Four New Compounds from *Sinacalia tangutica*

by **Ying Zhu***[a]), **Yan Zhao**[a]), **Guo-Du Huang**[a]), and **Wang-Suo Wu**[b])

[a]) State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China (phone: +86-931-3698769; fax: +86-931-8912582; e-mail: zhuy@lzu.edu.cn)

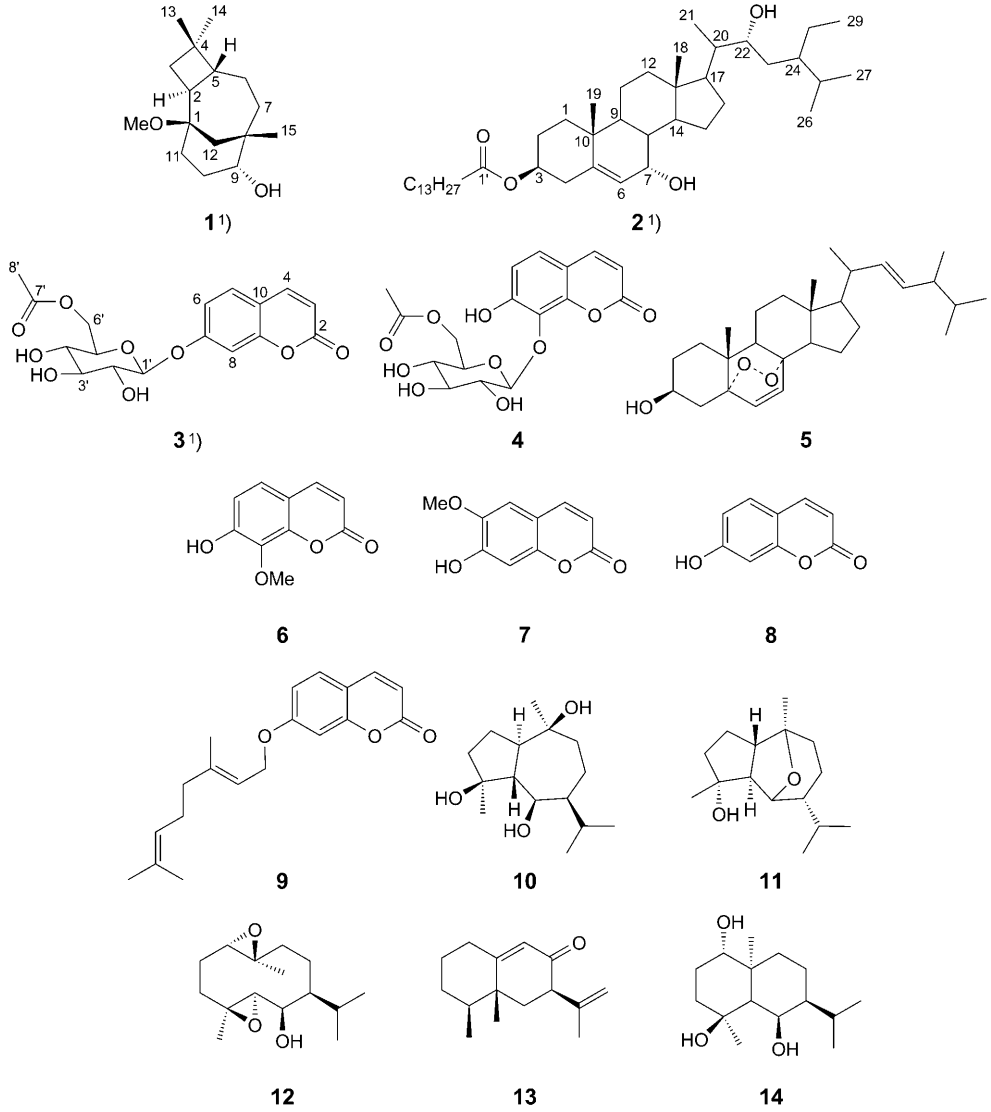
[b]) Radiochemistry Laboratory, Lanzhou University, Lanzhou 730000, P. R. China

Four new compounds, 9α-hydroxy-1β-methoxycaryolanol (**1**), stigmast-5-ene-7α,22α-diol-3β-tetradecanoate (**2**), 7-*O*-(6′-acetoxy-β-D-glucopyranosyl)coumarin (**3**), and 8-*O*-(6′-acetoxy-β-D-glucopyranosyl)-7-hydroxycoumarin (**4**), together with ten known compounds, were isolated from the aerial parts of *Sinacalia tangutica*. The structures of the new compounds were established by means of extensive spectroscopic analyses (1D- and 2D-NMR, EI-MS, HR-ESI-MS, as well as IR and UV) and by comparison of their spectroscopic data with those of structurally related compounds reported in the literature.

