Molecules **2014**, *19*, 6727-6736; doi:10.3390/molecules19056727

OPEN ACCESS

molecules

ISSN 1420-3049

www.mdpi.com/journal/molecules

Article

Four New Flavonol Glycosides from the Leaves of *Brugmansia suaveolens*

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Received: 31 March 2014; in revised form: 16 May 2014 / Accepted: 19 May 2014 / Published: 22 May 2014

Abstract: Four new flavonol glycosides were isolated from the leaves of *Brugmansia suaveolens*: kaempferol 3-*O*-β-D-glucopyranosyl-(1'''→2'')-*O*-α-L-arabinopyranoside (**1**), kaempferol 3-*O*-β-D-glucopyranosyl-(1'''→2'')-*O*-α-L-arabinopyranoside-7-*O*-į-D-glucopyranoside (**2**), kaempferol 3-*O*-β-D-[6'''-*O*-(*E*-caffeoyl)]-glucopyranosyl-(1'''→2'')-*O*-α-L-arabinopyranoside-7-*O*-β-D-glucopyranoside (**3**), and kaempferol 3-*O*-β-D-[2'''-*O*-(*E*-caffeoyl)]-glucopyranosyl-(1'''→2'')-*O*-α-L-arabinopyranoside-7-*O*-β-D-glucopyranoside (**4**). The structure elucidation was performed by MS, 1D and 2D NMR analyses.

Keywords: *Brugmansia suaveolens*; Solanaceae; acylated kaempferol glycosides

1. Introduction

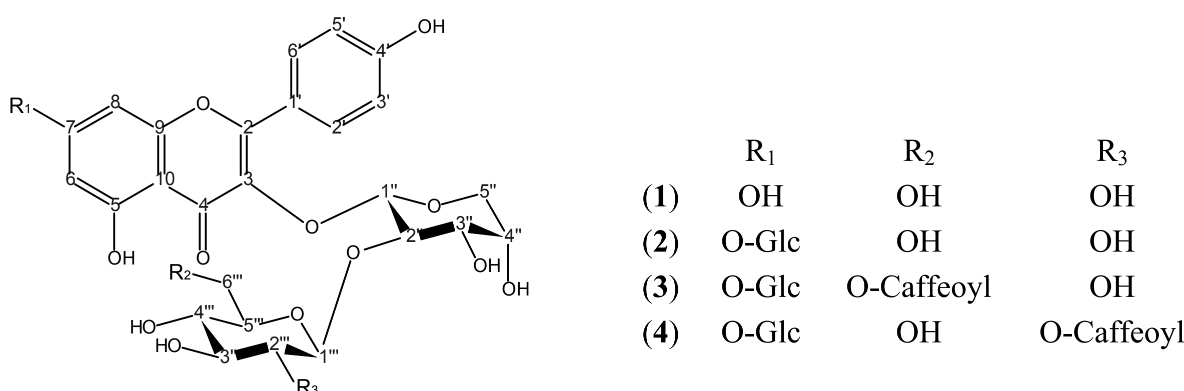
Brugmansia suaveolens (Humb. & Bonpl. ex. Willd.) Bercht. & C. Presl (Syn. *Datura suaveolens*), known also as angel's trumpet, is a flowering shrub of the Solanaceae family, native to the coastal rainforest regions of Southeast Brazil. Extracts from its leaves have been studied for their anti-inflammatory and wound healing activities [1,2]. Up until now, alkaloids [3–5] and essential oils [6]

have been reported as the main effective compounds. Moreover, in [7] the isolation of the flavonol glycosides kaempferol 3-*O*-α-L-arabinopyranoside and kaempferol 3-*O*-α-L-arabinopyranoside-7-*O*-β-D-glucopyranoside from the leaves of this species has been described. In this paper, the isolation and structure elucidation of four new kaempferol glycosides are reported for the first time.

2. Results and Discussion

Phytochemical investigation of the ethanolic extract of *B. suaveolens*, prepared from the leaves, yielded four new kaempferol glycosides, while neither of the compounds described by [7] were isolated in this work. Analysis of the spectroscopic data led to the identification of compounds **1**–**4** (Figure 1).

