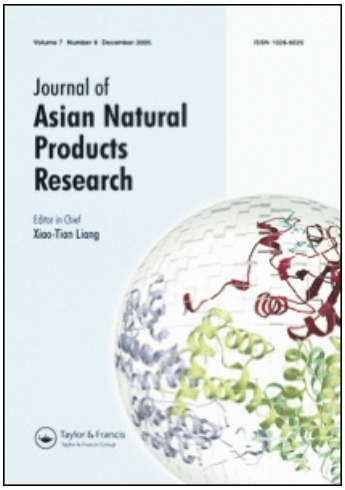

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Several chromones from the stems of *Polygonum aubertii* Henry

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NOTE

Several chromones from the stems of *Polygonum aubertii* Henry

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Two new 2-alkylchromanones, 2-tricosyl-2,5,7-trihydroxy-chromanone (**6**) and 2-pentacosyl-2,5,7-trihydroxy-chromanone (**7**), together with five known 2-alkylated chromones and chromanones (**1**–**5**), were isolated from the stems of *Polygonum aubertii* Henry. The structures of these compounds were established by spectroscopic methods including extensive 1D, 2D NMR (^{1}H-^{1}H COSY, HSQC, and HMBC), and HR-ESI-MS techniques. In addition, a plausible biosynthetic pathway for these compounds is described.

Keywords: *Polygonum aubertii*; Polygonaceae; chromone; chromanone

1. Introduction

The genus *Polygonum* (polygonaceae) comprises ca. 300 species, and is mainly distributed in the north temperate zone [1]. Most of these plant species were found to be of significant biological value for their cytotoxic, anti-inflammatory, and anti-microbial effects [2]. *Polygonum aubertii* Henry is well known as a scandent shrub and nectariferous plant [3,4]. Its rhizomes and stems are used in traditional herbal medicine for the treatment of pulmonary disease, cat fever, and rheumatoid arthritis, and improving acuity of vision [5–7]. So far as we know, previous phytochemical investigation on this plant revealed the presence of α-L-butylsorpyranoside, 2,4-diphenylpyrrole, stagmast-4-en-3-one, syringic acid, stagmast-5-en-3-ol-7-one, tetracosanoic acid, and β-sitosterol [7]. As a part of our ongoing research of the natural occurrence of herbal medicine from the northwestern plant resources of China, we studied deeply on the chemical constituents of the stems of *P. aubertii*. Two new 2-alkylchromanones, 2-tricosyl-2,5,7-trihydroxy-chromanone (**6**) and 2-pentacosyl-2,5,7-trihydroxy-chromanone (**7**), together with five known 2-alkylated chromones and chromanones (**1**–**5**) have been isolated. Herein, we report the isolation and structural elucidation of two new 2-alkylchromanones. The biosynthetic pathway of 2-alkylated chromone and chromanone was also inferred.

2. Results and discussion

The structures of chromone compounds **1**–**3** were elucidated as 5,7-dihydroxy-2-heptadecyl-chromone (**1**), 5,7-dihydroxy-2-nonadecyl-chromone (**2**), and 5,7-dihydroxy-2-heneicosyl-chromone (**3**) by comparison of their spectral data with those reported in the literature [8], and they were isolated for the first time from this resource. Acetylation of **1**–**3** obtained monoacetates

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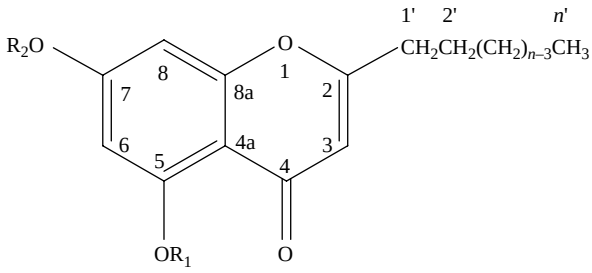
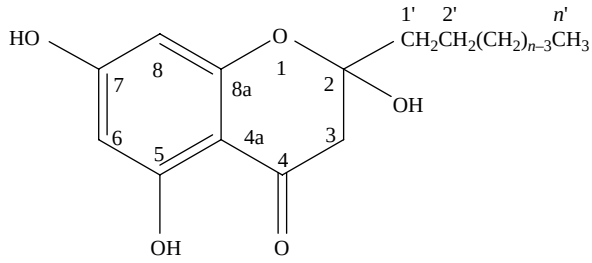


