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TWO AFZELECHIN GLYCOSIDES FROM *ARTHROMERIS MAIREI*

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Key Word Index—*Arthromeris mairei*; Polypodiaceae; roots; afzelechin glycoside; arthromerin A and B; multiflorin A; catharsis.

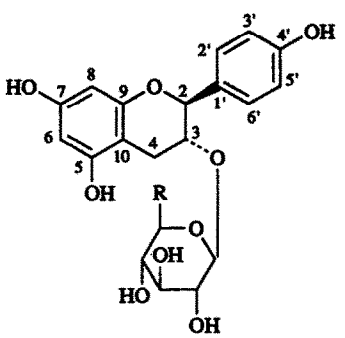
Abstract—Two new afzelechin glycosides named arthromerin A and B were isolated from the roots of *Arthromeris mairei*. Their structures were determined to be afzelechin-3-*O*-β-D-xylopyranoside and afzelechin-3-*O*-β-D-glucopyranoside, respectively. A purgative compound multiflorin A and another two known compounds were also isolated and identified.

INTRODUCTION

Arthromeris mairei, a Chinese purgative herb with little toxicity, is mainly used in the treatment of indigestion [1]. Its chemical constituents have not been previously reported. Our research on the polyphenol constituent of *A. mairei* led to the isolation of two new afzelechin glycosides named arthromerin A (**1**) and B (**2**). A purgative compound, kaempferol-3-*O*-(6-*O*-acetyl-glucopyranosyl)-(1→4)-α-L-rhamnopyranoside (multiflorin A, **3**) [2, 3] and another two known compounds, kaempferol-3-*O*-glucopyranosyl-(1→4)-α-L-rhamnopyranoside (**4**) [4] and β-sitosterol, were also isolated and identified. This paper deals with the isolation and structural elucidation of the two new glycosides.

RESULTS AND DISCUSSION

An ethanol extract of the roots of *A. mairei* was chromatographed on D101 resin with increasing concentrations of ethanol in water. The eluate with 10% ethanol was further separated and purified by column chromatography on silica gel to give arthromerins A and B.



R
1 H
2 CH_2OH

Arthromerin A (**1**) had the molecular formula $C_{20}H_{22}O_9$ which was supported by the $[M]^+$ at *m/z* 406 in the FD mass spectrum, and was shown to be polyphenolic by its colour reaction with 3% $FeCl_3$ in ethanol. The ^1H and ^{13}C NMR spectra of **1** showed the presence of an afzelechin moiety which was further confirmed by the following correlations in the ^1H–^1H COSY spectrum: δ4.92↔δ4.15↔δ2.82↔δ2.70↔δ4.15. The *p*-hydroxyphenyl group at C-2 was in *trans*-position to the hydroxy group at C-3 according to the large coupling constant of the H-2 signal ($J=6.7$ Hz) which was coincident with that of a (+)-catechin moiety ($J_{H-2}=7$ Hz) [5]. The ^1H–^1H COSY and ^{13}C NMR spectra of **1** revealed the presence of a β-D-xylopyranose residue. The H-1 signal of the xylopyranose residue resonated at higher field than that of quercetin-3,7-diglucopyranoside [4], but at the same field as that of 3-*O*-glucopyranosyl-4',7-dihydroxyflavanonol [4]. These findings confirmed the location of the xylopyranose residue at the C-3 position of the afzelechin moiety. This was further supported by the downfield shift of the C-3 signal of the afzelechin moiety in the ^{13}C NMR spectrum of **1** in comparison with that of a (+)-catechin moiety [5]. Acid hydrolysis of **1** gave xylose and afzelechin (**1a**). Arthromerin A was finally determined to be afzelechin-3-*O*-β-D-xylopyranoside.

Arthromerin B (**2**) had the molecular formula $C_{21}H_{24}O_{10}$ which was supported by its FD mass spectrum *m/z* 437 $[M+H]^+$ and elementary analysis, and was shown to be polyphenolic by its colour reaction with 3% $FeCl_3$ in ethanol. The ^1H and ^{13}C NMR spectra of **2** clearly revealed an afzelechin moiety as did those of **1**. The similarity of the coupling constant of the H-2 signal ($J=6.5$ Hz) to that of a (+)-catechin moiety demonstrated that the *p*-hydroxyphenyl group at C-2 was in a *trans*-position to that of the hydroxy group at C-3. The ^{13}C NMR spectrum of **2** revealed a β-D-glucopyranose residue. The similarities of the chemical shifts of the H-1 signal of the glucopyranose residue and that of the C-3 signal of the afzelechin moiety to those of **1** in the ^1H and ^{13}C NMR spectra determined the location of the glucopyranose residue at the C-3 position of the afzelechin moiety. Acid hydrolysis of **2** afforded glucose and **1a**.

Arthromerin B was determined to be afzelechin-3-*O*-*β*-D-glucopyranoside.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. ^1H–^1H COSY spectra were recorded at 400 MHz with TMS as int. standard.