Figure 1. Chemical structures of compounds **1**–**4** isolated from the leaves of *Brugmansia suaveolens*.



	R_1	R_2	R_3
(**1**)	OH	OH	OH
(**2**)	O-Glc	OH	OH
(**3**)	O-Glc	O-Caffeoyl	OH
(**4**)	O-Glc	OH	O-Caffeoyl

The molecular formula of compound **1** was determined as $C_{26}H_{28}O_{15}$ on the basis of FT-ICR-MS *m/z* 603.132636 $[M+Na]^+$ (calcd. *m/z* 603.13204 $[M+Na]^+$) and ESI-MS *m/z* 603.1 $[M+Na]^+$. The IR spectrum showed the characteristic absorption bands of hydroxyl (3248.2 cm^{-1}), carbonyl (1652.8 cm^{-1}), and phenyl groups (1574.4 cm^{-1}). The ^{1}H-NMR and ^{13}C-NMR spectra (see Table 1) are similar to those reported by [7]. The aromatic region of the ^{1}H-NMR spectrum of **1** showed four signals, namely, two broad singlets (δ 6.21 and δ 6.40) for the protons in ring A and two doublets (AA'BB' system) for ring B (δ 6.92 and δ 8.02, both with J = 8.6 Hz), which are typical for a kaempferol aglycone [7]. The middle region of the spectrum exhibited two anomeric signals due to the sugar units at δ 5.48 and δ 4.55. The coupling constant of the anomeric proton of the glucose (J = 7.8 Hz) was in accordance with a β-glycosidic linkage, while the coupling constant of the anomeric proton of the pentose (J = 3.3 Hz) indicated a α-glycosidic linkage [8]. Acid hydrolysis of **1** indicated D-glucose and L-arabinose, which were compared with an authentic sample by TLC analysis [9,10]. A further eleven protons were identified between δ 3.34 and δ 4.21 due to the sugar units [8]. The structural information concerning the attachment position of the aforementioned moieties was determined based on MS fragmentation and 2D-NMR analysis. The MS fragmentation of **1** showed no $[M+H-pentose]^+$ fragment, indicating that the pentose is bonded directly to the aglycone, and that the glucose unit is linked as the second sugar moiety [11,12]. The HMBC experiment of **1** exhibited a correlation of the anomeric proton H-1'' of α-L-arabinopyranose (δ 5.48) with C-3 (δ_{C3} 135.7), indicating the linkage of this sugar with the aglycone moiety. The interglycosidic linkage is shown by the correlation of the H-1''' (δ 4.55) of

β-D-glucopyranose with the C-2'' ($\delta_{C2''}$ 80.1) of α-L-arabinopyranose [13]. Based on the aforementioned spectroscopic data, the structure of **1** was assigned as a kaempferol 3-*O*-β-D-glucopyranosyl-(1'''→2'')-*O*-α-L-arabinopyranoside.

Table 1. ^{1}H-NMR, ^{13}C-NMR, and 2D-NMR spectral data for compounds **1** and **2**.

