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高山金粉蕨的黄酮类成分*

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摘要 从高山金粉蕨 (*Onychium contiggum*) 地上部分的甲醇抽提物中分到8个成分: 高山金粉蕨甲甙 (1), 高山金粉蕨乙甙 (2)、金粉蕨素 (3)、反式桂皮酸 (4), 瓦利甙 (5), β-谷甾醇 (6), 胡萝卜甙 (7) 和蔗糖 (8)。高山金粉蕨甲甙和乙甙是新成分, 反式桂皮酸系首次从金粉蕨属中分到。化学结构用一维和二维核磁共振技术确定。

关键词 高山金粉蕨, 中国蕨科, 黄酮, 黄酮甙
分类号 Q 946

Flavonoids from *Onychium contiggum*

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Abstract Eight compounds, contigoside A (1), contigoside B (2), onychin (3), trans - cinnamic acid (4), wallichoside (5), β - sitosterol (6), daucosterol (7), and sucrose (8) were isolated from the methanolic extract of the aerial parts of *Onychium contiggum*. Compound 1 and 2 were new ones. Trans - cinnamic acid (4) was isolated from *Onychium* for the first time. Their structures were assigned by a combination of one - and two - dimensional NMR techniques.

Key words *Onychium contiggum*, Sinopteridaceae, Flavone and flavone glycoside

Onychium, which is distributed mainly in eastern Asia, is a small genus with about 10 species (Sinopteridaceae family). Plants in this genus were used as traditional Chinese medicine for enteritis, jaundice, flu and fever and as toxicide (Zhou, 1988). The compounds isolated from *Onychium* include flavonoids, indanoids, chalcone and diterpenoids (Xu *et al*, 1993; Akabori *et al*, 1980; Hasegawa *et al*, 1974; Banerji *et al*, 1974; Ramakrishanan *et al*, 1974; Sengupta *et al*, 1976).

Chemical study on *Onychium contiggum* is not reported. The present paper describes the isolation, structural elucidation and identification of these eight constituents from this plant.

RESULTS AND DISCUSSIONS

Contigoside A (1), $C_{27}H_{30}O_{14}$, M^+ 578, has strong IR absorption for the hydroxyl groups

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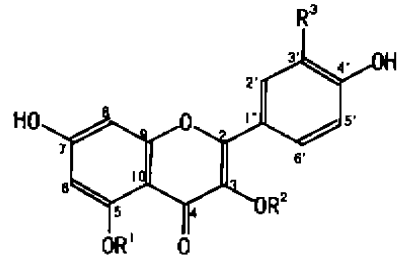
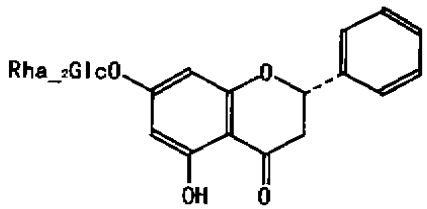
(3380 cm^{-1}) and the characteristic peaks due to the flavonol skeleton (1705, 1655, 1605, 1594, 1510, 970, 950, 915 cm^{-1}). This was further supported by typical UV spectrum at 201, 227, 244, 266, 288, 315 and 347 nm (logε: 4.46, 4.12, 4.09, 4.26, 3.89, 4.04 and 4.15) (Nomura *et al*, 1978). The ^{13}C NMR data (Table 2) also revealed the presence signals of a flavone skeleton and two rhamnose moiety signals. Its aglycone unit was very similar to that of 3,4',5,7 – tetrahydroxyflavone (kaempferol) (Wagner *et al*, 1976). The locations attached of two rhamnose units were deduced as follows. Comparison of ^{1}H NMR spectra of 1 with that of kaempferol showed the lack of extreme downfield characteristic signals for 5 – OH and 3 – OH ((12.5 – 10.6 ppm) due to the intramolecular hydrogen bonding (Roitman *et al*, 1993). Therefore, two rhamnose units could attach the 3 – and 5 – hydroxyl groups. This conclusion was supported by ^{13}C NMR data which showed the downfield shift of C – 2, C – 4, C – 6 and C – 10 signals from δ 146.8, 175.9, 98.2 and 103.1ppm in kaempferol to δ 157.15, 179.20, 100.09 and 107.12 ppm in 1, respectively (Markham et al, 1978). In addition, this conclusion was further confirmed by the detailed $^{1}H-^{1}H$ and $^{1}H-^{13}C$ COSY and COLOC analyses. On the basis of the above evidence, we assigned 1 as kaempferol – 3,5 – dirhamnoside, namely 2 – (4 – hydroxyphenyl) – 3,5 – di – (α – L – rhamnopyranosyloxy) – 7 – hydroxy – 4H – 1 – Benzopyran – 4 – one.