1. Introduction. – The genus *Sinacalia* belongs to the family Compositae and is widely distributed in the West China. It is a Chinese endemic genus and consists of only four species. *Sinacalia tangutica* (MAXIM) has long been used as a folk medicine for expectorant, anti-cough, antihistamine, antiradical and cathartic purposes [1]. Up to now, only the phytochemical constitutes of *S. tangutica* have been studied. A new flavan was isolated from *S. tangutica* distributing in the southeast of Gansu province [2]. Monoterpenes and caryophyllane sesquiterpene were obtained from this plant distributing in the central region of Gansu province [3]. An isopentenyl acetophenon derivative, eremophilane sesquiterpenes, cycloartene triterpenes and coumarins were reported from *S. tangutica* from the east of Qinghai province [4]. From the above information, we found that the chemical constitutes of *S. tangutica* had some regional differences.

Here, we report four new compounds, 9α-hydroxy-1β-methoxycaryolanol (**1**), stigmast-5-ene-7α,22α-diol-3β-tetradecanoate (**2**), 7-*O*-(6′-acetoxy-β-D-glucopyranosyl)coumarin (**3**), and 8-*O*-(6′-acetoxy-β-D-glucopyranosyl)-7-hydroxycoumarin (**4**), together with ten known compounds, including a steroid, **5**, four coumarins **6**–**9**, and five sesquiterpenes, **10**–**14**, from the aerial parts of *S. tangutica* distributing in the southwest of Gansu province. Among them, compounds **5**, **7**, and **9**–**14** were isolated from the title plant for the first time. This further gives evidence that the chemical compositions of plants have a relation with their growth environment.

2. Results and Discussion. – The structures of the known compounds were elucidated by comparing their physical and spectral data with those reported in the literature as 5α,8α-epidioxyergosta-6,22-dien-3β-ol (**5**) [5], 7-hydroxy-8-methoxycou-



marin (**6**) [6], 6-methoxy-7-hydroxycoumarin (**7**) [7], 7-hydroxycoumarin (**8**) [6], aurapten (**9**) [8], 1α,5β-guaiane-4β,6β,10β-triol (**10**) [9], chrysothol (**11**) [9], 1α,10β,4β,5α-diepoxy-7αH-germacran-6β-ol (**12**) [10], eremophila-9,11-dien-8-one (**13**) [11], 1α,4β,6β-trihydroxyeudesmane (**14**) [12].

Compound **1** was obtained as colorless crystals. The EI-MS showed the molecular-ion peak at *m*/*z* 252, and the molecular formula $C_{16}H_{28}O_2$ was deduced from the pseudomolecular-ion peak at *m*/*z* 270.2431 ($[M+NH_4]^+$, $C_{16}H_{32}NO_2^+$; calc. 270.2428)

[1]) Arbitrary atom numbering; for systematic names, see *Exper. Part.*

in the HR-ESI-MS, which indicated three degrees of unsaturation. The IR (film) spectrum showed absorption bands of a OH (3369.5 cm^{-1}) and a MeO group (2853.9 cm^{-1}). The ^{13}C-NMR (DEPT) spectra (*Table 1*) gave 16 C-atoms, including three Me, six CH_2, and three CH groups, including one oxymethine group (δ(C) 72.4, *d*), along with three quaternary C-atoms, including one oxygenated C-atom (δ(C) 75.3, *s*), and one MeO group. The signals of the three Me groups, δ(C) 30.4 (*q*), 26.7 (*q*), and 20.6 (*q*) were characteristic signals for a caryolane sesquiterpene [13][14]. In the ^{1}H,^{1}H-COSY experiment, the key correlations of H–C(2) (δ(H) 2.10–2.14, *m*) with H_b–C(3) (δ(H) 1.62–1.66, *m*) and H–C(5) (δ(H) 1.88–1.94, *m*); H_b–C(6) (δ(H) 1.33–1.37, *m*) with H–C(5) (δ(H) 1.88–1.94, *m*) and H_a–C(7) (δ(H) 1.10–1.14, *m*); and H_a–C(10) (δ(H) 1.76–1.80, *m*) with H–C(9) (δ(H) 3.45, *dd*) and H_b–C(11) (δ(H) 1.68–1.70, *m*) were observed. These findings further confirmed that **1** has a caryolane sesquiterpene skeleton with each a OH and a MeO substituent. The positions of the MeO and OH groups were determined by the HMBC correlations of MeO (δ(H) 3.16, *s*) with C(1) (δ(C) 75.3, *s*) and Me(15) (δ(H) 0.91, *s*) and H_b–C(11) (δ(H) 1.68–1.70, *m*) with C(9) (δ(C) 72.4, *d*), indicating that the MeO group and the OH group were linked at C(1) and C(9), respectively.