1. $R_1 = R_2 = H$ $n = 17$
2. $R_1 = R_2 = H$ $n = 19$
3. $R_1 = R_2 = H$ $n = 21$
1a. $R_1 = H$ $R_2 = Ac$ $n = 17$
2a. $R_1 = H$ $R_2 = Ac$ $n = 19$
3a. $R_1 = H$ $R_2 = Ac$ $n = 21$
1b. $R_1 = Ac$ $R_2 = Ac$ $n = 17$
2b. $R_1 = Ac$ $R_2 = Ac$ $n = 19$
3b. $R_1 = Ac$ $R_2 = Ac$ $n = 21$



4. $n = 19$
5. $n = 21$
6. $n = 23$
7. $n = 25$

Figure 1. The structures of compounds **1**–**7**.

1a–**3a** and diacetates **1b**–**3b**. Their structures were elucidated as 7-acetoxy-2-alkyl-5-hydroxy-chromone (**1a**–**3a**) and 2-alkyl-5,7-diacetoxy-chromone (**1b**–**3b**) (Figure 1) and the NMR spectral data were also assigned by extensive spectroscopic studies including 1D and 2D NMR for the first time (Table 1).

Compounds **4**–**7** were isolated as a white amorphous powder. The HR-ESI-MS of compounds **4**–**7** exhibited four quasi-molecular ion peaks at *m/z* 463.3416 $[M\mathbf{4} + H]^+$, 491.3726 $[M\mathbf{5} + H]^+$, 519.4033 $[M\mathbf{6} + H]^+$, and 547.4343 $[M\mathbf{7} + H]^+$, suggesting that **4**–**7** were a mixture of homologs. Accordingly, the

Table 1. ^1H (400.13 MHz) and ^{13}C (100.62 MHz) NMR spectral data of compounds **1a**–**3a** and **1b**–**3b** in $CDCl_3$.

	1a–**3a**		**1b**–**3b**	
No.	δ_H	δ_C	δ_H	δ_C
2		171.4		168.8
3	6.07 (1H, s)	108.5	6.01 (1H, s)	110.8
4		182.9		176.3
4a		108.7		114.7
5	12.72 (OH, s)	157.1		150.1
6	6.50 (1H, d, 2.0)	105.2	6.78 (1H, d, 2.4)	113.3
7		155.6		153.6
8	6.67 (1H, d, 2.0)	100.8	7.18 (1H, d, 2.4)	108.9
8a		161.9		157.9
$1'$	2.58 (2H, t, 8.0)	34.3	2.54 (2H, t, 7.6)	33.8
5-CO				169.5
5-CH_3			2.41 (3H, s)	21.2
7-CO		168.4		168.1
7-CH_3	2.30 (3H, s)	21.2	2.33 (3H, s)	21.1

Table 2. ^{1}H (400.13 MHz) and ^{13}C (100.62 MHz) NMR spectral data of compounds **4**–**7** in acetone-d_6.

No.	δ_H	δ_C	No.	δ_H	δ_C
2	3.20 (OH, s)	102.5	7		166.4
3	2.62 (1H, s), 2.95 (1H, s)	44.6	8	5.89 (1H, d, 2.0)	95.4
4		195.8	8a		160.9
4a		101.9	1′	1.90 (m)	40.6
5		163.5	2′-(n − 1)′	1.26 − 1.40 (m)	28.4 − 31.7
6	5.86 (1H, d, 2.0)	95.6	n′	0.85 (3H, t, 6.8)	13.4

