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Two New Flavonol Glycosides from *Knoxia corymbosa*

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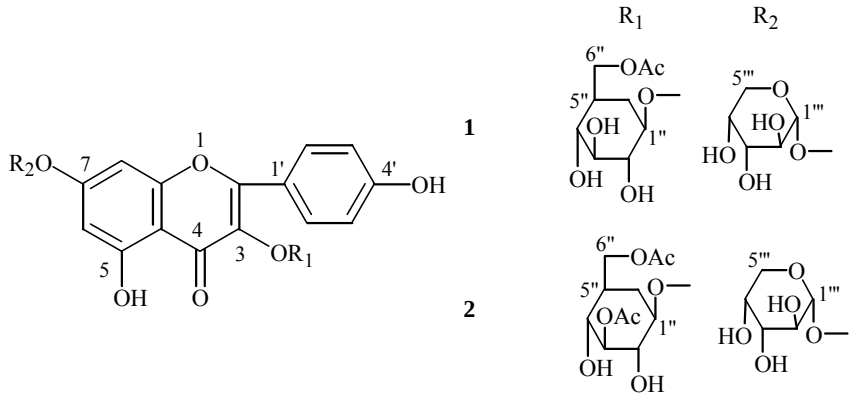
Abstract: Two new flavonol glycosides (**1** and **2**) together with two known flavonoides (**3** and **4**), were isolated from the whole plant of *Knoxia corymbosa* willd. The structures of **1** and **2** were elucidated as kaempferol-7-*O*-α-L-arabinosyl-3-*O*-β-D-6″-acetylglucopyranoside and kaempferol -7-*O*-α-L-arabinosyl-3-*O*- β -D-3″,6″-diacetylglucopyranoside respectively.

Keywords: *Knoxia corymbosa*, flavonol glycoside, kaempferol-7-*O*-α-L-arabinosyl-3-*O*-β-D-6″-acetylglucopyranoside, kaempferol-7-*O*-α-L-arabinosyl-3-*O*-β-D-3″,6″-diacetylglucopyranoside.

Knoxia corymbosa willd. is a perennial herbaceous plant distributed in south China. Its whole plant has been used as a folk medicine for the treatment of watery diarrhea, dropsy[1]. During our investigation of the chemical constituents of the title plant, four flavonoides **1**-**4** were isolated from its *n*-BuOH extract. The structures of these compounds were determined as kaempferol-7-*O*-α-L-arabinosyl-3-*O*-β-D-6″-acetylgluco pyranoside (**1**), kaempferol-7-*O*-α-L-arabinosyl-3-*O*-β-D-3″,6″-diacetylglucopyranoside (**2**), kaempferol-3-*O*-glucopyranoside (**3**)[2] and kaempferol-3-*O*-6″-acetylglucopyranoside (**4**)[3] mainly by 1D and 2D NMR experiments. Compounds **1** and **2** are two new flavo nolglycosides.

Figure 1 The structures of compound **1** and **2**



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Compound **1** was obtained as white amorphous powder, $[\alpha]_D^{23}$ –20.41 (c 0.196, DMSO). Its molecular formula was established to be $C_{28}H_{30}O_{16}$ by negative HR-FABMS (found 621.1458, calcd. 621.1455). The peaks of UVλ_{max} (DMSO) 346, 267 nm and IR (KBr) 3473, 3392, 3219 (OH), 1660 (α, β unsaturated C=O) and 1601, 1588 (aromatic ring) cm^{-1} indicated that **1** was an aromatic compound. ^1H and ^{13}C NMR spectra (**Table 2** and **1**) suggested that it has the similar skeleton with kaempferol[2]. The characteristic signals of NMR at δ_H 5.5-3.0 ppm and δ_C 105-60 ppm, accompanied with ^1H-^1H COSY and HMQC experiments indicated the presence of one β-D-glucose and one α-L-arabinose. The correlations of δ_H 5.39 (H-1″) with δ_C 133.8 (C-3) and 5.06 (H-1‴) with 163.2 (C-7) in HMBC showed that the β-D-glucose was linked at 3-OH while the α-L-arabinose was linked at 7-OH. In addition, the correlations of δ_H 4.11 and 3.96 (H-6″) with δ_C 170.1 (OAc) indicated that an acetoxyl substitute at C-6″ position. Therefore, **1** was identified as kaempferol-7-*O*-α-L-arabinosyl-3-*O*-β-D-6″-acetylglucopyranoside.

Compound **2** was obtained as yellow needle prisms, $[\alpha]_D^{25}$ –18.03 (c 0.638, DMSO). Its molecular formula ($C_{30}H_{32}O_{17}$) was determined by negative HR-FABMS (found 663.1546, calcd. 663.1561). In comparison with compound **1**, the spectra (^1H, ^{13}C, COSY, HMQC and HMBC) are quite similar except one more acetyl signal in compound **2**. By analysis of the HMBC spectrum, the correlation of δ_H 4.86 (H-3″) with δ_C 170.0 (OAc) indicated that acetoxyl was linked at C-3″ position. Thus, compound **2** was elucidated as kaempferol-7-*O*-α-L-arabinosyl-3-*O*-β-D-3″, 6″-diacetylglucopyranoside.

Table 1 The assignment of ^{13}C NMR signals of compounds **1** and **2** (125MHz, δ in ppm)

No.	**1**	**2**	No.	**1**	**2**
C-2	156.4	156.4	1″	101.4	101.1
C-3	133.8	133.6	2″	75.4	72.3
C-4	177.9	177.8	3″	76.5	77.4
C-5	161.2	161.2	4″	70.2	68.0
C-6	99.7	99.7	5″	74.4	74.0
C-7	163.2	163.2	6″	63.1	62.7
C-8	94.8	94.8	3″-O$\underline{C}$OCH$_3$	/	170.0
C-9	157.4	157.5	3″-OCO$\underline{C}$H$_3$	/	21.4
C-10	105.8	105.8	6″-O$\underline{C}$OCH$_3$	170.1	170.1
C-1′	121.0	120.9	6″-OCO$\underline{C}$H$_3$	20.5	20.5
C-2′	131.2	131.3	1‴	100.5	100.5
C-3′	115.5	115.5	2‴	70.4	70.4
C-4′	160.5	160.6	3‴	72.7	72.7
C-5′	115.5	115.5	4‴	67.8	67.8
C-6′	131.2	131.3	5‴	66.2	66.2

Table 2 ^{1}H NMR spectral data for compounds **1** and **2** in DMSO-d_6 (500 MHz, δ in ppm)

No.	1	2
H-6	6.43 (d, J=1.8 Hz)	6.44 (d, J= 1.9 Hz)
H-8	6.79 (d, J=1.8 Hz)	6.79 (d, J= 1.9 Hz)
H-2′	8.04 (d, J=8.8 Hz)	8.03 (d, J= 9.0 Hz)
H-3′	6.89 (d, J=8.8 Hz)	6.90 (d, J= 9.0 Hz)
H-5′	6.89 (d, J=8.8 Hz)	6.90 (d, J=9.0 Hz)
H-6′	8.04 (d, J=8.8 Hz)	8.03 (d, J= 9.0 Hz)
OH-5	12.57 (s)	12.53 (s)
OH-4′	10.24 (s)	10.24 (s)
H-1″	5.39 (d, J=7.1 Hz)	5.48 (d, J=7.7 Hz)
H-1‴	5.06 (d, J= 6.5 Hz)	5.06 (d, J= 6.7 Hz)

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