Contigoside B (2), $C_{21}H_{20}O_{12}$, M 464, has strong IR absorption for the hydroxyl groups (3350 cm^{-1}), and the characteristic peaks due to the flavone skeleton (1655, 1600, 1555, 1508, 995, 935 cm^{-1}). This was further supported by typical UV spectrum at 206, 258.5, 296 and 363 nm (logε: 4.



	R^1	R^2	R^3
1	Rha	Rha	H
2	H	Glc	OH



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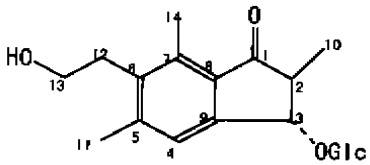

5

Fig Chemical Constituents of *Onychium contiguum*

55, 4.28, 3.94, 4.17) (Nomura *et al*, 1978). The ^{13}C NMR data (Table 2) also revealed the pres-

ence of a flavonol skeleton and an glucose moiety. Its aglycone unit was very similar to that of 3,3',4',5,7 - pentahydroxyflavone (quercetol) (Wagner *et al*, 1976). The location attached of glucose unit was deduced as follows. Comparison of ^1H NMR spectra of 2 with that of quercetol showed the lack of extreme downfield characteristic signal for 3 - OH (~ δ10.6 ppm) due to the intramolecular hydrogen bonding (Roitman *et al*, 1993). Therefore, this glucose unit could be suggested to the 3 - hydroxyl group. This conclusion was supported by ^{13}C NMR data which showed two downfield shift of C - 2 and C - 4 signals from δ 146.9 and 175.8 ppm in quercetol to δ 157.74 and 178.86 ppm in 2 (Markham et al, 1978). On the basis of the above evidence, 2 was determined as quercetol - 3 - glucoside, namely 2 - (3,4 - dihydroxyphenyl) - 3 - (β - D - glucopyranosyloxy) - 5,7 - dihydroxy - 4H - 1 - Benzopyran - 4 - one.

EXPERIMENTAL

General. Kofler melting points were uncorrected; Optical ratations were taken on a Jasco - 20C digital polarimeter. IR were recorded on KBr discs with a Perkin - Elmer 577 spectrometer. UV were obtained in EtOH on a UV - 210A spectrometer. EIMS (positive) were measured on a VG Auto Spec - 3000 spectrometer with direct inlet 70 or 20 eV. NMR were run on a Bruker AM - 400 spectrometer using TMS as internal standard; chemical shift values are reported in δ units (pyridine - d_5 and $CDCl_3$). Coupling constants (J) were expressed in Hz.

Plant Material. The aerial parts of *Onychium contiggum* were collected in Shiyang, Dayao County, Yunnan, China in September, 1989, and were identified by Prof. Sugong Wu, a botanist of the Kunming Institute of Botany, the Chinese Academy of *Sciences*. A voucher specimen was deposited in the Herbarium of the institute.

Extraction and isolation. 2 kg dried and powdered of *Onychium contiggum* were extracted with MeOH three times at room temperature for a week. after removal the solvent in vacuum, the residue was subjected on Si gel column chromatography and eluted with gradient $CHCl_3$ - CH_3COCH_3 and $CHCl_3$ - MeOH system. Nine compounds, contigoside A (1) (14 mg, 0.0007%), contigoside B (2) (10 mg, 0.0005%), onychin (3) (3.0 g, 0.15%), contigol (4 mg, 0.0002%), cinnamic acid (4) (12 mg, 0.0006%), wallichoside (5) (56 mg, 0.0028%), β - sitosterol (6), daucosterol (7) and sucrose (8) were obstained (See Figure 1). Some components were further purified by recrystallization and prep. TCL (silica gel).

