Phenylpropanoid-Substituted Catechins and Epicatechins from *Smilax china*

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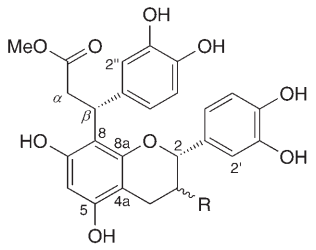
The four new phenylpropanoid-substituted catechins **1**, **3**, and **4** and 3-epicatechin (**2**), together with seven analogues, were isolated from the AcOEt extract of *Smilax china* L. (catechin = (2*R*,3*S*)-2-(3,4-dihydroxyphenyl)-3,4-dihydro-2*H*-2-benzopyran-3,5,7-triol). Their structures were determined by means of spectroscopic analyses, including HR-MS, IR, ^{1}H- and ^{13}C-NMR, and 2D experiments (COSY, HSQC, and HMBC), and comparison with known related compounds.

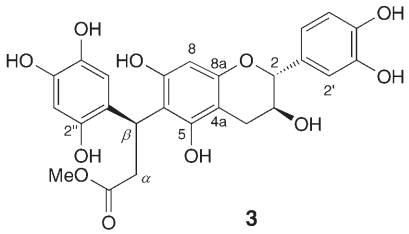
Introduction. – *Smilax china* (family Liliaceae), known as 'Ba Qia' (or 'Jin Gang Teng') in Chinese, is widely spread in the southern area of China. In traditional Chinese medicine (TCM), the efficacy of *S. china* is regarded as dispelling wind-evil, eliminating damp, and detoxicating and eliminating stasis to activate blood circulation [1]. In China, this plant has been used for treatment of diverse diseases, such as bone- and muscle-aching pain, furunculosis, tumors, inflammatory diseases (especially for pelvic inflammation and chronic pelvic inflammation) [2][3]. *S. china* has been proved to have anti-inflammatory activity [4][5] and to be rich in steroidal saponins [6–9]. Recent pharmacological studies suggested that *S. china* has neuroprotective effects, which may be associated with catechin and epicatechin [10][11]. Catechins and epicatechins have been confirmed to have anticyclooxygenase and anticarcinogenesis [12–14], antifungal and antimicrobial [15], as well as antioxidant activities [16].

The polyphenolic constituents (catechins and epicatechins) of *S. china* have not yet been investigated. Thus, in the present study, the four new phenylpropanoid-substituted catechins **1**, **3**, and **4** and 3-epicatechin **2** were isolated from the rhizome of *S. china* and characterized, together with seven analogues. To the best of our knowledge, this is the first report on these analogues of catechin (= (2*R*,3*S*)-2-(3,4-dihydroxyphenyl)-3,4-dihydroxy-2*H*-1-benzopyran-3,5,7-triol) and 3-epicatechin from the genus *Smilax*.

Results and Discussion. – The air-dried and powdered tubers were extracted with 70% EtOH to give rise to the crude extract (350 g). The total extract was suspended in H_2O and successively extracted with AcOEt and BuOH. The AcOEt fraction was separated by column chromatography and semi-prep. HPLC into a series of phenyl-



1 R = –OH
2 R = ····OH



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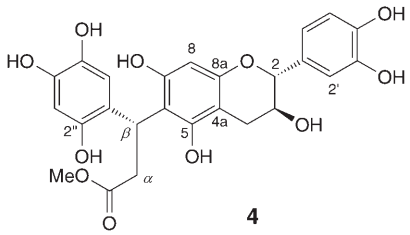

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propanoid-substituted catechins and epicatechins, including the three new catechins **1**, **3**, and **4**, the new 3-epicatechin **2**, and seven known analogues. The structures of the known compounds were confirmed by comparison of their physical and spectral data with the published ones, such as cinchonain 1a [17][19], cinchonain 1b [17][19], catechin-(7,8-bc)-4β-(3,4-dihydroxyphenyl)-dihydropyran-2(3*H*)-one [18], catechin-3β-hydroxy-(1*R*-3,4-dihydroxyphenyl)pyranone [19], cinchonain 1c [17][19], catechin-3β-hydroxy-(1*S*-3,4-dihydroxyphenyl)pyranone [19], and (–)-epicatechin [18].

