Phytochemistry, Vol. 20, No. 11, pp. 2601–2602, 1981.
Printed in Great Britain.

0031-9422/81/112601-02 $02.00/0

AROMATIC ESTERS FROM *SOLIDAGO DECURRENS*

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(*Received* 27 *March* 1981)

Key Word Index—*Solidago decurrens;* Compositae; benzyl benzoates; cinnamyl angelates.

Abstract—From *Solidago decurrens* several new benzyl benzoates and two cinnamyl angelates were variously isolated from stems, flower and root.

The Chinese folk medicinal plant *Solidago decurrens* Lour.,† a subsp. of *S. virgaurea*. L. (Compositae, tribe Astereae), has long been used as antibacterial and anti-inflammatory agent. Earlier investigations on this genus revealed the presence of acetylenic compounds [1], sesquiterpenes [2], diterpenes [3–6] and benzyl benzoate derivatives [7], but *S. decurrens* so far has not been investigated chemically. We now have isolated ten compounds, namely sitosterol, two isomers of acetylenic compounds (**1a** and **1b**) and seven benzyl benzoates (**2**–**8**). Compounds **2** [7], **3** [7] and **4**, **5** and **6** [8] were obtained from flowers and **2**, **3** and **6**–**8** from roots. The constituents of the stems are nearly the same as those of the flowers. The spectral data of **4** and **5** were similar to those of **2** and **3**. The structures clearly followed from the MS spectra and the ^{1}H NMR data (Table 1), especially if compared with those of **2** and **3**. Compounds **7** and **8** only were present in the roots, their molecular formulae being $C_{18}H_{22}O_6$ and $C_{17}H_{20}O_5$, respectively. The structures clearly followed from the ^{1}H NMR data (Table 2). Saponification of **7** afforded 3,5-dimethoxy-4-hydroxycinnamic alcohol (**9**).

Table 1. ^{1}H NMR spectral data of compounds **4** and **5** (400 MHz, $CDCl_3$, TMS as internal standard)

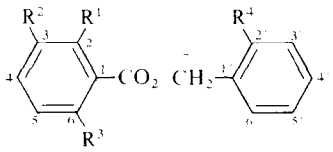
	4	**5**
H-3	6.55 *d*	
H-4 }	7.25 *m*	6.87 *d*
H-5 }		6.58 *d*
H-3′	6.88 *br d*	6.88 *br d*
H-4′	7.28 *m*	7.28 *ddd*
H-5′	6.94 *ddd*	6.94 *br dd*
H-6′	7.47 *dd*	7.47 *dd*
H-7′	5.45 *s*	5.45 *s*
OMe	3.81 *s*	3.84 *s*
	3.77 *s*	3.81 *s*
	3.77 *s*	3.79 *s*
		3.77 *s*

J (Hz): 4,5 = 3′,4′ = 4′,5′ = 5′,6′ = 8; 4′,6 = 2.

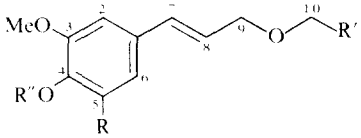
MeCH=CH[C≡C]$_2$**CH=CHCO$_2$**Me

c *c* **1a**

c *t* **1b**



	2	**3**	**4**	**5**	**6**
R^1	OMe	OMe	OMe	OMe	OH
R^2	H	OMe	H	OMe	H
R^3	OMe	OMe	OMe	OMe	OMe
R^4	H	OMe	OMe	OMe	



7 R = H, R′ = Ang, R″ = Ac
8 R = OMe, R′ = Ang, R″ = Ac
9 R = OMe, R′ = H, R″ = H

†*Solidago decurrens* is named Yi-Zhi-Huang-Hua in China (meaning that the plant produces a yellow flower).