	1 [a]					**2** [b]				
Position	**δ_H (*J* in Hz)**		**δ_C**	**COSY**	**HMBC**	**δ_H (*J* in Hz)**		**δ_C**	**COSY**	**HMBC**
2			158.5					155.9		
3			135.7					134.3		
4			179.7					177.7		
5			161.6					160.2		
6	6.21	Brs	99.9	H-8	C-7,8,10	6.44	Brs	99.3	H-8	C-5,7,8,10
7			166.0					162.9		
8	6.40	Brs	94.7	H-6	C-6,7,9,10	6.79	Brs	94.6	H-6	C-6,7,9,10
9			159.0					156.6		
10			105.8					105.6		
1'			122.6					120.3		
2'	8.02	d (8.6)	132.4	H-3'	C-2,4'	8.10	d (8.4)	131.1	H-3'	C-2,4'
3'	6.92	d (8.6)	116.5	H-2'	C-1′,4'	6.91	d (8.4)	115.4	H-2'	C-1',4'
4'			163.1					160.2		
5'	6.92	d (8.6)	116.5	H-6′	C-1',4'	6.91	d (8.4)	115.4	H-6'	C-1',4'
6'	8.02	d (8.6)	132.4	H-5′	C-2, 4'	8.10	d (8.4)	131.1	H-5′	C-2, 4'
Ara-O-3										
1''	5.48	d (3.3)	101.3	H-2''	C-3	5.61	d (3.1)	98.9	H-2''	C-3
2''	4.21	dd (5.4,3.4)	80.1	H-1'',3''		4.07	M	78.7	H-1'',3''	
3″	3.96	dd (5.4,6.4)	71.3	H-2'',4''		3.86	M	68.7	H-2'',4''	
4''	3.86	M	66.6	H-3'',5''		3.70	M	64.1	H-3'',5''	
5_a''	3.23	M	63.4	H-4″		3.07	M	61.2	H-4''	
5_b″	3.73	M				3.51	brd (11.1)			
Glc-Ara										
1'''	4.55	d (7.8)	105.4	H-2'''	C-2''	4.37	d (7.5)	103.8	H-2'''	C-2''
2'''	3.25	brd (7.8)	75.2	H-1''',3'''		2.97	M	73.6	H-1''',3'''	
3'''	3.38	M	78.1	H-2''',4'''		3.17	M	76.7	H-2''',4'''	
4'''	3.34	M	71.4	H-3''',5'''		3.12	M	69.7	H-3''',5'''	
5'''	3.36	M	78.0	H-4''', 6'''		3.43	M	77.1	H-4''', 6'''	
6_a'''	3.78–3.82	M	62.7	H-5'''		3.43	brd (11.5)	60.9	H-5‴	
6_b'''						3.59	M			
Glc-O-7										
1''''						5.07	d (7.1)	99.8	H-2''''	C-7
2''''						3.25	M	73.1	H-1'''',3''''	
3''''						3.30	M	76.4	H-2'''',4''''	
4''''						3.17	M	69.6	H-3'''',5'''',	
5''''						3.12	M	76.8	H-4'''',6''''	
6_a''''						3.70	M	60.6	H-5''''	
6_b''''						3.43	M			

[a] MeOH-d_4; [b] DMSO-d_6; ^{13}C-NMR measured in 100 MHz; ^{1}H-NMR measured in 600 MHz.

Compound **2** was established as $C_{32}H_{38}O_{20}$ on the basis of FT-ICR-MS *m/z* 765.184176 $[M+Na]^+$ (calcd. *m/z* 765.18486 $[M+Na]^+$) and ESI-MS *m/z* 765.0 $[M+Na]^+$. The IR spectrum revealed signals of hydroxyl (3365.8 cm^{-1}), carbonyl (1653.8 cm^{-1}), and phenyl groups (1605.3 cm^{-1}). The ^{1}H-NMR and ^{13}C-NMR (see Table 1) spectra are similar to those of **1**. In the middle region of the spectrum, one additional anomeric signal was identified, due to a new sugar unit at δ 5.07. The coupling constant of this anomeric proton (J = 7.1 Hz) was in accordance with a β-glycosidic linkage. The sugar units of compound **2** were determined as D-glucose and L-arabinose by TLC comparison with authentic samples after acid hydrolysis [9,10]. As in **1**, the HMBC experiment of **2** exhibited correlation between the anomeric proton H-1'' (δ 5.61) and C-3 (δ_{C3} 134.3), and between H-1'''' (δ 5.07) and C-7 (δ_{C7} 162.9), indicating, respectively, the linkage of α-L-arabinopyranose and of β-D-glucopyranose with the aglycone. Additionally, the interglycosidic linkage is shown by the correlation of the H-1''' (δ 4.37) of another β-D-glucopyranose with the C-2'' ($\delta_{C2''}$ 78.7) of α-L-arabinopyranose [13]. Therefore, compound **2** was identified as a kaempferol 3-*O*-β-D-glucopyranosyl-(1'''→2'')-*O*-α-L-arabinopyranoside-7-*O*-β-D-glucopyranoside.