molecular formulas were established as $C_{28}H_{46}O_5$ for **4**, $C_{30}H_{50}O_5$ for **5**, $C_{32}H_{54}O_5$ for **6**, and $C_{34}H_{58}O_5$ for **7**. The IR spectrum showed characteristic absorption bands of hydroxyl groups at 3376 cm^{-1}, an α,β-unsaturated ketone at 1658 cm^{-1}, and an aromatic ring at 1605, 1509, and 1467 cm^{-1}, as well as phenyl groups at 1356, 1375 cm^{-1}. The UV spectrum also confirmed the existence of these unsaturated functional groups with the absorption maxima at 221, 227, and 333 nm. The ^{1}H NMR spectrum (Table 2) displayed two aromatic protons at δ_H 5.86 (d, 1H, $J = 2.0$ Hz, H-6) and 5.89 (d, 1H, $J = 2.0$ Hz, H-8) in a meta-position, indicating the existence of a tetrasubstituted aromatic ring. The NMR spectral data at δ_C 163.5 (C-5), 166.4 (C-7), and 160.9 (C-8a) were attributed to the A-ring in 5,7-dioxygenated flavonoid, and data at δ_C 102.5 (C-2), 44.6 (CH_2-3), and 195.8 (C-4), as well as protons at δ_H 2.62 and 2.95 (H_2-3) were attributable to a saturated C-ring in flavanone [9]. Except for the aromatic ring signals, the rest of the signals at δ_H 0.85 (t, 3H, $J = 6.8$ Hz) and 1.26–1.40 (m) being made up of a methyl group and a long aliphatic chain suggested that the compounds were not flavanones but 2,5,7-trihydroxy-chromanones, substituted at C-2 with a saturated alkyl group. The numbers of the saturated alkyl chains could be confirmed as $C_{19}H_{39}$ for **4**, $C_{21}H_{43}$ for **5**, $C_{23}H_{47}$ for **6**, $C_{25}H_{51}$ for **7** by four quasi-molecular ion peaks in the HR-ESI-MS spectrum. The results could also be supported by the corresponding ^{13}C NMR spectral data (Table 2). In the HMBC spectrum, the H-3 proton showed ^{2}J correlation with a carbonyl carbon (δ_C 195.8) and with an oxygen-bearing quaternary carbon at δ_C 102.5 (C-2). A methylene multiplet at δ_H 1.90 (C-1′) showed ^{2}J correlation with C-2, which confirmed the attachment of the side chain at C-2 (Figure 2). Based on the above analysis, the structures of compounds **4**–**7** were identified as 2-nonadecyl-2,5,7-trihydroxy-chromanone (**4**), 2-heneicosyl-2,5,7-trihydroxy-chromanone (**5**), 2-tricosyl-2,5,7-trihydroxy-chromanone (**6**), and 2-pentacosyl-2,5,7-trihydroxy-chromanone (**7**) [8]. However, the stereo configuration of C-2 in compounds **4**–**7** could not be confirmed. Among them, compounds **4** and **5** are described for the first time in *P. aubertii*. Compounds **6** and **7** are new ones.

A plausible hypothesis concerning the biosynthesis of 2-alkylated chromone and chromanone is shown in Figure 3. The pathway is initiated by the Aldol-type condensation of malonyl-coenzyme A (malonyl-CoA). In addition, a fatty acid (unit **A**) is produced with the acyl chain growing by two-carbon units in each round

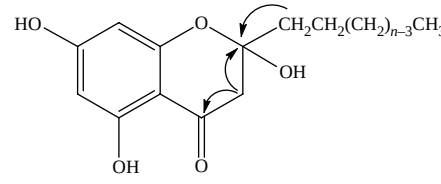


Figure 2. Key HMBC correlations of **4**–**7**.

