

New Acetylated Flavonol Glycosides from *Knoxia corymbosa*

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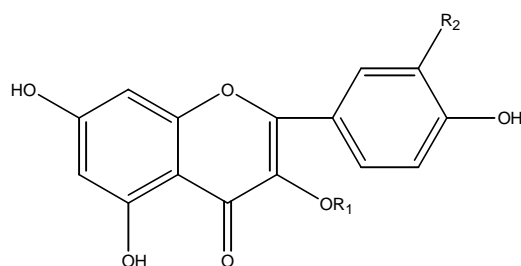
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Abstract: Two new diacetylated flavonol glycosides, kampferol-3-O- β -3'', 6''-diacetylglucopyranoside and quercetin-3-O- β -3'', 6''-diacetylglucopyranoside were isolated from *knoxia corymbosa*. Their structures were elucidated by spectroscopic evidents.

Keywords: Acetylated flavonol glycosides, *Knoxia corymbosa*.

In our continued investigation on the bioactive compounds of *Knoxia corymbosa*¹, another two new diacetylated flavonol glycosides, kampferol-3-O- β -3'', 6''-diacetylglucopyranoside and quercetin-3-O- β -3'', 6''-diacetylglucopyranoside were isolated from its EtOAc extraction.

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



1 R₁=3, 6-diacetylglucose, R₂=H

2 R₁=3, 6-diacetylglucose, R₂=OH

Compound **1** was isolated as yellow needles. Its formula, C₂₅H₂₄O₁₃, was determined by HRFAB-MS, found. 531.1130 (calcd.531.1138) as well as ¹³C NMR data. The ¹H NMR spectrum (DMSO-*d*₆) showed kaempferol's characteristic proton signals (**Table 2**) at 6.87(d, 2H, J=8.8Hz, H-3', 5'), 7.97(d, 2H, J=8.8Hz, H-2', 6'), 6.44(d, 1H, J=1.7Hz, H-8), and 6.21(d, 1H, J=1.7Hz, H-6)². The ¹³C NMR spectrum data also

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clearly indicated one flavonol skeleton and one glucose unit. Besides there is the information of two acetyl carbon signals in the ^{13}C NMR spectrum. Compared with our previous reported compound kaempferol-7-*O*- α -L-arabinosyl-3-*O*- β -D-3'', 6''-diacetyl glucopyranoside³, we deduced that the acetyls were linked to C-3''(δ 77.0) and C-6''(δ 62.3). The ^1H - ^1H COSY, HMQC and HMBC data proved our deduction. The presence of cross peaks between $\text{H}_{\text{Glc-1}}$ (δ 5.46, $J=7.2\text{Hz}$) and C-3 (δ 133.0) confirmed that the glucose unit was link at C-3. So compound **1** was identified as kampferol-3-*O*- β -D-3'', 6''-diacetylglucopyranoside.

Compound **2** was obtained as yellow needle prisms. Its formula was determined as $\text{C}_{25}\text{H}_{24}\text{O}_{14}$ by analysis its ^{13}C NMR spectrum data accompanied by FAB/MS which shows its quasi molecular ion peaks at m/z 548 and fragment ion at m/z 191. The analysis of its ^{13}C NMR data (**Table 1**) suggested that compound **2** has the similar skeleton with quercetin-3-*O*- β -D-glucopyranoside⁴. Its sugar unit was quite similar to compound **1** but quite different with the known compound quercetin-3-*O*- β -D-3'', 6''-diacetylgalacto pyranoside⁵.

Table 1 The assignment of ^{13}C NMR signals of compounds **1** and **2**

No.	1 ^a	2 ^b	No.	1 ^a	2 ^b
2	156.4	156.7	5'	115.1	116.5
3	133.0	133.3	6'	130.8	121.2
4	177.2	177.6	1''	100.9	101.0
5	161.2	161.6	2''	71.9	72.1
6	98.8	99.1	3''	77.0	77.5
7	164.3	164.6	4''	67.7	67.9
8	93.8	93.9	5''	73.6	73.9
9	156.7	157.0	6''	62.3	62.6
10	103.9	104.2	3''-OCOCH ₃	169.8	170.2
1'	120.7	121.8	3''-OCOCH ₃	20.1	21.4
2'	130.8	115.5	6''-OCOCH ₃	169.7	170.0
3'	115.1	145.1	6''-OCOCH ₃	21.0	20.4
4'	160.1	148.9	/	/	/

Table 2 ^1H NMR spectral data for **1** and **2**

No.	1 ^a	2 ^b
H-6	6.21(d, $J=1.7\text{Hz}$)	6.24(d, $J=2.1\text{Hz}$)
H-8	6.44(d, $J=1.7\text{Hz}$)	6.45(d, $J=2.1\text{Hz}$)
H-2'	7.97(d, $J=8.8\text{Hz}$)	7.58(m)
H-3'	6.87(d, $J=8.8\text{Hz}$)	/
H-5'	6.87(d, $J=8.8\text{Hz}$)	6.94 (d, $J=8.8\text{Hz}$)
H-6'	7.97(d, $J=8.8\text{Hz}$)	7.58(m)
OH-5	12.51(s)	12.60(s)
OH-7	10.89(s)	10.93(s)
OH-3'	/	9.75(s)
OH-4'	10.25(s)	9.27(s)
H-1''	5.46(d, $J=7.2\text{Hz}$)	5.49(d, $J=7.8\text{Hz}$)

^a ^1H NMR and ^{13}C NMR spectra was obtained at 500 and 125MHz, δ in ppm, $\text{DMSO}-d_6$

^b ^1H NMR and ^{13}C NMR spectra was obtained at 300 and 75MHz, δ in ppm, $\text{DMSO}-d_6$

Considering the above evidence, compound **2** was characterized as quercetin-

3-*O*- β -D-3'', 6''-diacetyl glucopyranoside.

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Received 9 December, 2002