Table 1. *^{1}H-, ^{13}C-NMR* (DEPT)[a]), *and HMBC Data of* **1**[1]) ($CDCl_3$, δ in ppm, *J* in Hz)

	δ(H)	δ(C)	HMBC (C → H)
C(1)		75.3 (*s*)	Me(15), H_b–C(11), CH_2(12), MeO
H–C(2)	2.10–2.14 (*m*)	38.6 (*d*)	Me(13), Me(14), CH_2(11), CH_2(12)
CH_2(3)	a: 1.50–1.58 (*m*)	27.9 (*t*)	Me(13)
	b: 1.62–1.66 (*m*)		
C(4)		35.3 (*s*)	Me(13), Me(14), H_a–C(3)
H–C(5)	1.88–1.94 (*m*)	44.7 (*d*)	Me(13), Me(14), H_a–C(6)
CH_2(6)	a: 1.14–1.18 (*m*)	20.8 (*t*)	H_b–C(7)
	b: 1.33–1.37 (*m*)		
CH_2(7)	a: 1.10–1.14 (*m*)	35.8 (*t*)	Me(15), H_b–C(12), H_b–C(6)
	b: 1.44–1.48 (*m*)		
C(8)		39.0 (*s*)	Me(15), CH_2(12), H_b–C(7)
H–C(9)	3.45 (*dd*, *J* = 11.7, 3.6)	72.4 (*d*)	Me(15), CH_2(12), H_b–C(11)
CH_2(10)	a: 1.76–1.80 (*m*)	28.0 (*t*)	H_a–C(12), H_a–C(11)
	b: 2.00–2.10 (*m*)		
CH_2(11)	a: 1.52–1.57 (*m*)	36.1 (*t*)	H_b–C(12)
	b: 1.68–1.70 (*m*)		
CH_2(12)	a: 1.38 (*d*, *J* = 12.3)	40.3 (*t*)	Me(15), H_a–C(11), H_b–C(7)
	b: 1.51 (*d*, *J* = 12.9)		
Me(13)	1.00 (*s*)	20.6 (*q*)	Me(14), H_b–C(3)
Me(14)	0.98 (*s*)	30.4 (*q*)	Me(14), H_a–C(3)
Me(15)	0.91 (*s*)	26.7 (*q*)	CH_2(12)
MeO–C(1)	3.16 (*s*)	50.1 (*q*)	

[a]) Assignments made by ^{1}H,^{1}H-COSY, HSQC, and HMBC experiments.

The relative configuration of **1** was elucidated by an NOE experiment, in combination with the interpretation of the coupling constants. Irradiation of the Me(15) resulted in enhancements of H_b–C(12) at δ(H) 1.51 (+2.21 %) and H–C(9)

(+1.42%), irradiation of H–C(9) led to enhancements of Me(15) (+2.47%) and H–C(5) (+3.91%), and irradiation of MeO–C(1) resulted in the enhancement of H_b–C(12) at δ(H) 1.51 (+2.77%). Assuming Me(15) to be β-oriented, as in all natural caryolane sesquiterpenes, H–C(9), H–C(5), H_b–C(12), and MeO–C(1) should be β-configured. The coupling constant of H–C(9) (J(9,10a) = 11.7) further confirmed the β-configuration. Accordingly, the structure of **1** was elucidated to be 9α-hydroxy-1β-methoxycaryolanol[1]).

Compound **2** was obtained as colorless villiform crystal. The HR-ESI-MS showed an $[M+Na]^+$ peak at m/z 679.5646 (calc. 679.5636), corresponding to the molecular formula $C_{43}H_{76}O_4$. The IR (film) spectrum showed absorption bands of OH groups (3407.2 cm^{-1}), an ester CO group (1733.4 cm^{-1}), and a C=C bond (1640.1 cm^{-1}). The ^{1}H-NMR spectrum (*Table 2*) exhibited the six typical Me-group signals of the stigmastane skeleton: two *singlet*s at δ(H) 0.70 and 1.00 (Me(18) and Me(19), resp.), three *doublet*s at δ(H) 0.92, 0.87 and 0.77 (Me(21), Me(26), and Me(27), resp.), and one *triplet* at δ(H) 0.88 (Me(29)), as well as three oxygenated CH groups: a *multiplet* at δ(H) 4.63–4.67, a broad *singlet* at δ(H) 3.84, and a broad *doublet* at δ(H) 3.70. The ^{13}C-NMR (DEPT) spectra (*Table 2*) showed six typical stigmastane skeleton Me groups (δ(C) 11.6 (*q*), 18.2 (*q*), 12.3 (*q*), 17.5 (*q*), 20.6 (*q*), and 11.9 (*q*)) [15], three oxygenated CH groups (δ(C) 73.0 (*d*), 65.2 (*d*), 71.2 (*d*)), two olefinic C-atoms (δ(C)

