503.
[15] D. Ferreira, J. P. J. Marais, D. Slade, L. A. Walker. *J. Nat. Prod.* **2004**, *67*, 174–178.
[16] K. H. Kim, E. Moon, S. U. Choi, S. Y. Kim, K. R. Lee. *Phytochemistry* **2013**, *92*, 113–121.
[17] J. H. Wu, Y. T. Tung, S. C. Chien, S. Y. Wang, Y. H. Kuo, L. F. Shyur, S. T. Chang. *J. Agric. Food Chem.* **2008**, *56*, 1567–1573.
[18] A. Benavides, C. Bassarello, P. Montoro, W. Vilegas, S. Piacente, C. Pizza. *Phytochemistry* **2007**, *68*, 1277–1284.
[19] I. C. du Preez, D. G. Roux. *J. Chem. Soc.* **1970**, 1801–1804.
[20] R. P. Borris. *J. Ethnopharmacol.* **1996**, *51*, 29–38.
[21] D. E. Moerman. *J. Ethnopharmacol.* **1996**, *52*, 1–22.
[22] S. Kumar, A. K. Pandey. *Scientific World Journal* **2013**, 1–16.
[23] M. Arayama, S. Uesugi, K. Tanaka, H. Maeda, T. Nehira, K. Kimura, M. Hashimoto. *Tetrahedron* **2016**, *72*, 1031–1035.
[24] Y. Shiono, T. Murayama, K. Takahashi, K. Okada, S. Katohda, M. Ikeda. *Biosci. Biotechnol. Biochem.* **2005**, *69*, 287–292.
[25] R. Schaffer, in *The Carbohydrates: Chemistry and Biochemistry* (Eds: W. Pigman, D. Horton), Academic Press, New York, London, **1972**, pp. 69–111.

Supporting information

Additional supporting information may be found in the online version of this article at the publisher's web site.