Contigoside A (1), $C_{27}H_{30}O_{14}$ M 578, yellow needle crystals (MeOH), mp. 259 ~ 261℃; UV λ_{max}^{EtOH}(logε): 201 (4.46), 227 (4.12), 244 (4.09), 266 (4.26), 288 (3.89), 315 (4.04), 347 (4.15) nm; IR λ_{max}^{KBr}: 3380, 1705, 1655, 1605, 1594, 1510, 1490, 1444, 1370, 1345, 1305, 1280, 1206, 1176, 1130, 1090, 1055, 1025, 970, 950, 915, 836, 820, 810 cm^{-1}; EIMS 70eV m/z (%): 286 $[M - 2 \times Rha]^+$ (100), 269, 257, 241, 229, 213, 201, 184, 153, 128, 121, 99, 93, 85, 73, 58, 43; HRMS m/z (%): 578.1714 $[M]^+$ (100), Calc. for $C_{27}H_{30}O_{14}$ 578.1636,

431 [M - Rha - 1]$^+$ (94), 415 (15), 339 (35), 325 (56), 311 (34), 283 (10), 80 (8); ^{1}H NMR (C_5D_5N) δ: See Table 1; ^{13}C NMR (C_5D_5N) δ: See Table 2; ^{13}C - ^{1}H COSY and COLOC spectra See Table 3.

Contigoside B (2), $C_{21}H_{20}O_{12}$, yellow needle crystals (MeOH), mp. 206 ~ 208℃; UVλ_{max}^{EtOH} (logε): 206 (4.55), 258.5 (4.28), 296 (3.94), 363 (4.17) nm; IR ν_{max}^{KBr}: 3350, 1655, 1600, 1555, 1508, 1490, 1440, 1353, 1292, 1266, 1200, 1168, 1085, 1055, 1010, 995, 935, 810, 710, 655, 645, 595 cm^{-1}; EIMS 70eV m/z (%): 396 (45), 382 (5), 302 [M - Glc]$^+$ (100), 285 (2), 273 (8), 229 (6), 193 [302 - B - ring]$^+$ (2), 153 (18), 137 (35), 128 (22), 109 [B - ring]$^+$ (20), 81 (25), 73 (38), 69 (70), 55 (51), 43 (58); ^{1}H NMR (C_5D_5N) δ: See Table 1; ^{13}C NMR (C_5D_5N) δ: See Table 2.

Onychin (3), $C_{27}H_{32}O_{13}$, white needle crystals (MeOH), mp. 279 ~ 280℃; $[\alpha]^{24.5}$ - 112.93° (MeOH, C 0.29), UVλ_{max}^{EtOH}(logε): 213 (4.46), 286 (4.26), 330 (3.50) nm; IRλ_{max}^{KBr}: 3410, 3350, 1636, 1630, 1567, 1485, 1440, 1383, 1285, 1270, 1220, 1175, 1150, 1080, 1042, 1025, 972, 880, 846, 812, 770, 743 cm - 1; EIMS 70eV m/z (%): 564 [M]$^+$ (0.7), 418 [M - Rha]$^+$ (0.5), 400 [M - Rhamnose]$^+$ (1.2), 328 (0.7), 256 [M - Glc - Rha]$^+$ (100), 238 (6), 179 [256 - B - ring]$^+$ (43), 152 (37), 124 (27), 104 (23), 85 (34), 77 (B - ring, 19), 71 (37), 60 (30); ^{1}H NMR (C_5D_5N) δ: See Table 1; ^{13}C NMR (C_5D_5N) δ: See Table 2.