The molecular formula $C_{41}H_{44}O_{23}$ of compound **3** was deduced based on FT-ICR-MS *m/z* 927.215977 $[M+Na]^+$ (calcd. *m/z* 927.21656 $[M+Na]^+$) and ESI-MS *m/z* 927.7 $[M+Na]^+$. The absorption bands of the hydroxyl (3309.5 cm^{-1}), carbonyl (1651.9 cm^{-1}), and phenyl groups (1598.2 cm^{-1}) were observed in IR analysis. The ^{1}H-NMR and ^{13}C-NMR spectra (see Table 2) were similar to those of **2**, including again three anomeric signals. Acid hydrolysis of **3** suggests D-glucose and L-arabinose as sugar moieties, which was confirmed by comparison with authentic samples by TLC analysis [9,10]. Additionally, **3** showed two further signals at δ 6.41 and δ 7.81 (both d, J = 15.8 Hz), which are indicative of olefinic protons of a *trans*-caffeoyl group [14,15]. The HMBC experiment exhibited correlation between the anomeric proton H-1'' of α-L-arabinopyranose (δ 6.41) and C-3 (δ_{C3} 137.0), and between the anomeric proton H-1''''' (δ 5.78) and C-7 (δ_{C7} 163.6), showing direct linkages of these sugars moieties with aglycone. The correlation of the H-2'' (δ 5.07) of α-L-arabinopyranose with the C-1''' ($\delta_{C1'''}$ 106.7) of another β-D-glucopyranose indicates a linkage between these sugar moieties. The ^{1}H-NMR spectrum of **3** exhibited the downfield shift of the signals corresponding to methylene protons H_2-6''' to δ 4.90–5.03, indicating an acylation at this position [14]. The HMBC experiment confirmed the linkage of the caffeic acid to C-6''' of β-D-glucopyranose by a correlation between the H-$6_{a'''}$ and H-$6_{b'''}$ (δ 4.90–5.03) of this sugar unit and C=O ($\delta_{C\text{-}1''''}$ 167.4) of the caffeic acid moiety. Based on detailed analysis of the NMR spectra, the structure of compound **3** was determined as a kaempferol 3-*O*-β-D-[6'''-*O*-(*E*-caffeoyl)]-glucopyranosyl-(1'''→2'')-*O*-α-L-arabinopyranoside-7-*O*-β-D-glucopyranoside.

Compound **4** was determined as $C_{41}H_{44}O_{23}$ based on FT-ICR-MS *m/z* 927.216170 $[M+Na]^+$ (calcd. *m/z* 927.21656 $[M+Na]^+$) and ESI-MS *m/z* 927.1 $[M+Na]^+$. The IR spectrum showed bands of hydroxyl (3263.2 cm^{-1}) and phenyl groups (1586.6 cm^{-1}). The ^{1}H-NMR and ^{13}C-NMR spectra (see Table 2) are similar to those of **3**. Compound **4** showed again three anomeric signals and also two further signals at δ 6.25 and δ 7.47 (both d, J = 15.7 Hz), which were assigned to the olefinic protons of a *trans*-caffeoyl group [14,15]. Acid hydrolysis of **4**, followed by TLC comparison with authentic samples, indicated the presence of D-glucose and L-arabinose [9,10]. The HMBC experiment of **4** exhibited correlation between the anomeric proton H-1'' of α-L-arabinopyranose (δ 5.58) and C-3 (δ_{C3} 134.5), and between the anomeric proton H-1''''' of a β-D-glucopyranose unit (δ 5.06) and C-7 (δ_{C7} 162.9),

showing the linkages of these sugar units to the kaempferol moiety. The interglycosidic linkage is shown by the correlation of H-1''' (δ 4.68) of another β-D-glucopyranose with C-2'' ($\delta_{C2''}$ 78.7) of α-L-arabinopyranose [13]. The ^{1}H-NMR spectrum of **4** exhibited also a downfield shift of the signal corresponding to H-2''' at δ 4.60, indicating an acylation at the C-2''' position. The HMBC experiment confirmed the assignment of the caffeic acid moiety to C-2''' of β-D-glucopyranose by a correlation between the H-2''' (δ 4.60, t, *J* = 8.7 Hz) of this sugar unit and the C=O ($\delta_{C\text{-}1''''}$ 165.6) of the caffeic acid moiety.