Table 2. *^{1}H- and ^{13}C-NMR* (DEPT) *Data*[a]) *of* **2**[1]) ($CDCl_3$, δ in ppm, J in Hz)

	δ(H)	δ(C)		δ(H)	δ(C)
CH_2(1)	a: 1.12–1.16 (*m*)	36.7 (*t*)	H–C(17)	1.14–1.18 (*m*)	52.8 (*d*)
	b: 1.82–1.89 (*m*)		Me(18)	0.70 (*s*)	11.6 (*q*)
CH_2(2)	a: 1.52–1.60 (*m*)		Me(19)	1.00 (*s*)	18.2 (*q*)
	b: 1.88–1.92 (*m*)	29.7 (*t*)	H–C(20)	1.68–1.72 (*m*)	42.5 (*d*)
H–C(3)	4.63–4.67 (*m*)	73.0 (*d*)	Me(21)	0.92 (*d*, *J* = 6.9)	12.3 (*q*)
CH_2(4)	2.34 (br. *d*, *J* = 9.9)	37.9 (*t*)	H–C(22)	3.70 (br. *d*, *J* = 9.9)	71.2 (*d*)
C(5)		145.4 (*s*)	CH_2(23)	a: 1.02–1.08 (*m*)	29.7 (*t*)
H–C(6)	5.62 (*d*, *J* = 5.1)	124.6 (*d*)		b: 1.21–1.28 (*m*)	
H–C(7)	3.84 (br. *s*)	65.2 (*d*)	H–C(24)	1.26–1.30 (*m*)	41.4 (*d*)
H–C(8)	1.26–1.30 (*m*)	37.5 (*d*)	H–C(25)	1.72–1.80 (*m*)	28.6 (*d*)
H–C(9)	1.42–1.46 (*m*)	42.4 (*d*)	Me(26)	0.87 (*d*, *J* = 7.2)	17.5 (*q*)
C(10)		37.5 (*s*)	Me(27)	0.77 (*d*, *J* = 7.2)	20.6 (*q*)
CH_2(11)	a: 1.20–1.28 (*m*)	24.3 (*t*)	CH_2(28)	a: 1.00–1.08 (*m*)	23.6 (*t*)
	b: 1.98–2.02 (*m*)			b: 1.20–1.29 (*m*)	
CH_2(12)	a: 1.15–1.20 (*m*)	39.1 (*t*)	Me(29)	0.88 (*t*, *J* = 7.0)	11.9 (*q*)
	b: 1.92–2.00 (*m*)		C(1′)		173.2 (*s*)
C(13)		42.5 (*s*)	CH_2(2′)	2.26 (*t*, *J* = 7.3)	34.6 (*t*)
H–C(14)	1.64–1.66 (*m*)	49.0 (*d*)	CH_2(3′)	1.56–1.63 (*m*)	25.0 (*t*)
CH_2(15)	a: 1.18–1.22 (*m*)	20.6 (*t*)	CH_2(4′–11′)	1.25 (br. *s*)	29.1–29.7[b]) (*t*)
	b: 1.82–1.88 (*m*)		CH_2(12′)	1.25 (br. *s*)	31.9 (*t*)
CH_2(16)	a: 1.26–1.30 (*m*)	27.5 (*t*)	CH_2(13′)	1.25 (br. *s*)	22.7 (*t*)
	b: 1.60–1.66 (*m*)		Me(14′)	0.85 (*t*, *J* = 7.2)	14.1 (*q*)

[a]) Assignments made by ^{1}H,^{1}H-COSY, HSQC, and HMBC experiments. [b]) Overlapped signals.

124.6 (*d*), 145.4 (*s*)), one ester CO group (δ(C) 173.2 (*s*)), and some aliphatic C-atoms (δ(C) 34.6 (*t*), 25.0 (*t*), 29.1–29.7 (*t*), 31.9 (*t*), 22.7 (*t*), 14.1 (*q*)). Furthermore, comparison of the ^{1}H- and ^{13}C-NMR data of **2** with stigmast-5-ene-3β,7α,22α-triol reported in literature [16], showed that they both are very similar, except that a fatty acid moiety appeared in **2**. Compared with those of stigmast-5-ene-3β,7α,22α-triol, the signals of H–C(3) and C(3) in **2** were both shifted downfield (δ(H): from 3.59 to 4.63–4.67; δ(C): from 71.3 (*d*) to 73.0 (*d*)). This suggested that the fatty acid moiety was attached at C(3). In the HMBC experiment, a correlation between CH_2(2′) with C(3) was observed, and this further confirmed that the fatty acid was linked at C(3) position by an ester bond. The HR-ESI-MS showed a peak at *m*/*z* 411.3612 ($[M - C_{14}H_{28}O_2 - H_2O + H]^+$; calc. 411.3621), and the EI-MS spectrum showed fragment peaks at *m*/*z* 429 ($[M - C_{14}H_{27}O_2]^+$) and 229 ($[C_{14}H_{29}O_2]^+$), which indicated that the fatty acid moiety contains 14 C-atoms. Hence, the structure of **2** was assigned as stigmast-5-ene-7α,22α-diol-3β-tetradecanoate[1]).

