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Flavonoids from Tartary Buckwheat Seeds

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Nine flavonoids were isolated from the seeds of tartary buckwheat. Their structures were eulcidated as quercetin (**1**), rutin (**2**), vitexin (**3**), orientin (**4**), hyperin (**5**), tricin-7-O-β-D-glucopyranoside (**6**), chrysoeriol (**7**), tectochrysin (**8**) and luteolin-7-O-β-D-glucopyranoside (**9**), by means of spectroscopic methods, especially by ^{1}H and ^{13}C NMR, FAB-MS and GC, as well as by chemical methods and comparison with literature data.

Key Words: Tartary buckwheat seed, Flavonoid.

INTRODUCTION

Flavonoids are a group of naturally occurring plant compounds that serve many functions *e.g.*, antioxidant, anti-tumor, antiinflammatory, antituberculosis, antimalarial, antimicrobial and antiviral, *etc.*[1,2]. The seeds of tartary buckwheat (*Fagopyrum tataricum* Gaertn.) serve as a rich source of flavonoids and have been popularly recognized as an excellent selective antioxidant and hypolipidaemic nutrient food in China and many other countries of the world[3]. In order to make full use of tartary buckwheat, our recent research led to the isolation of 9 flavonoids from the seeds of tartary buckwheat.

EXPERIMENTAL

Acid hydrolysis of compounds and determination of the absolute configuration of the monosaccharide: A solution of compound (5.0 mg, **2-6** and **9**) in 2 mol/L HCl-dioxane (1:1, 1 mL) was refluxed in a water bath at 90 ºC for 2 h. After removal of dioxane, the solution was extracted with EtOAc (1 mL × 3). The aqueous layer was neutralized by passing through an Amberlite MB-3 resin column eluted with H_2O, then concentrated and dried to furnish a monosaccharide residue. Then, the sugars were detected by TLC analysis [$CHCl_3$-CH_3OH-H_2O-HOAc (15:6:2:3), detection solution: aniline-phthalic acid] against the standard samples. The residue was dissolved in pyridine (0.2 mL) and then a pyridine solution (0.3 mL) of L-cysteine methyl ester hydrochloride (5 mg) was added to the solution. The mixture was kept at 60 ºC for 1.5 h, dried *in vacuo* and trimethylsilylated with hexamethyldisilazane-trimethylchlorosilane (HMDS-TMCS) (0.1 mL) at 60 ºC for 1 h. After being partitioned between *n*-hexane (0.5 mL) and H_2O (0.5 mL), the *n*-hexane extract was concentrated and analyzed by GC under the following conditions: HP-5 MS fused silica capillary column (30 m × 0.25 mm, film thinkness 0.25 μm), column temperature at 230 ºC, injection temperature at 250 ºC, N_2 as carrier gas. The sugars were confirmed by comparison of the retention times of their derivatives with standard samples [retention time, D-glucose (21.7 min), D-galactose (25.4 min) and L-rhamnose (19.1 min)]. The presence of L-rhamnose in **2**, D-galactose in **5**, D-glucose in **2, 3, 4, 6** and **9** were detected.

RESULTS AND DISCUSSION

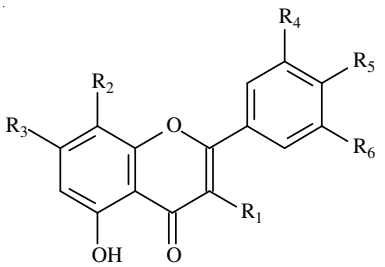
The seeds of tartary buckwheat were collected in September 2010 from Ring County of China and extracted three times with 95 % aqueous EtOH at room temperature. The extract was dissoved in 50 % aqueous EtOH and extracted with petroleum ether and EtOAc. The EtOAc extract was separated by repeated column chromatography (Silica-gel, Diaion HP-20 and Sephadex LH-20) and recrystallization to give nine flavonoid compounds. On the basis of chemical (acid hydrolysis) and spectral analyses (UV, IR, MS and NMR) and comparison with the literature data, their structures were elucidated as quercetin (**1**)[4,5], rutin (**2**)[6,7], vitexin (**3**)[8], orientin (**4**)[9], hyperin (5)[10,11], tricin-7-O-β-D-glucopyranoside (6)[12], chrysoeriol (7)[13,14], tectochrysin (**8**)[15] and luteolin-7-O-β-D-glucopyranoside (**9**)[16,17]. Although quercetin, rutin, vitexin, orientin and hyperin have been previously isolated from tartary buckwheat[18], this is first report on the occurrence of tricin-7-O-glucopyranoside,