Compound **1**, a brown powder, had the molecular formula $C_{25}H_{24}O_{10}$ as deduced from its HR-ESI-MS (*m*/*z* at 507.1245 for $C_{25}H_{24}NaO_{10}^{+}$). The IR spectrum revealed the absorption bands of OH (3402 cm^{-1}) and COOH (1708 cm^{-1}) groups. The structure of **1** was elucidated as an 8-[(1*R*)-1-(3,4-dihydroxyphenyl)-3-methoxy-3-oxopropyl]-substituted catechin[1]) by its ^{1}H- and ^{13}C-NMR (*Table 1*), HSQC, and HMBC data. The configuration of **1** was determined by comparison of the CD data (*Fig. 1*) with those of several chinchonains isolated from *Chincona succirubra* [17–19].

The ^{13}C-NMR, DEPT, and HSQC data of **1** established the presence of 25 C-signals, due to one Me, one C=O, two CH_2, and nine CH groups, and to twelve quaternary C-atoms. The occurrence of a catechin skeleton in the molecule could be easily deduced from the characteristic signals at δ(H) 4.41 (*d*, J = 8.4 Hz, H–C(2)) and 3.85–3.90 (*m*, H–C(3)), as well as the signals at δ(C) 82.6 (C(2)) and 68.0 (C(3)) [19]. The signals at δ(H) 3.04 (*dd*, J = 7.6 and 16.0 Hz, 1 H–C(α)), 3.12 (*dd*, J = 8.4 and 16.0 Hz, 1 H–C(α)), and 4.81 (*t*, J = 8.4 Hz, H–C(β)), and at δ(C) 173.7 (C=O), as well as an extra set of *ABX*-type aromatic protons at δ(H) 6.5–6.8 indicated the presence of a phenylpropanoid (C_6–C_3) unit [17]. Detailed analysis of the ^{13}C-NMR data of **1** suggested the presence of a C_6–C_3 substituent, located at C(8) through a C–C bond [17], which was supported by the HMBC cross-peaks H–C(α)/C(8), H–C(β)/C(8), and H–C(β)/C(8a)]. The configuration at C(β) was determined by comparing the

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

Table 1. *^{1}H- and ^{13}C-NMR Data* (400 and 100 MHz, resp.; $(D_6)Me_2CO + D_2O$), *of* **1** *and* **2**. δ in ppm, J in Hz.

	1		**2**	
	δ(H)	δ(C)	δ(H)	δ(C)
H–C(2)	4.41 (*d*, *J* = 8.4)	82.6	4.91 (br. *s*)	78.5
H–C(3)	3.85–3.90 (*m*)	68.0	4.25–4.29 (*m*)	65.9
CH_2(4)	2.44 (*dd*, *J* = 9.2, 16.4), 2.84 (*dd*, *J* = 5.6, 16.0)	28.9	2.76 (*dd*, *J* = 6.4, 16.8), 2.9 (*dd*, *J* = 8.8, 17.2)	28.4
C(4a)		100.6		99.1
C(5)		154.4		154.2
H–C(6)	6.01 (*s*)	96	6.12 (*s*)	95.8
C(7)		154.4		154.2
C(8)		110		109.3
C(8a)		154.4		154.2
C(1′)		131.7		131.3
H–C(2″)	6.9 (*d*, *J* = 1.6)	115.3	7.08 (br. *s*)	115.2
C(3′)		145.3		144.4
C(4′)		145.1		144.2
H–C(5′)	6.77 (*d*, *J* = 8.0)	114.8	6.86 (br. *s*)	114.2
H–(6′)	6.72 (*dd*, *J* = 1.6, 8.0)	119.8	6.86 (br. *s*)	119.2
C(1″)		137.1		136.7
H–C(2″)	6.79 (*d*, *J* = 2)	115.9	6.96 (*d*, *J* = 2)	115.4
C(3″)		144.5		144.1
C(4″)		143.1		142.6
H–C(5″)	6.5 (*d*, *J* = 8.0)	115	6.70 (*d*, *J* = 8.0)	115
H–C(6″)	6.53 (*dd*, *J* = 1.6, 8.0)	119.6	6.71 (*dd*, *J* = 1.6, 8.0)	118.4
$CH_2(\alpha)$	3.04 (*dd*, *J* = 7.6, 16.0), 3.12 (*dd*, *J* = 8.4, 16.0)	38.7	3.21 (*dd*, *J* = 1.6, 7.6), 3.21 (*dd*, *J* = 1.6, 7.6)	38.4
H–C(β)	4.81 (br. *t*, *J* = 8.4)	36.2	5.1 (br. *t*, *J* = 8.8)	35.7
C=O		173.7		174.7
MeO	3.43 (*s*)	51	3.57 (*s*)	51.3