Compound **3** was obtained as an amorphous white powder. Its molecular formula was determined as $C_{17}H_{18}O_9$ from the HR-ESI-MS signal at 384.1297 ($[M + NH_4]^+$; calc. 384.1289). The IR (KBr) spectrum showed the absorption bands of an OH group (3422.7 cm^{-1}), a CO group (1735.5 cm^{-1}), and an aromatic moiety (1620.6 and 1510.7 cm^{-1}). The ^{13}C-NMR (DEPT) and ^{1}H-NMR spectra showed the presence of a CO signal at δ(C) 170.9 (*s*) and five typical H-atoms of a coumarin skeleton (6.30 (*d*, *J* = 9.3, H–C(3)), 8.00 (*d*, *J* = 9.3, H–C(4)), 7.63 (*d*, *J* = 8.5, H–C(5)), 6.96 (*d*, *J* = 8.5, H–C(6)), 7.02 (*s*, H–C(8)) [6], a signal for an AcO group, and glucosyl signals (*Table 3*). From the above information, compound **3** was deduced as a coumarin glucoside. The signal of the anomeric H-atom of glucosyl at δ(H) 5.07 (*d*, *J* = 7.2) indicated that the glucosyl moiety was bound in β-configuration. By comparison with the NMR data reported in literature, the sugar moiety was identified as D-glucose [17]. The HMBC experiment showed a correlation between the anomeric H-atom H–C(1′) at δ(H) 5.07 of the glucosyl moiety and C(7) at δ(C) 160.6 (*s*) of the coumarin skeleton, which suggested that the glucosyl moiety was located at C(7). The correlations between the CO group of AcO at δ(C) 170.9 and CH_2(6′) at δ(H) 4.26 and 4.00–4.06 of the glucosyl moiety, inferred that the AcO group was linked at C(6′). Meanwhile, the signals for C(6′) (δ(C) 64.0 (*t*)) and C(5′) (δ(C) 74.4 (*d*)) were shifted downfield and upfield, respectively [18] due to the influence of the AcO group. This further confirmed the position of the AcO group. From the above evidences, the structure of **3** was elucidated as 7-*O*-(6′-acetoxy-β-D-glucopyranosyl)coumarin[1]).

Compound **4** was isolated as a yellowish gum. Its molecular formula $C_{17}H_{18}O_{10}$ was determined on the basis of the pseudomolecular-ion peak at *m*/*z* 405.0792 ($[M + Na]^+$; calc. 405.0792) in the HR-ESI-MS. The IR (KBr) spectrum showed the absorption bands of OH groups (3423.8 cm^{-1}), CO groups (1723.7 cm^{-1}), and an aromatic moiety (1613.6 and 1506.2 cm^{-1}). The ^{13}C-NMR (DEPT) spectra of **3** and **4** were similar, except for the signals of C(7), C(8), and C(9) (*Table 3*). The signals of two oxygenated aromatic C-atoms at δ(C) 153.9 (*s*) and 132.1 (*s*) indicated a 7,8-disubstituted coumarin, which was confirmed by the disappearance of the signal at δ(H) 7.02 for H–C(8) of **3** in the ^{1}H-NMR spectrum. In the HMBC experiment, correlations were observed between the anomeric H-atom H–C(1′) at δ(H) 4.86 of the glucosyl moiety and C(8) at δ(C) 132.1 (*s*) of the coumarin skeleton, which suggested that the glucosyl moiety was

Table 3. *^{1}H- and ^{13}C-NMR* (DEPT) *Data of* **3** *and* **4**[1]) (δ in ppm, *J* in Hz)