Table 2. ^{1}H-NMR, ^{13}C-NMR, and 2D-NMR spectral data for compounds **3** and **4**.

	3 [c]					**4** [b]				
Position	**δ_H (*J* in Hz)**		**δ_C**	**COSY**	**HMBC**	**δ_H (*J* in Hz)**		**δ_C**	**COSY**	**HMBC**
2			157.2					154.4		
3			137.0					134.5		
4			178.8					177.6		
5			161.7					160.5		
6	6.72	brs	100.0	H-8	C-5,7,8,10	6.43	Brs	98.7	H-8	C-7
7			163.6					162.9		
8	6.92	brs	94.6	H-6	C-6,7,9,10	6.76	Brs	94.0	H-6	C-7,10
9			156.6					155.9		
10			106.7					106.0		
1'			121.8					121.2		
2'	8.44	d (8.6)	131.8	H-3'	C-2,4'	8.06	d (8.6)	131.0	H-3'	C-2
3'	7.26	d (8.6)	116.2	H-2'	C-1',4'	6.81	d (8.6)	115.4	H-2'	C-1',4'
4'			162.0					160.5		
5'	7.26	d (8.6)	116.2	H-6'	C-1',4'	6.81	d (8.6)	115.4	H-6'	C-1',4'
6'	8.44	d (8.6)	131.8	H-5'	C-2,4'	8.06	d (8.6)	131.0	H-5'	C-2
Ara-O-3										
1''	6.41	d (5.0)	100.4	H-2''	C-3	5.58	d (3.4)	98.7	H-2''	C-3
2''	5.07	m	80.7	H-1'',3''		4.09	M	78.7	H-1'',3''	
3''	4.67	m	70.9	H-2'',4''		3.85	M	68.6	H-2'',4''	
4''	4.47	m	66.0	H-3'',5''		3.50	M	63.7	H-3'',5''	
5_a''	4.38	m	62.1	H-4''		3.00	brd (11.6)	60.6	H-4''	
5_b''	4.56	brd (11.9)				3.50	M			
Glc-Ara										
1'''	5.28	d (7.5)	106.7	H-2'''	C-2''	4.68	d (7.8)	101.5	H-2'''	C-2''
2'''	4.12	m	75.1	H-1''',3'''		4.60	M	73.1	H-1''',3'''	C-1''''
3'''	4.05	m	78.1	H-2''',4'''		3.48	M	73.6	H-2''',4'''	
4'''	4.15	m	70.9	H-3''',5'''		3.25	M	69.5	H-3''',5'''	
5'''	4.05	m	75.4	H-4''',6'''		3.30	M	76.4	H-4''',6'''	
6_a'''	4.90–5.03	m	63.9	H-5'''	C-1''''	3.50–3.70	M	60.3	H-5'''	
6_b'''										
Caffeoyl										
1''''			167.4					165.6		
2''''	6.41	d (15.8)	114.6	H-3''''	C1''''	6.25	d (15.7)	113.9	H-3''''	C1''''

Table 2. *Cont.*

	3 [c]					4 [b]				
Position	δ_H (*J* in Hz)		δ_C	**COSY**	**HMBC**	δ_H (*J* in Hz)		δ_C	**COSY**	**HMBC**
3''''	7.81	d (15.8)	145.6	H-2''''	C-1'''', 2'''''	7.47	d (15.7)	145.0	H-2''''	C-1'''', 2'''''
1'''''			126.6					125.4		
2'''''	7.40	brs	115.6		C-3''''	7.07	Brs	114.9		C-3''''
3'''''			145.6					145.7		
4'''''			147.2					148.7		
5'''''	7.12	d (8.0)	116.3	H-6'''''		6.90	d (8.6)	115.8	H-6'''''	
6'''''	6.95	d (8.0)	121.8	H-5'''''		6.96	brd (8.0)	121.2	H-5'''''	
Glc-O-7										
1''''''	5.78	d (7.2)	101.3	H-2''''''	C-7	5.06	d (7.4)	99.8	H-2''''''	C-7
2''''''	4.30	m	74.6	H-1'''''',3''''''		3.20	M	72.5	H-1'''''',3''''''	
3''''''	4.40	m	78.9	H-2'''''',4''''''		3.28	M	76.8	H-2'''''',4''''''	
4''''''	4.30	m	71.0	H-3'''''',5''''''		3.25	M	69.8	H-3'''''',5''''''	
5''''''	4.30	m	78.1	H-4'''''',6''''''		3.40	M	77.1	H-4'''''',6''''''	
6_a''''''	3.71	m	63.4	H-5''''''		3.50-3.70	M	60.3	H-5''''''	
6_b''''''	4.50	m								

[b] DMSO-d_6; [c] Pyridine-d_5; ^{13}C-NMR measured in 100 MHz; ^{1}H-NMR measured in 600 MHz.