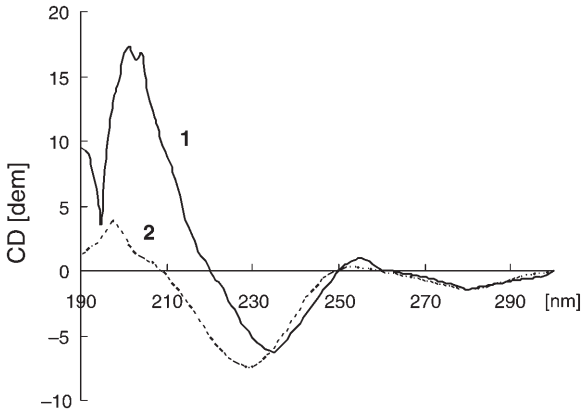

Fig. 1. *CD Spectra of* **1** *and* **2**

circular dichroism (CD) data and curve (*Fig. 1*) of **1** with those of several cinchonains [17–19]. According to the literature, CD bands are mainly due to the chirality center C(β) and unaffected by the stereogenic centers C(2) and C(3). Furthermore, these CD data showed strong negative *Cotton* effects at 228 and 291 nm and a positive one at 252 nm. Hence, the configuration of the aryl substituent at C(β)) could be determined to be β.

Compound **2** exhibited the molecular formula $C_{25}H_{24}O_{10}$ as established by its HR-ESI-MS (*m/z* at 507.1254 for $C_{25}H_{24}NaO_{10}^{+}$) and analysis of the NMR data (*Table 1*), indicating that the molecular formula of **2** was the same as that of **1**. Moreover, the NMR data of **2** were very similar to those of **1**, the only difference being another configuration at C(3). The ^{1}H-NMR spectrum of **2** showed the characteristic 3-epicatechin protons (δ(H) 4.91 (br. *s*) and 4.25–4.29 (*m*)) [17]. The position of each functional group was determined by detailed analysis of NMR data and 2D-NMR techniques. Furthermore, the configuration of the aryl substituent at C(β) was β, according to the CD curve (*Fig. 1*) which was similar to that of **1**. Thus, the structure of compound **2** was established as an 8-[(1*R*)-1-(3,4-dihydroxyphenyl)-3-methoxy-3-oxopropyl]-substituted 3-epicatechin[1]). However, it should be noted that the structure of an analogue (isolated from *Antirhea acutata*) was inaccurately deduced in a recently published report [13], due to comparison with data published in 1982 which had been revised in 1993 [17][19]. Therefore, the configuration of this analogue should be revised, *i.e.*, the configuration of its aryl substituent at C(β) should be α and not β [13].

Compound **3** was obtained as a brown powder and shown to possess the molecular formula $C_{25}H_{24}O_{11}$ by HR-ESI-MS (*m/z* at 523.1086 for $C_{25}H_{24}NaO_{11}^{+}$). Its IR spectrum was almost identical with that of compound **1**, compatible with the same functional groups. From the ^{1}H- and ^{13}C-NMR (*Table 2*), HMBC, and CD data (*Fig. 2*), the structure of **3** was deduced to be a 6-[(1*S*)-3-methoxy-3-oxo-1-(2,4,5-trihydroxyphenyl)propyl]-substituted catechin[1]).