	3 δ(H)[a])	**4** δ(H)[a])	**4** δ(H)[b])	**3** δ(C)[a])	**4** δ(C)[b])
C(2)				160.9 (*s*)	160.0 (*s*)
H–C(3)	6.30 (*d*, *J* = 9.3)	6.06 (*d*, *J* = 9.3)	6.20 (*d*, *J* = 9.5)	113.9 (*d*)	112.5 (*d*)
H–C(4)	8.00 (*d*, *J* = 9.3)	7.83 (*d*, *J* = 9.3)	7.88 (*d*, *J* = 9.5)	144.9 (*d*)	144.4 (*d*)
H–C(5)	7.63 (*d*, *J* = 8.5)	7.20 (*d*, *J* = 8.7)	6.88 (*d*, *J* = 8.7)	130.1 (*d*)	125.1 (*d*)
H–C(6)	6.96 (*d*, *J* = 8.5)	6.72 (*d*, *J* = 8.7)	7.35 (*d*, *J* = 8.7)	114.3 (*d*)	113.5 (*d*)
C(7)				160.6 (*s*)	153.9 (*s*)
H–C(8)	7.02 (*s*)	–	–	103.8 (*d*)	132.1 (*s*)
C(9)				155.7 (*s*)	148.5 (*s*)
C(10)				114.0 (*s*)	112.9 (*s*)
H–C(1′)	5.07 (*d*, *J* = 7.2)	4.80 (*d*, *J* = 7.8)	4.86 (*d*, *J* = 7.5)	100.2 (*d*)	105.9 (*d*)
H–C(2′)	3.20–3.25 (*m*)	3.22–3.26 (*m*)	3.59–3.61 (*m*)	73.7 (*d*)	74.2 (*d*)
H–C(3′)	3.25–3.30 (*m*)	3.17–3.20 (*m*)[c])	3.51–3.58 (*m*)	77.0 (*d*)	76.5 (*d*)
H–C(4′)	3.12–3.20 (*m*)	3.17–3.20 (*m*)[c])	3.43 (*dd*, *J* = 8.7, 9.9)	70.4 (*d*)	70.5 (*d*)
H–C(5′)	3.68–3.72 (*m*)	3.27–3.30 (*m*)	3.64–3.67 (*m*)	74.4 (*d*)	74.7 (*d*)
CH_2(6′)	4.26 (*d*, *J* = 11.7)	4.10 (*m*)	4.22 (*dd*, *J* = 11.7, 6.6)	64.0 (*t*)	63.6 (*t*)
	4.00–4.06 (*m*)		4.32 (*dd*, *J* = 11.7, 2.1)		
C(7′)				170.9 (*s*)	170.5 (*s*)
Me(8′)	2.00 (*s*)	1.86 (*s*)	1.97 (*s*)	21.3 (*q*)	20.0 (*q*)
OH–C(2′)	5.48 (*d*, *J* = 4.8)				
OH–C(3′)	5.24 (*d*, *J* = 4.5)				
OH–C(4′)	5.33 (*d*, *J* = 5.4)				

[a]) In (D_6)DMSO. [b]) In (D_6)acetone. [c]) Overlapped signals.

located at C(8). The correlations between CH_2(6′) (δ(H) 4.22 and 4.32) of the glucosyl moiety and the CO group of AcO (δ(C) 170.5, *s*) suggested that the AcO group was located at C(6′) of the glucosyl moiety. From the above information, the OH group was unambiguously located at C(7) (δ(C) 153.9, *s*). Thus, the structure of **4** was elucidated as 8-*O*-(6′-acetoxy-β-D-glucopyranosyl)-7-hydroxycoumarin[1]).

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 200–300 mesh, *Qingdao Marine Chemical Factory*, China). TLC and prep. TLC (PTLC): SiO_2 *GF_{254}* (10–40 μm, *Qingdao Marine Chemical Factory*), detection at 254 nm UV light or by heating after spraying with 5% H_2SO_4 in EtOH (*v*/*v*). Melting points: *Kofler* melting point apparatus, uncorrected. Optical rotations: *Perkin-Elmer 341* polarimeter. UV Spectra: *Shimadzu spectrometer UV-260*, λ_{max} (log ε), in nm. IR Spectra: *Nicolet NEXUS-670* FT-IR spectrometer, in cm^{-1}. NMR Spectra: *Varian Mercury plus-300* spectrometer at 300 (^{1}H-NMR) and 75 MHz (^{13}C-NMR), δ in ppm, *J* in Hz. EI-MS: *HP 5988A* GC/MS instrument, in *m*/*z*. HR-ESI-MS: *Bruker Daltonics APEX-II* mass spectrometer.

Plant Material. The whole plant of *Sinacalia tangutica* was collected in Linxia City of Gansu Province, China, in August 2005 and identified by Prof. *Guo-Liang Zhang*, Department of Life Science, Lanzhou University. A voucher specimen (No. St20050801) has been deposited with the State Key Laboratory of Applied Organic Chemistry, Lanzhou University.