Table 2. ^{1}H NMR spectral data of compounds **7**–**9** (400 MHz, $CDCl_3$, TMS as int. standard)

	7	8	9
H-2 }		6.65 *s*	6.63 *s*
H-5 }	7.00 *m*	—	—
H-6 }		6.65 *s*	6.63 *s*
H-7	6.63 *br d*	6.61 *br d*	6.52 *br d*
H-8	6.26 *dt*	6.24 *dt*	6.23 *dt*
H-9	4.72 *dd*	4.73 *dd*	4.32 *br d*
OCOR	6.24 *br q*	6.24 *br q*	—
	2.06 *br s*	2.06 *br s*	—
OMe	3.86 *s*	3.86 *s*	3.91 *s*
		3.86 *s*	3.91 *s*
OAc	2.11 *s*	2.11 *s*	—

J (Hz): 7,8 = 16; 8,9 = 7.5.

Derivatives of benzyl benzoate have been isolated from several Compositae (*Ageratina* [9], *Aster* [8], *Hirpicum* [10] and *Solidago* [7]), while angelates of cinnamic alcohols were isolated for the first time.

EXPERIMENTAL

The air-dried plant material (voucher deposited in the Shanghai Inst. of Materia Medica) was extracted with Et_2O and the extracts obtained first separated by CC (Si gel) and further by TLC (Si gel) (Et_2O–petrol, 1:1). Known compounds were identified by comparing the IR and ^{1}H NMR spectra with those of authentic material.

The 3 g extract from flowers (equal to 100 g plant material) afforded 90 mg **2**, 15 mg **3**, 10 mg **4**, 45 mg **5**, while the extract from 200 g roots gave 100 mg **2**, 15 mg **3**, 90 mg **6**, 10 mg **7** and 15 mg **8**, 14 mg sitosterol, 60 mg **1a** and 20 mg **1b**.

2-Methoxybenzyl-2,3,6-trimethoxybenzoate (**4**). Colourless crystals, mp 100°, UV $\lambda_{max}^{(Et_2O)}$ nm: 278; MS *m/z* (rel. int.): 332 $[M]^+$ (83) ($C_{18}H_{20}O_6$), 195 $[C_{10}H_{11}O_4]^+$ (88), 137 $[C_8H_9O_2]^+$ (16), 121 $[C_8H_9O]^+$ (100); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (COOR), 1600, 1490 (aromatic).

2-Methoxybenzyl-2,6-dimethoxybenzoate (**5**). Colourless crystals, mp 73°; MS *m/z* (rel. int.): 302 $[M]^+$ (14) ($C_{17}H_{18}O_5$), 165 $[C_9H_9O_3]^+$ (100), 121 $[C_8H_9O]^+$ (54); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1725 (COOR), 1600, 1495 (aromatic).

3,5-Dimethoxy-4-acetoxycinnamyl angelate (**7**). Colourless crystals, mp 110°; MS *m/z* (rel. int.): 334.1416 $[M]^+$ (10) ($C_{18}H_{22}O_6$), 252 $[C_{13}H_{16}O_5]^+$ (25), 83 $[C_5H_7O]^+$ (100); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1738 (COOR), 1596, 1490 (aromatic), 1645 (C=C).

3-Methoxy-4-acetoxycinnamyl angelate (**8**). Colourless oil, MS *m/z* (rel. int.): 304.1311 $[M]^+$ (7) ($C_{17}H_{20}O_5$), 222 $[C_{12}H_{14}O_4]^+$ (14), 83 $[C_5H_7O]^+$ (100); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735 (COOR), 1590, 1500 (aromatic), 1645 (C=C).

4 mg **7** was saponified with KOH in EtOH yielding 1 mg 3,5-dimethoxy-4-hydroxycinnamic alcohol (**9**); MS *m/z* (rel. int.): 210 $[M]^+$ (100) ($C_{11}H_{14}O_4$), 193 $[C_{11}H_{13}O_3]^+$ (8), 167 $[C_9H_{11}O_3]^+$ (81).

Acknowledgements—Z.C. thanks the Alexander von Humboldt Foundation for a stipend, and Mrs. S. L. Huang, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, for identification of the plant material.

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