The ^{13}C-NMR and DEPT data indicated the presence of one Me, one C=O, two CH_2, and eight CH groups, and of thirteen quaternary C-atoms, which is different from compound **1**. The catechin skeleton

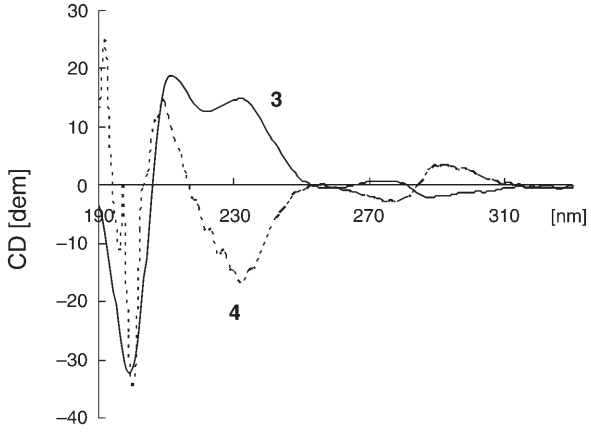

Fig. 2. *CD Spectra of* **3** *and* **4**

Table 2. *^{1}H- and ^{13}C-NMR Data* (400 and 100 MHz, resp.; $(D_6)Me_2CO + D_2O$) *of* **3** *and* **4**. δ in ppm, J in Hz.

	3		**4**	
	δ(H)	δ(C)	δ(H)	δ(C)
H–C(2)	4.68 (*d*, *J* = 7.2)	81.8	4.68 (*d*, *J* = 7.6)	81.8
H–C(3)	4.12–4.16 (*m*)	67.1	4.12–4.16 (*m*)	67.1
CH_2(4)	2.72 (*dd*, *J* = 8.4, 16.0), 3.11 (*dd*, *J* = 5.6, 16.0)	27.6	2.73 (*dd*, *J* = 8.8, 16.8), 3.09 (*dd*, *J* = 5.6, 16.4)	27.7
C(4a)		100		100
C(5)		151.4		151.3
C(6)		104.4		104.3
C(7)		153.7		153.7
H–C(8)	6.23 (*s*)	97.1	6.23 (*s*)	97
C(8a)		154		154
C(1′)		131		130.8
H–C(2′)	6.97 (*d*, *J* = 2.0)	114.7	6.96 (*d*, *J* = 2.0)	114.8
C(3′)		145		145
C(4′)		145.1		145
H–C(5′)	6.89 (*d*, *J* = 8.0)	115.4	6.87 (*d*, *J* = 8.0)	115.3
H–C(6′)	6.81 (*dd*, *J* = 2, 8.4)	119.3	6.80 (*dd*, *J* = 2.0, 8.0)	119.3
C(1″)		115		115
C(2″)		145.2		145.2
H–C(3″)	6.69 (*s*)	103.8	6.70 (*s*)	103.8
C(4″)		144.9		144.8
C(5″)		141.3		141.4
H–C(6″)	6.79 (*s*)	114.3	6.79 (*s*)	114.2
$CH_2(\alpha)$	2.50 (*dd*, *J* = 8.8, 14.0), 2.78 (*dd*, *J* = 4.4, 14.4)	43.6	2.49 (*dd*, *J* = 8.8, 14.0), 2.78 (*dd*, *J* = 4.0, 14.0)	43.5
H–C(β)	4.52 (*dd*, *J* = 4.4, 8.4)	30.4	4.51 (*dd*, *J* = 4.0, 8.0)	30.1
C=O		172.7		172.7
MeO	3.66 (*s*)	51.4	3.66 (*s*)	51.4

and a C_6–C_3 (phenylpropanoid) unit located at C(6) were deduced from the ^{1}H- and ^{13}C-NMR data and comparison with literature values [17–19]. Furthermore, this was supported by the cross-peaks H–C(β)/C(5), CH_2(4)/C(5), H–C(2)/C(8a), CH_2(4)/C(8a) and H–C(8)/C(8a) in the HMBC plot. The C_6–C_3 unit contained a trihydroxy-substituted phenyl substituent, as confirmed by the ^{1}H-NMR spectrum at δ(H) 6.69 (*s*) and 6.79 (*s*). The HMBC cross-peak H–C(6″)/C(β) indicated that the three OH groups were positioned at C(2″), C(4″), and C(5″). The configuration of the aryl substituent at C(β) was determined to be α, based on the CD curve (*Fig. 2*) which showed positive *Cotton* effects at 228 and 273 nm and a negative one at 291 nm.