Therefore, the structure of **4** was assigned as a kaempferol 3-*O*-β-D-[2'''-*O*-(*E*-caffeoyl)]-glucopyranosyl-(1'''→2'')-*O*-α-L-arabinopyranoside-7-*O*-β-D-glucopyranoside.

3. Experimental Section

3.1. General

NMR spectra 1D (^{1}H, ^{13}C, and DEPT-135) and 2D (^{1}H-^{1}H COSY, HSQC, HMBC) were recorded with MeOH-d_4, DMSO-d_6 or pyridine-d_5 on Bruker AMX-600 (600 MHz and 150 MHz) and Bruker AMX-400 (400 MHz and 100 MHz) spectrometers (Bruker BioSpin GmbH, Rheinstetten, Germany). LC-ESI-MS was carried out on an electrospray Finnigan MAT P4000 HPLC-DAD system connected to a Finningan LCQ™ Duo ion Trap mass spectrometer (Thermo Electron GmbH, Karlsruhe, Germany). Analytical HPLC was performed with a L-7100 Pump (Merck-HITACHI-LaChrom); UV-Vis detector L7420 (Merck-HITACHI-LaChrom); HPLC D-7000 HSM software with a D7000 data interface. HR-MS (FT-ICR) was performed on a Bruker APEXII (electrospray ionization). The UV spectra were measured in a Hewlett-Packard HP 1090 HPLC-DAD system in MeOH. The IR spectra were obtained on a Perkin Elmer Spectrum One (ATR Technology, Shelton, CT, USA). Sephadex LH-20 (6 × 50 cm) (particle size 25–100 mm, Sigma Chemical Co., Munich, Germany); Thin layer chromatography (TLC) (Silica Gel 60 F254 (0.25 mm) Merck (Darmstadt, Germany); RP-TLC aluminum sheets 20 × 20 cm, RP-18 F254 Merck); Flash chromatography (LaFlash, VWR International, Darmstadt, Germany), RP-18 (25–40 µm) column (5 × 20 cm), with gradient MeOH–H_2O (10:90 → 100:0, *v/v*); Analytical HPLC, LiChrospher RP-18 column (5 × 100 mm; 5 µm), mobile phase (A) MeOH–ACN–FA (95:5:0.1, *v/v/v*) and (B) gradient of MeOH–ACN–FA (95:5:0.1→85:15:0.1, *v/v/v*).

3.2. Plant Material

Leaves of *Brugmansia suaveolens* were collected in Santa Maria, Rio Grande do Sul, Brazil in January 2008. The plant was identified by botanist Gilberto Zanetti. A voucher specimen was deposited in the herbarium of the Department of Biology at the Federal University of Santa Maria, Brazil, under reference number SMDB12520.