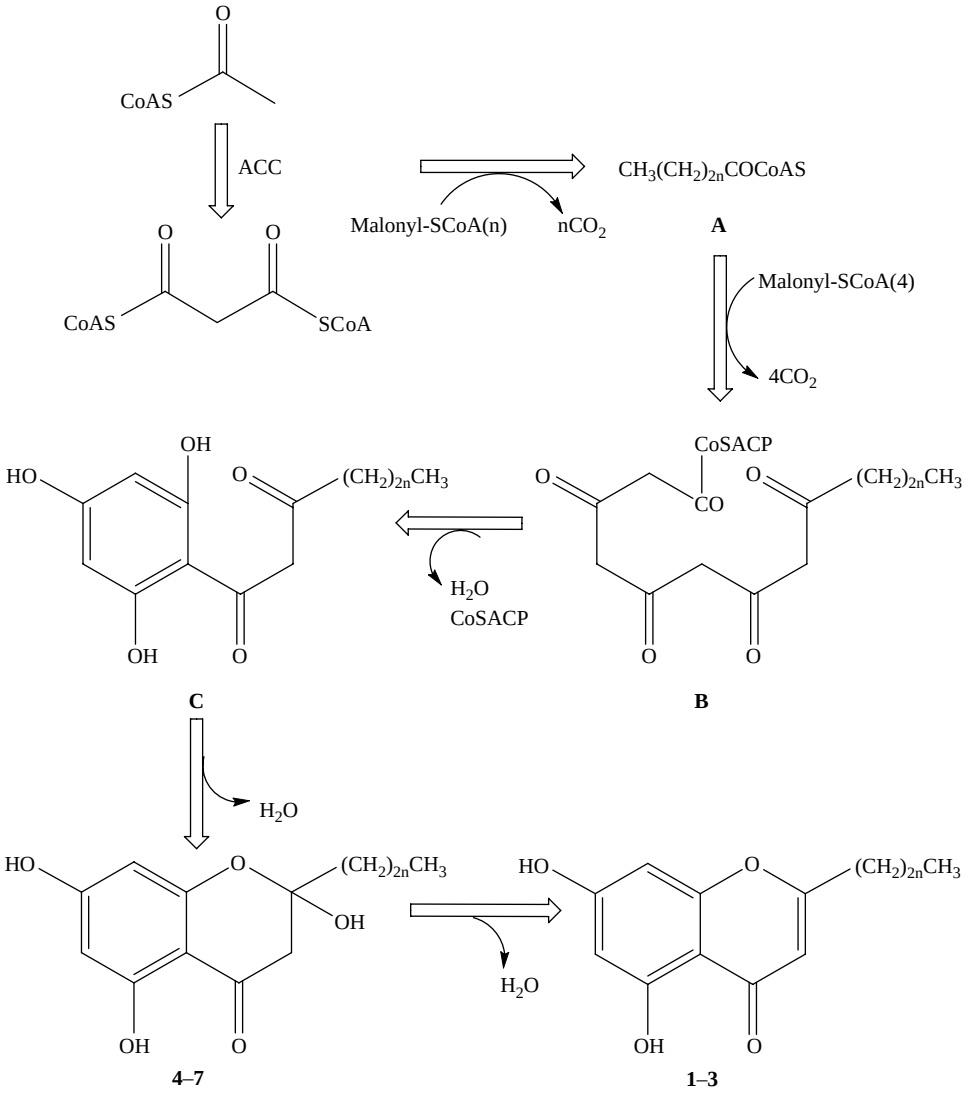


Figure 3. Predicted biosynthesis pathways of compounds **1**–**7**.

[10–13]. Then, unit **A** extends four times of malonyl-CoAs to 3-oxoacyl-(acyl carrier proteins) without the reductive removal of oxygens, yields a polyoxomethylene intermediate **B**. The Claisen-type ring closure of intermediate **B** yields unit **C** [14]. Then, the concerted liberation of ACP and decarboxylation from unit **C** furnish 2-alkylchromanone (compounds **4**–**7**). The dehydration of 2-alkylchromanone can give 2-alkylchromone (compounds **1**–**3**).

3. Experimental

3.1 General experimental procedures

Melting point was recorded on an X-4 digital micro-melting apparatus and is uncorrected. Optical rotation was measured on a Perkin-Elmer 241 automatic polarimeter. UV spectra were

determined on a Shimadzu UV-240 ultraviolet spectrograph and IR spectra on a Nicolet170SX FT-IR spectrophotometer. Both 1D and 2D NMR spectra were determined on a Varian INOVA-400 FTNMR instrument operating at 400.13 and 100.62 MHz, respectively, with TMS as the internal reference. The chemical shift values are reported in ppm (δ) units and the coupling constants (J) are in Hz; HR-ESI-MS were carried out on a Bruker APEX II spectrometer. Silica gel (200–300 mesh) for column chromatography (CC) and GF_{254} (10–40 mesh) for TLC were purchased from Qingdao Marine Chemical Group Co., Qingdao, China.

3.2 Plant material

The stems of *P. aubertii* Henry were collected in the city of Lanzhou, Gansu Province, China, in February 2001, and identified by Dr Huan-Yang Qi. A voucher specimen (No. 2006P01) has been deposited in the Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China.