Compound **4** had the molecular formula $C_{25}H_{24}O_{11}$ as assigned by the HR-ESI-MS, *i.e.*, the same as compound **3**. Its IR and ^{1}H- and ^{13}C-NMR data (*Table 2*) were almost identical to those of **3**. Accordingly, compound **4** should be a stereoisomer of **3**. The major differences between **3** and **4** were their optical rotation and CD spectra (*Fig. 2*), due to the configuration at C(β). The CD plot (*Fig. 2*) exhibited negative *Cotton* effects at 228 and 273 nm and a positive one at 291 nm, opposite to those of compound **3**. Based on the above deduction, compound **4** was identified as a 6-[(1*R*)-3-methoxy-3-oxo-1-(2,4,5-trihydroxyphenyl)propyl]-substituted catechin[1]).

Experimental Part

General. All solvents used for the isolation were of anal. grade. Column chromatography (CC): silica gel *H* (200–300 mesh; *Haiyang Chemical Co., Ltd*, Qingdao), *MCI* gel (*Mitsubishi Chemical Corporation*, Tokyo, Japan), and *Sephadex LH-20* (*Amersham Biosciences*). TLC: Silica gel *60 PF_{254}* (*Merck*); detection by UV and 10% H_2SO_4/EtOH spraying reagent followed by heating at 105° for 1–2 min. HPLC: *Agilent 1100* system, equipped with an *Agilent DAD* spectrophotometer and an auto-sampler; *Alltima C18* column (10 × 250 mm) for semi-prep. analysis and *Agilent Zobax-C18* column (4.6 × 250 mm) for analysis. Optical rotation: *Perkin-Elmer 341* polarimeter; in MeOH at 22°. UV Spectra: *Shimadzu UV-240* spectrophotometer; in MeOH; λ_{max} (log ε) in nm. CD Spectra: *Jasco J-20* spectropolarimeter; in MeOH. IR Spectra: *Perkin-Elmer 577* spectrometer; in cm^{-1}. NMR Spectra: *Bruker AM-400* spectrometer; at 400 (^1H) and 100 MHz (^{13}C); in (D_6)Me_2CO or (D_6)DMSO with $SiMe_4$ as internal standard; δ in ppm and *J* in Hz; ^1H,^1H-COSY, HSQC, HMBC, and NOESY by using the standard pulse sequences. HR-ESI-MS: *Finnigan-LC-Q^{DECA}* instrument; in *m*/*z*.

Plant Material. Fresh tubers of *S. china* L. were kindly provided by *Qing-Hua Liu*, senior engineer at the Jiangxi College of Traditional Chinese Medicine, and identified by *Xue-Wen Lai*, associate-professor at the same college. The tubers were collected from Jiangxi Province, P. R. China, in March 2006. A voucher specimen (SC0252006) was deposited at the Shanghai Research Center for Modernization of Traditional Chinese Medicine, Shanghai Institute of Materia Medica, SIBS, CAS.