3.3. Extraction and Isolation

The air-dried and powdered leaves (1.087 g) of *B. suaveolens* were exhaustively extracted with EtOH (7 L, 30 h) in a Soxhlet apparatus. The EtOH extract was concentrated under vacuum at 40 °C and lyophilized to yield 359.94 g, which was treated with MeOH at −20 °C giving a soluble fraction of 344.82 g after solvent removal. Of this extract, 6.18 g was subjected to column chromatography with Sephadex LH-20 and MeOH as mobile phase at a flow rate of 1 mL/min. A total of 300 fractions of 10 mL each were collected and controlled by TLC using silica gel with toluene–MeOH–DEA (8:1:1, *v/v/v*) and RP-18 with MeOH–H_2O (1:1, *v/v*); Anisaldehyde-H_2SO_4 was used for detection. Those fractions with a similar profile were combined, yielding 11 fractions (A→K). Fraction G (80 mg) was chromatographed by RP-18 CC using MeOH–H_2O (1:1, *v/v*) to give five combined sub-fractions ($G_{1.1}$-$G_{1.5}$). A sub-fraction $G_{1.2}$ was fractioned again by RP-18 CC with MeOH–H_2O (1:2, *v/v*) to provide three sub-fractions ($G_{1.2.1}$-$G_{1.2.3}$). Sub-fraction $G_{1.2.1}$ was further purified by HPLC using a gradient of MeOH–ACN–FA (95:5:0.1→85:15:0.1, *v/v/v*), yielding compound **2** (10.3 mg). Fraction I (41.1 mg) was chromatographed by RP-18 gel CC using MeOH–H_2O (1:1, *v/v*) to give three combined sub-fractions ($I_{1.1}$-$I_{1.3}$). Sub-fraction $I_{1.2.2}$ was further purified by HPLC using a gradient of MeOH–ACN–FA (95:5:0.1→85:15:0.1, *v/v/v*) to afford compound **3** (4.5 mg). Fraction H (100 mg) was separated by flash chromatography RP-18 with gradient MeOH–H_2O (10:90 → 100:0, *v/v*) to give four combined sub-fractions ($H_{1.1}$-$H_{1.4}$). Sub-fraction $H_{1.4}$ (47.8 mg) was further purified by RP-18 CC using MeOH–H_2O (1:1, *v/v*) yielding 3.2 mg of compound **1**. Sub-fraction $H_{1.2}$ (35.2 mg) was applied to HPLC using a gradient of MeOH–ACN–FA (95:5:0.1→85:15:0.1, *v/v/v*), affording 11.1 mg of compound **3** and 3.5 mg of compound **4**.

3.4. Acid Hydrolysis

An amount of 2 mg per compound **1**–**4** was dissolved in EtOH–HCl 10% (10 mL) and refluxed at 80 °C for 2 h. The mixture was diluted in water (10 mL) and extracted with EtOAc (3 × 3 mL). The aglycone and sugar moieties were identified by TLC analysis and compared with authentic samples, D(+)-glucose, L(+)-arabinose, and kaempferol used as standards (Sigma-Aldrich, Munich, Germany). Silica gel (Merck), mobile phase for aglycone $CHCl_3$–EtOAc–MeOH (14:3:3, *v/v/v*) detected with $AlCl_3$, and mobile phase for sugars EtOH 96%–NH_4OH 25%–H_2O (20:1:4, *v/v/v*) detected with aniline phthalate [9,10].

Kaempferol 3-O-β-D-glucopyranosyl-(1'''→2'')-O-α-L-arabinopyranoside (**1**). Yellow amorphous powder. ESI-MS: positive ions *m/z* (rel. int.): 603.1 $[M+Na]^+$ (54); 581.0 $[M+H]^+$ (52); 419.0 $[M+H−glucose]^+$ (43); 401.1 $[M+H−glucose−H_2O]^+$ (13); 287.2 $[aglycone+H]^+$ (100). FT-ICR-MS

(ESI): [Measured: 603.132636]$^+$ (calculated mass for $C_{26}H_{28}O_{15}Na^+$: 603.13204). UV λ max (nm) MeOH: 265, 346. ^{1}H-NMR, ^{13}C-NMR, COSY, and HMBC: Table 1.

Kaempferol 3-O-β-D-glucopyranosyl-(1'''→2'')-O-α-L-arabinopyranoside-7-O-β-D-glucopyranoside (**2**). Yellow amorphous powder. ESI-MS: positive ions *m/z* (rel. int.): 765.0 [M+Na]$^+$ (10); 742.8 [M+H]$^+$ (22); 580.9 [M+H−glucose]$^+$ (29); 448.8 [M+H−arabinose−glucose]$^+$ (100); 418.9 [M+H−glucose−glucose]$^+$ (100); 400.9 [M+H−glucose−glucose−H_2O]$^+$ (7); 287.1 [aglycone+H]$^+$ (82). FT-ICR-MS (ESI): [Measured: 765.184176]$^+$ (calculated mass for $C_{32}H_{38}O_{20}Na^+$: 765.18486). UV λ max (nm) MeOH: 265, 345. ^{1}H-NMR, ^{13}C-NMR, COSY, and HMBC: Table 1.