Extraction and isolation. Dried and powdered roots of *Arthromeris mairei* (Branse) Ching. (1.9 kg), which were collected in the suburban district of Kunmin, Yunnan Province of China and identified by the Kunmin Institute of Medicine Inspection where the voucher specimen is deposited, were extracted with 95% EtOH (3 l × 2) and concd to give an extract (265 g). A portion (50 g) of the EtOH extract was subjected to CC on D101 resin with increasing concns of EtOH in H_2O. A portion (1.26 g) of the eluate with 90% EtOH (4.9 g) was chromatographed on silica gel (200–300 mesh) with increasing concns of MeOH in $CHCl_3$. The frs containing arthromerin A (**1**) and B (**2**) were further purified by CC on silica gel to give **1** (100 mg) and **2** (100 mg). A portion (1.5 g) of the eluate with 30% EtOH (3.1 g) was purified over silica gel with 20% MeOH in $CHCl_3$ to yield **4** (561 mg). A portion (2 g) of the eluate with 50% EtOH (13.1 g) was sepd by silica gel CC with 20% MeOH in $CHCl_3$ to give **3** (649 mg) and **4** (100 mg).

Arthromerin A (**1**). Off-white powder. $[\alpha]_D^{25}$ −3.79° (MeOH; *c* 1). FDMS *m/z* 406 $[M]^+$. UV λ_{max}^{MeOH} nm (log *ε*): 209 (6.4), 275 (5.4), 318 (4.9). ^1H NMR: Table 1. ^{13}C NMR: Table 2.

Acid hydrolysis of **1**. Compound **1** (40 mg) in 6% HCl (3 ml) was refluxed at 70° for 3 hr, and then neutralised with Na_2CO_3. After drying by distillation, the residue was redissolved in MeOH. Inorganic salts were removed by filtration. The filtrate was mixed with silica gel and subjected to CC on silica gel (200–300 mesh) with 20% MeOH in $CHCl_3$ to yield afzelechin (**1a**) (4 mg). This compound showed a positive colour reaction with 3% $FeCl_3$ in EtOH. FDMS *m/z* 298 $[M+Na+H]^+$, 257 $[M-OH]^+$. ^{13}C NMR: Table 2. The filtrate was subjected to PC with an authentic sample to find xylose [EtOAc–pyridine–H_2O(6:4:3), R_f = 0.53].

Table 1. ^1H NMR spectral data for compounds **1** and **2** [300 MHz, *δ*, *J* (in Hz) in parentheses, acetone-d_6 + D_2O]

H	1	2
2	4.92 *d* (6.7)	4.91 *d* (6.5)
3	4.15 *m*	4.21 *m*
4	2.82 *dd* (5.4, 16.4)	2.82 *dd* (4.7, 16.2)
4′	2.70 *dd* (7.0, 16.4)	2.71 *dd* (6.9, 16.2)
6	6.04 *d* (2.3)	6.04 *br s*
8	5.91 *d* (2.3)	5.91 *br s*
2′, 6′	7.25 (2H) *d* (8.5)	7.26 (2H) *d* (8.1)
3′, 5′	6.84 (2H) *d* (8.5)	6.84 (2H) *d* (8.1)
Xylose or glucose residue		
1	4.19 *d* (7.1)	4.26 *d* (8.5)
2	3.10 *dd* (7.1, 8.4)	*
3	3.28 *d* (8.4)	*
4	3.48 *m*	3.11 *t* (8.4)
5	3.85 *dd* (5.0, 11.4)	*
5′	3.19 *dd* (9.6, 11.4)	—
6	—	3.84 *br d* (11.4)
6′	—	3.62 *dd* (5.1, 11.4)

*3.32, complex, 3H in total.

Table 2. ^{13}C NMR spectral data for compounds **1**, **1a** and **2** (75 MHz, *δ*, acetone-d_6 + D_2O)

C	1	1a	2
2	79.9 (1)*	77.3	79.8 (1)
3	76.4 (1)	69.7	75.8 (1)
4	27.5 (2)	25.0	26.8 (2)
5	156.4 (0)[a]	155.6[b]	156.4 (0)[c]
6	96.2 (1)	96.1	96.2 (1)
7	157.1 (0)[a]	157.2[b]	157.0 (0)[c]
8	95.3 (1)	94.0	95.4 (0)
9	157.7 (0)[a]	157.8[b]	157.6 (0)[c]
10	100.1 (0)	100.5	100.1 (0)
1′	130.9 (0)	130.0	131.1 (0)
2′ 6	129.0 (1)	129.0	129.0 (1)
3′ 5	115.9 (1)	115.1	115.9 (1)
4′	158.1 (0)[a]	159.9[b]	157.9 (0)[c]
Xylose or glucose residue			
1	104.1 (1)		103.8 (1)
2	73.9 (1)		74.8 (1)
3	76.4 (1)		77.5 (1)
4	70.5 (1)		71.4 (1)
5	65.8 (2)		77.5 (1)
6	—		62.9 (2)

*Number of bonded H in parentheses, determined by DEPT spectra.

[a–c] Values with the same superscript are interchangeable.

Arthromerin B (**2**). Off-white powder. $[\alpha]_D^{25}$ −3.03° (MeOH; *c* 1), (found: C, 57.6; H, 5.7. $C_{21}H_{24}O_{10}$ requires: C, 57.8; H, 5.5%). FDMS *m/z* 437 $[M+H]^+$. UV λ_{max}^{MeOH} nm (log *ε*): 212 (6.6), 275 (5.6), 322 (4.9). ^1H NMR: Table 1. ^{13}C NMR: Table 2.

Acid hydrolysis of **2**. **2** (3 mg) in 6% HCl (0.5 ml) was refluxed at 70° for 3 hr and then subjected to silica gel TLC with an authentic sample to find **1a** [$CHCl_3$–MeOH (8:1), R_f = 0.62], and subjected to PC with an authentic sample to find glucose [EtOAc–pyridine–H_2O (6:4:3), R_f = 0.45].

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