Extraction and Isolation. The shade-dried and powdered tubers of *S. china* (3 kg) were completely extracted with 70% EtOH. Then, the EtOH was evaporated and the resulting residue (350 g) was suspended in H_2O and then successively extracted with AcOEt and BuOH. The AcOEt fraction (80 g) was subjected to CC (silica gel; $CHCl_3$/MeOH 10:1 → 2:1): *Fractions 1–4*. *Fr. 1* was subjected to CC (silica gel, $CHCl_3$/MeOH 25:1): (−)-epicatechin. *Fr. 2* was separated by CC (*MCI* gel, MeOH/H_2O 1:1 → 1:0): *Fr. 2a–2d*. *Fr. 2a* was submitted to repeated CC (silica gel $CHCl_3$/MeOH 20:1; *Sephadex LH-20*), followed by semi-prep. HPLC: **1** (14 mg), **2** (8 mg), and cinchonain **1a** (60 mg). *Fr. 2b* yielded cinchonain **1b** (30 mg) and catechin-(7,8-bc)-4*β*-(3,4-dihydroxyphenyl-dihydropyran-2(3*H*)-one (10 mg), *Fr. 2c* afforded **3** (8 mg), catechin-3*β*-hydroxy-(1*R*-3,4-dihydroxyphenyl)pyranone (25 mg), and cinchonain **1c** (6 mg), and *Fr. 2d* gave **4** (5 mg) and catechin-3*β*-hydroxy-(1*S*-3,4-dihydroxyphenyl)pyranone (7 mg).

*8-[(1*R*)-1-(3,4-Dihydroxyphenyl)-3-methoxy-3-oxopropyl]catechin* (=*(β*R,2R,3S)-*β,2-Bis(3,4-dihydroxyphenyl)-3,4-dihydro-3,5,7-trihydroxy-2*H*-1-benzopyran-8-propanoic Acid Methyl Ester*; **1**): Brown powder. $[\alpha]_D^{22} = -9$ (*c* = 0.1, MeOH). UV (MeOH): 214 (4.56), 282 (3.97). IR (KBr): 3402, 1708, 1620, 1524, 1452, 1284, 818. ^1H- and ^{13}C-NMR: *Table 1*. HR-ESI-MS (pos.): 507.1245 ($[M+Na]^+$; calc. 507.1267).

*8-[(1*R*)-1-(3,4-Dihydroxyphenyl)-3-methoxy-3-oxopropyl]-3-epicatechin* (=*(β*R,2R,3R)-*β,2-Bis(3,4-dihydroxyphenyl)-3,4-dihydro-3,5,7-trihydroxy-2*H*-1-benzopyran-8-propanoic Acid Methyl Ester*; **2**): Brown powder. $[\alpha]_D^{22} = -43$ (*c* = 0.1, MeOH). UV (MeOH): 214 (4.59), 282 (3.92). IR (KBr): 3425, 1714, 1625, 1518, 1447, 1282, 817. ^1H- and ^{13}C-NMR: *Table 1*. HR-ESI-MS (pos.): 507.1254 ($[M+Na]^+$; calc. 507.1267).

*6-[(1*S*)-3-Methoxy-3-oxo-1-(2,4,5-trihydroxyphenyl)propyl]catechin* (=*(β*S,2R,3S)-*2-(3,4-Dihydroxyphenyl)-3,4-dihydro-3,5,7-trihydroxy-β-(2,4,5-trihydroxyphenyl)-2*H*-1-benzopyran-6-propanoic Acid Methyl Ester*; **3**): Brown powder. $[\alpha]_D^{22} = +54$ (*c* = 0.1, MeOH). UV (MeOH): 203 (4.76), 282 (3.86). IR (KBr): 3420, 1718, 1620, 1513, 1457, 1289, 816. ^1H- and ^{13}C-NMR: *Table 2*. HR-ESI-MS (pos.): 523.1086 ($[M+Na]^+$; calc. 523.1216).

*6-[(1*R*)-3-Methoxy-3-oxo-1-(2,4,5-trihydroxyphenyl)propyl]catechin* (=*(β*R,2R,3S)-*2-(3,4-Dihydroxyphenyl)-3,4-dihydro-3,5,7-trihydroxy-β-(2,4,5-trihydroxyphenyl)-2*H*-1-benzopyran-6-propanoic Acid Methyl Ester*; **4**). Brown powder. $[\alpha]_D^{22} = -27$ (*c* = 0.05, MeOH). UV (MeOH): 203 (4.53), 282 (3.68). IR (KBr): 3422, 1712, 1616, 1504, 1450, 1278, 819. ^1H- and ^{13}C-NMR: *Table 2*. HR-ESI-MS (pos.): 523.1058 ($[M+Na]^+$; calc. 523.1216).

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