Table 1 ^{1}H NMR spectra data of compounds (1), (2), and (3) in C_5D_5N

Hydrogen	1	2	3
H - 6	6.77 d, 1.7	6.69 d, 16.	6.68 d, 2.0
H - 8	6.96 d, 1.7	6.66 d, 1.6	6.74 d, 2.0
H - 2′	8.05 dd, 8.6, 0.6	8.43 d, 2.0	7.54 d, 7.6
H - 3′	7.28 d, 8.6		7.40 t, 7.6
H - 4′			7.35 t, 7.6
H - 5′	7.28 d, 8.6	7.28 d, 8.4	7.40 t, 7.6
H - 6′	8.05 dd, 8.6, 0.6	8.01 dd, 8.4, 2.0	7.54 d, 7.6
5 - OH		12.64 s	12.46 s
H - 2β			5.40 dd, 13.2, 3.2
H - 3α			3.20 dd, 17.2, 13.2
H - 3β			2.87 dd, 17.2, 3.2
Glc - 1 - H		6.12 d, 6.6	5.71 d, 7.6
Glc - 5 - H		3.99 ddd,	4.05 ddd,
Glc - H_5		4.38 - 4.15	
Rha - 1 - H	6.28 s		6.40 s
Rha - 2 - H	5.09 br s		4.80 d, 2.0
Rha - H_3	4.61 - 4.16		
Rha - Me	1.43 d, 6.1		1.78 d, 6.0
Rha - 1′ - H	6.25 s		
Rha - 2′ - H	4.71 br s		
Rha - H'_3	4.65 - 4.49		
Rha - Me′	1.64 d, 6.0		

Table 2 ^{13}C NMR spectra data of compounds (1), (2), and in C_5D_5N

Carbon	1	2	3
2	157.15 s	157.74 s	79.50 d
3	136.16 s	135.50 s	43.45 t
4	179.20 s	178.86 s	196.62 s
5	162.49 s	162.86 s	164.53 s
6	100.09 d	100.04 d	97.94 d
7	162.99 s	166.23 s	166.31 s
8	94.94 d	94.77 d	96.30 d
9	158.48 s	157.95 s	163.41 s
10	107.12 s	105.31 s	104.43 s
1′	121.64 s	122.51 s	139.34 s
2′	131.58 d	116.40 d	126.85 d
3′	116.48 d	146.93 s	129.15 d
4′	161.90 s	150.80 s	129.06 d
5′	116.48 d	118.10 d	129.15 d
6′	131.58 d	122.75 d	126.85 d
Glucose			
Glc－1		104.84 d	99.48 d
－2		76.19 d	77.87 d
－3		78.68 d	79.20 d
－4		71.52 d	74.12 d
－5		78.97 d	78.89 d
－6		62.80 t	62.11 t
Rhamnose			
Rha－1	103.98 d		102.49 d
－2	71.97 d		72.44 d
－3	72.58 d		72.79 d
－4	73.29 d		71.17 d
－5	72.10 d		69.93 d
－Me	18.30 q		18.89 q
Rha－1′	100.40 d		
－2′	71.82 d		
－3′	72.41 d		
－4′	73.60 d		
－5′	71.45 d		
－Me′	18.60 q		

Trans－cinnamic acid (4), $C_9H_8O_2$, white amorphous crystals (MeOH), UVλ_{max}^{EtOH}(logε): 203.5 (4.27), 208.5 (4.14), 215.5 (4.22), 221.5 (4.17), 271 (4.17) nm; IR ν_{max}^{KBr}: 3048, 3018, 2820, 2700, 2590, 2520, 1680, 1625, 1572, 1490, 1446, 1416, 1340, 1310, 1285, 1223, 1203, 1175, 1065, 1025, 982, 970, 930, 870, 765, 705, 675, 596, 545, 484, 370 cm^{-1}; EIMS 20eV m/z (%): 148 $[M]^+$ (100), 131 $[M-OH]^+$ (42), 120 (13), 103 $[M-COOH]^+$ (80), 91 (40), 77 $[Benzene]^+$ (83), 65 (7), 51 (20), 40 (3); ^1H NMR ($CDCl_3$) δ: 7.80 (1H, d, J=16.0Hz, β－H), 6.45 (1H, d, J=16.0Hz, α－H), 7.56 (2H, m, 2,6－H), 7.40 (3H, m, 3,4,5－H); ^{13}C NMR ($CDCl_3$) δ: 172.56 (s, COOH), 147.10 (d, β－C), 117.