Extraction and Isolation. Air-dried of the aerial parts of *S. tangutica* (6.0 kg) were powdered and extracted with MeOH for five times (7 d each time) at r.t. The residue (790 g) was obtained after removing the solvent under reduced pressure. The residue was suspended in H_2O and partitioned with

$CHCl_3$, AcOEt, and BuOH, resp. The $CHCl_3$-soluble extract was concentrated to give a dark green viscous residue (145 g). This residue was subjected to CC (SiO_2; 1849 g) with gradient elution, with petroleum ether (PE; 60–90°)/acetone, and finally washing with MeOH. *Fr. 3* (30:1, 10 g) was further subjected to CC (SiO_2), eluting with PE/$CHCl_3$ (1:1), and further purified by PTLC (cyclohexane/AcOEt 3:1): **13** (5 mg). *Fr. 4* (20:1, 3.5 g) was purified by CC (SiO_2) with PE/acetone (20:1) and PE/AcOEt (10:1) successively: **9** (4 mg). *Fr. 5* (15:1, 2 g) was purified by repeated CC (SiO_2) with PE/AcOEt (10:1), PE/$CHCl_3$ (1:1), $CHCl_3$/AcOEt (15:1), and $CHCl_3$/acetone (15:1), successively: **1** (9 mg), **2** (5 mg, recrystallized from $CHCl_3$), **5** (2 mg), **11** (12 mg). *Fr. 6* (10:1, 2 g) was separated by CC (SiO_2) with $CHCl_3$/acetone (15:1) and $CHCl_3$/AcOEt (8:1) successively: **6** (10 mg), **8** (20 mg, recrystallized from $CHCl_3$), and **12** (6 mg). *Fr. 7* (5:1, 10 g) was purified by CC (SiO_2) with $CHCl_3$/AcOEt (5:1), PE/AcOEt (2:1), and PE/acetone (2:1), successively: **7** (3 mg) and **14** (4 mg). *Fr. 8* (3:1, 8 g) was purified by CC (SiO_2) with PE/AcOEt (1:1): **10** (12 mg).

The AcOEt-soluble part (45 g) was subjected to CC (SiO_2; 845 g), eluting sequentially with $CHCl_3$/MeOH (30:1–0:1): **3** (7 mg). Further purification by PTLC ($CHCl_3$/MeOH/H_2O 10:1:0.05) led to the isolation of **4** (4 mg).

9α-Hydroxy-1β-methoxycaryolanol (=*(1*R,*2*S,*5*R,*8*S,*9*R*)-1-Methoxy-4,4,8-trimethyltricyclo-[6.3.1.0^{2,5}]dodecan-9-ol*; **1**). Colorless crystals. M.p. 94–95° (acetone). $[\alpha]_D^{20} = +20$ ($c = 0.113$, $CHCl_3$). IR (film): 3369.5, 2930.3, 2853.9, 1600.0, 1458.0, 1210.8. ^{1}H- and ^{13}C-NMR (DEPT): *Table 1*. EI-MS: 252 (1, M^+), 220 (3, $[M - MeOH]^+$), 193 (71), 141 (100), 123 (42). HR-ESI-MS: 270.2431 ($[M + NH_4]^+$, $C_{16}N_{32}NO_2^+$; calc. 270.2428).

Stigmast-5-ene-7α,22α-diol-3β-tetradecanoate (=*(3β,7α,22*R*)-7,22-Dihydroxystigmast-5-en-3-yl Tetradecanoate*; **2**). Colorless villiform crystal. M.p. 99–100° (acetone). $[\alpha]_D^{20} = -35$ ($c = 0.233$, $CHCl_3$). IR (film): 3407.3, 2925.1, 2855.3, 1733.4, 1640.1, 1461.3, 1024.0. ^{1}H- and ^{13}C-NMR: *Table 2*. EI-MS: 429 (0.5, $[M - C_{14}H_{27}O_2]^+$), 229 (1.6, $[C_{14}H_{29}O_2]^+$), 155 (11, $[C_{11}H_{23}]^+$), 157 (3.6, $[C_{10}H_{21}O]^+$), 141 (13, $[C_{10}H_{21}]^+$), 127 (19, $[C_9H_{19}]^+$), 113 (19, $[C_8H_{17}]^+$), 99 (26, $[C_7H_{15}]^+$), 85 (51, $[C_6H_{13}]^+$), 71 (65, $[C_5H_{11}]^+$), 57 (100, $[C_4H_9]^+$), 43 (75, $[C_3H_7]^+$). HR-ESI-MS: 679.5646 ($[M + Na]^+$, $C_{43}H_{76}NaO_4^+$; calc. 679.5636), 411.3612 ($[C_{29}H_{46}O + H]^+$; calc. 411.3621).