Kaempferol 3-O-β-D-[6'''-O-(E-caffeoyl)]-glucopyranosyl-(1'''→2'')-O-α-L-arabinopyranoside-7-O-β-D-glucopyranoside (**3**). Yellow amorphous powder. ESI-MS: positive ions *m/z* (rel. int.): 927.7 [M+Na]$^+$ (13); 904.8 [M+H]$^+$ (74); 742.9 [M+H−caffeic acid]$^+$ (21); 580.8 [M+H−caffeic acid−glucose]$^+$ (24); 448.9 [M+H−caffeic acid−arabinose−glucose]$^+$ (100); 418.8 [M+H−caffeic acid−glucose−glucose]$^+$ (7); 324.8 [caffeic acid+glucose−H]$^+$ (8); 287.1 [aglycone+H]$^+$ (37); 162.9 [caffeic acid−OH]$^+$ (8). FT-ICR-MS (ESI): [Measured: 927.215977]$^+$ (calculated mass for $C_{41}H_{44}O_{23}Na^+$: 927.21656). UV λ max (nm) MeOH: 265, 328. ^{1}H-NMR, ^{13}C-NMR, COSY, and HMBC: Table 2.

Kaempferol 3-O-β-D-[2'''-O-(E-caffeoyl)]-glucopyranosyl-(1'''→2'')-O-α-L-arabinopyranoside-7-O-β-D-glucopyranoside (**4**). Yellow amorphous powder. ESI-MS: positive ions *m/z* (rel. int.): 927.1 [M+Na]$^+$ (42); 904.9 [M+H]$^+$ (26); 742.9 [M+H−caffeic acid]$^+$ (10); 581.0 [M+H−caffeic acid−glucose]$^+$ (14); 448.9 [M+H−caffeic acid−arabinose−glucose]$^+$ (49); 419.1 [M+H−caffeic acid−glucose−glucose]$^+$ (6); 324.9 [caffeic acid+glucose−H]$^+$ (25); 287.2 [aglycone+H]$^+$ (100); 162.9 [caffeic acid−OH]$^+$ (24). UV λ max (nm) MeOH: 265, 330. FT-ICR-MS (ESI): [Measured: 927.216170]$^+$ (calculated mass for $C_{41}H_{44}O_{23}Na^+$: 927.21656). ^{1}H-NMR, ^{13}C-NMR, COSY, and HMBC: Table 2.

4. Conclusions

The four kaempferol glycosides isolated from the leaves of *B. suaveolens* are described for the first time in Nature. The similarities of the chemical structures suggest a common biosynthetic pathway with the constituents reported by [7] for the same plant species. Additional studies considering their biosynthesis should be performed to clarify this issue.

Supplementary Materials

Supplementary materials can be accessed at: http://www.mdpi.com/1420-3049/19/5/6727/s1.

Acknowledgments

We thank Mrs. Ledi Marchi for helping to collect plant material, and botanist Gilberto Zanetti of the Department of Industrial Pharmacy, Federal University of Santa Maria, Brazil, for the localization and identification of the species. We acknowledge the Department of Organic Chemistry, University of

Tübingen, Germany for running the NMR spectra. This work was supported by the government of Baden-Württemberg (*Zukunftsoffensive IV "Förderung von Innovation und Exzellenz"*).

Author Contributions

Fabiana Geller was mainly responsible for the plant collection and extraction, isolation, structure elucidation, and writing the article. Renato Murillo was in charge of interpreting the NMR spectra. Lisa Steinhauser and Klaus Albert were responsible for providing the facilities for NMR analysis. Berta Heinzmann was the main person responsible for plant collection and extraction, and also performed a critical revision of the article. Irmgard Merfort was involved in the design of the project, the structure elucidation and the critical revision of the article. Stefan Laufer was responsible for obtaining funding, for the design of the project and for the final approval of the article.

Conflicts of Interest

The authors declare no conflict of interest.

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Sample Availability: Not available.

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