3.3 Extraction and isolation

The air-dried stems of *P. aubertii* (7.0 kg) were extracted with 95% aqueous EtOH three times at room temperature for 7 days. The combined extracts were concentrated *in vacuo*. The residue (310.0 g) was suspended in 1000 ml water, and then extracted successively with petroleum ether (PE), ethyl acetate, and *n*-butanol. The PE extract (65.0 g) was subjected to CC over silica gel (1.0 kg, 100–200 mesh), eluting with PE–acetone (v/v = 30:1, 20:1, 15:1, 10:1, 8:1, 5:1, 3:1, 2:1, 1:1, each about 8.0 liters) to afford nine fractions (A1–A9) after concentration at reduced pressure. Fraction A1 was subjected to a silica gel CC eluted with PE–EtOAc (v/v, 2:1) to give compounds **1**–**3** (14.7 mg), after being purified by pre-TLC with PE–acetone (v/v, 2:1). Compounds **4**–**7** (115 mg) were subsequently purified from fraction A3, by silica gel CC eluting with $CHCl_3$–EtOAc (v/v, 20:1).

3.3.1 Compounds *4–7*

2-Alkyl-2,5,7-trihydroxy-chromanones (**4**–**7**), $C_{28}H_{46}O_5$ (**4**), $C_{30}H_{50}O_5$ (**5**), $C_{32}H_{54}O_5$ (**6**), $C_{34}H_{58}O_5$ (**7**); white amorphous powder; mp 108–109°C; $[\alpha]_D^{18} + 6$ ($c = 0.1$, acetone); UV (CH_3OH) λ_{max} (log ε): 221, 227, 333 nm; IR (film) ν_{max}: 3376, 1658, 1605, 1509, 1467, 1375, 1356 cm^{-1}; ^1H and ^{13}C NMR spectral data, see Table 2; HR-ESI-MS: *m/z* 463.3416 $[M\mathbf{4} + H]^+$ (calcd for $C_{28}H_{47}O_5$, 463.3418), 491.3726 $[M\mathbf{5} + H]^+$ (calcd for $C_{30}H_{51}O_5$, 491.3731), 519.4033 $[M\mathbf{6} + H]^+$ (calcd for $C_{32}H_{55}O_5$, 519.4044), and 547.4343 $[M\mathbf{7} + H]^+$ (calcd for $C_{34}H_{59}O_5$, 547.4357).

3.4 Acetylation of compounds *1–3*

Acetylation was done in pyridine and acetic anhydride (1:1) for 12 h at room temperature. The mono- and di-acetylated products **1a**–**3a** and **1b**–**3b** were obtained.

3.4.1 Compounds *1a–3a*

7-Acetoxy-2-alkyl-5-hydroxy-chromones (**1a**–**3a**), $C_{28}H_{42}O_5$ (**1a**), $C_{30}H_{46}O_5$ (**2a**), $C_{32}H_{50}O_5$ (**3a**); white amorphous powder; ^1H and ^{13}C NMR spectral data, see Table 1; HR-ESI-MS: *m/z* 459.3121 $[M\mathbf{1a} + H]^+$ (calcd for $C_{28}H_{43}O_5$, 459.3105), 487.3415 $[M\mathbf{2a} + H]^+$ (calcd for $C_{30}H_{47}O_5$, 487.3418), and 515.3721 $[M\mathbf{3a} + H]^+$ (calcd for $C_{32}H_{52}O_5$, 515.3731).

3.4.2 Compounds *1b–3b*

2-Alkyl-5,7-diacetoxy-chromones (**1b**–**3b**), $C_{30}H_{44}O_6$ (**1b**), $C_{32}H_{48}O_6$ (**2b**), $C_{34}H_{52}O_6$ (**3b**); white amorphous powder; ^1H and ^{13}C NMR spectral data, see Table 1; HR-ESI-MS: *m/z* 501.3222 $[M\mathbf{1b} + H]^+$ (calcd for $C_{30}H_{45}O_6$, 501.3211), 529.3523

$[M\mathbf{2b} + H]^+$ (calcd for $C_{32}H_{49}O_6$, 529.3524), and 557.3844 $[M\mathbf{3b} + H]^+$ (calcd for $C_{34}H_{53}O_6$, 557.3837).

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