7-O-*(6′-Acetoxy-β-*D*-glucopyranosyl)coumarin* (=*2-Oxo-2*H*-chromen-7-yl 6*-O*-Acetyl-β-*D*-glucopyronoside*; **3**). Amorphous white powder. $[\alpha]_D^{20} = -125$ ($c = 0.14$, MeOH). UV (MeOH): 212 (1.65), 316 (1.22). IR (KBr): 3422.7, 2922.3, 1735.5, 1620.6, 1510.7, 1077.2, 1041.4, 609.9. ^{1}H- and ^{13}C-NMR: *Table 3*. EI-MS: 366 (0.23, M^+), 205 (13.6, $[C_8H_{13}O_6]^+$), 162 (100, $[C_8H_{13}O_6 - MeCO]^+$), 43 (58, $[MeCO]^+$). HR-ESI-MS: 384.1297 ($[M + NH_4]^+$, $C_{17}H_{22}NO_9^+$; calc. 384.1289).

8-O-*(6′-Acetoxy-β-*D*-glucopyranosyl)-7-hydroxycoumarin* (=*7-Hydroxy-2-oxo-2*H*-chromen-8-yl 6*-O*-Acetyl-β-*D*-glucopyranoside*; **4**): Yellowish gum. $[\alpha]_D^{20} = -40$ ($c = 0.05$, MeOH). UV (MeOH): 227 (3.67), 321 (2.81). IR (KBr): 3423.8, 2932.9, 1723.7, 1613.6, 1506.2, 1075.9, 620.5. ^{1}H- and ^{13}C-NMR: *Table 3*. EI-MS: 382 (0.6, M^+), 205 (4, $[C_8H_{13}O_6]^+$), 162 (3, $[C_8H_{13}O_6 - MeCO]^+$), 144 (4, $[C_9H_4O_2]^+$), 43 (83, $[MeCO]^+$). HR-ESI-MS: 405.0792 ($[M + Na]^+$, $C_{17}H_{18}NaO_{10}^+$; calc. 405.0792).

The authors express their gratitude to the *Natural Science Foundation of Gansu Province* (No. ZS001-A25-002-Z), the *Natural Science Foundation of China* (NSFC) (No. J0630962/J0109) and the grant from the *State Key Laboratory of Applied Organic Chemistry at Lanzhou University.*

REFERENCES

[1] 'A Dictionary of the Traditional Chinese Medicines', Jiangsu College of New Medicine, Shanghai Science and Technology Press, Shanghai, 1977, p. 549.
[2] M.-J. Mao, J.-L. Qian, B. Jiang, *Chin. Chem. Lett*. **2005**, *16*, 1056.
[3] X. Liu, Q.-X. Wu, Y.-P. Shi, *J. Chin. Chem. Soc*. **2005**, *52*, 369.
[4] Z.-L. Liu, X. Tian, *Bull. Korean. Chem. Soc.* **2004**, *25*, 1078.
[5] J.-M. Yue, S.-N. Chen, Z.-W. Lin, H.-D. Sun, *Phytochemistry* **2001**, *56*, 801.
[6] A. Chatterjee, S. Sarkar, J. N. Shoolery, *Phytochemistry* **1980**, *19*, 2219.
[7] S. P. Gunasekera, G. A. Cordell, N. R. Farnsworth, *J. Nat. Prod.* **1980**, *43*, 285.
[8] T. Kinoshita, K. Firman, *Chem. Pharm. Bull*. **1996**, *44*, 1261.

[9] A. A. Ahmed, M.-E. F. Hegazy, N. M. Hassan, M. Wojcinska, J. Karchesy, P. W. Pare, T. J. Mabry, *Phytochemistry* **2006**, *67*, 1547.
[10] J. F. Sanz, J. A. Marco, *Phytochemistry* **1991**, *30*, 2788.
[11] M. Neuenschwander, A. Neuenschwander, E. Steinegger, *Helv. Chim. Acta* **1979**, *62*, 627.
[12] J. Kitajima, K. Kimizuka, Y. Tanaka, *Chem. Pharm. Bull.* **2000**, *48*, 77.
[13] I. G. Collado, J. R. Hanson, A. J. Macías-Sánchez, *Tetrahedron* **1996**, *52*, 7961.
[14] W. R. Abraham, L. Ernst, H. A. Arfmann, *Phytochemistry* **1990**, *29*, 757.
[15] E.-W. Li, K. Gao, Z.-J. Jia, *Chin. Chem. Lett.* **2004**, *15*, 194.
[16] Y. Li, M. Ishibashi, M. Satake, X. Chen, Y. Oshima, Y. Ohizumi, *J. Nat. Prod.* **2003**, *66*, 696.
[17] R.-Q. Mei, Q. Lu, Y.-F. Hu, H.-Y. Liu, F.-K. Bao, Y. Zhang, Y.-X. Cheng, *Helv. Chim. Acta* **2008**, *91*, 90.
[18] C. Bertrand, N. Fabre, C. Moulis, *Fitoterapia* **2004**, *75*, 242.

Received April 8, 2008