34 (d, α-C), 134.05 (s, C-1), 128.94 (d, C-2), 128.36 (d, C-3), 130.72 (d, C-4), 128.36 (d, C-5), 128.94 (d, C-6).

Wallichoside (5), $C_{20}H_{28}O_8$, mp. 199~201℃; UVλ_{max}^{EtOH}(logε): 219 (4.50), 258 (4.12), 299 (3.28) nm; IR ν_{max}^{KBr}: 3530, 3380, 3310, 3200, 1707, 1696, 1598, 1350, 1224, 1082, 1063, 1045, 1035, 1016, 916, 895, 876 cm^{-1}; EIMS 20eV m/z (%): 234 $[M-162]^+$(2), 216 $[M-glucose]^+$(27), 203 $[234-CH_2OH]^+$(3), 185 $[216-CH_2OH]^+$(100), 173 (7), 142 (5), 131 (2), 103 (5), 73 (80), 60 (45), 40 (18); ^1H NMR (C_5D_5N) δ: 7.74 (1H, s, 4-H), 5.08 (1H, d, 3.4, 3β-H), 3.96 (2H, t, 7.4, 13-H_2), 3.12 (2H, t, 7.4, 12-H_2), 3.09 (1H, dq, 7.2, 3.4, 2α-H), 2.80 (3H, s, 14-Me), 2.29 (3H, s, 11-Me), 1.61 (3H, d, 7.2, 10-Me), 5.24 (1H, d, 7.8, Glc-1-H), 4.14 (1H, dd, 7.8, 8.0, Glc-2-H), 4.36 (1H, t, 8.0, Glc-3-H), 4.32 (1H, t, 8.0, Glc-4-H), 4.05 (1H, ddd, 8.0, 5.1, 2.1, Glc-5-H), 4.60 (1H, dd, 11.7, 2.1, Glc-6-Ha), 4.45 (1H, dd, 11.7, 5.1, Glc-6-Hb). ^{13}C NMR (C_5D_5N) δ: 205.83 (s, C-1), 52.40 (d, C-2), 84.03 (d, C-3), 126.31 (d, C-4), 136.77 (s, C-5), 144.66 (s, C-6), 138.69 (s, C-7), 132.12 (s, C-8), 151.08 (s, C-9), 21.15 (q, C-10), 14.06 (q, C-11), 33.08 (t, C-12), 61.09 (t, C-13), 13.94 (q, C-14), 105.79 (d, Glc-1), 75.42 (d, Glc-2), 78.44 (d, Glc-3), 71.74 (d, Glc-4), 78.61 (d, Glc-5), 62.87 (t, Glc-6).

Table 3 ^{13}C-^1H COSY and COLOC spectra of Contigoside A (1) in C_5DN

Assignment	^1H NMR	^{13}C NMR	COLOC observed
H-2		157.15 s	
H-3		136.16 s	
H-6	6.77 d, 1.7	100.09 d	C-5, C-7, C-8, C-10
H-8	6.69 d, 1.7	94.94 d	C-6, C-7, C-9, C-10
H-2′, 6′	8.05 dd, 8.6, 0.6	131.58 d	C-2
H-3′, 5′	7 28 d, 8.6	116.48 d	C-1′
H-4′		161.90 s	
Rha-1-H	6.28 s	103.98 d	C-3, Rha-3 5-C
-2-H	5.09 br s	71.97 d	
-3-H	4.61 dd, 9.3, 3.2	72.58 d	
-4-H	4.30 t, 9.3	73.29 d	
-5-H	4.16 dq, 9.3, 6.1	72.10 d	
-6-Me	1.43 d, 6.1	18.30 q	
Rha-1′-H	6.25 s,	100.40 d	C-5, Rha′-3′, 5′-C
-2′-H	4.71 br s	71.82 d	
-3′-H	4.65 dd, 9.2, 3.2	72.41 d	
-4′-H	4.39 t, 9.2	73.60 d	
-5′-H	4.29 dq, 9.2, 6.0	71.45 d	
-6′-Me	1.64 d, 6.0	18.60 q	

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