TABLE-1
^{1}H-NMR DATA OF COMPOUNDS **1-9** (δ_H in DMSO-d_6, 400 MHz, *J*: Hz)

Proton	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
3			6.76 (s)	6.64 (s)		7.01 (s)	6.88 (s)	6.68 (s)	6.74 (s)
6	6.18 (d, 2.0)	6.21 (d, 2.0)	6.28 (s)	6.25 (s)	6.19 (d, 2.4)	6.92 (d, 1.9)	6.22 (d, 2.0)	6.39 (d, 2.1)	6.43 (d, 1.9)
8	6.38 (d, 2.0)	6.40 (d, 2.0)			6.41 (d, 2.4)	6.43 (d, 1.9)	6.49 (d, 2.0)	6.51 (d, 2.1)	6.79 (d, 1.9)
2'	7.62 (d, 2.0)	7.51 (d, 2.1)	7.99 (d, 8.1)	7.48 (d, 2.0)	7.51 (d, 1.7)	7.32 (s)	7.54 (m)	7.85 (m)	7.41 (d, 2.1)
3'			6.88 (d, 8.1)					7.48 (m)	
4'								7.54 (m)	
5'	6.88 (d, 8.1)	6.82 (d, 8.2)	6.88 (d, 8.1)	6.85 (d, 8.4)	6.81 (d, 8.4)		6.98 (d, 8.4)	7.48 (m)	6.88 (d, 8.0)
6'	7.56 (dd, 8.1, 2.0)	7.60 (dd, 8.2, 2.1)	7.99 (d, 8.1)	7.52 (dd, 8.4, 2.0)	7.66 (dd, 8.4, 1.7)	7.32 (s)	7.54 (dd, 8.4, 2.0)	7.85 (m)	7.46 (dd, 8.0, 2.1)
C_5-OH	12.48 (s)	12.58 (s)	13.21 (s)	13.16 (s)	12.62 (s)		12.95 (s)	12.71 (s)	12.98 (s)
OCH_3						3.85 (s)	3.90 (s)	3.89 (s)	
Anomeric H									
Glu		5.41 (d, 7.9)	4.68 (d, 7.6)	4.67 (d, 7.8)		5.02 (d, 7.4)			5.08 (d, 7.5)
Rha		4.38 (br s)							
Gal					5.36 (d, 7.8)				

TABLE-2
^{13}C-NMR (DEPT) DATA OF COMPOUNDS **1-9** (δ_C in DMSO-d_6, 100 MHz)

Carbon	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
2	146.8 (C)	156.6 (C)	163.9 (C)	164.1 (C)	156.2 (C)	164.5 (C)	163.8 (C)	163.8 (C)	164.3 (C)
3	135.6 (C)	133.4 (C)	102.4 (CH)	102.3 (CH)	133.8 (C)	103.9 (CH)	103.8 (CH)	104.3 (CH)	103.4 (CH)
4	175.6 (C)	177.2 (C)	182.1 (C)	182.0 (C)	177.6 (C)	182.1 (C)	181.9 (C)	182.2 (C)	181.9 (C)
5	160.1 (C)	161.2 (C)	161.1 (C)	160.5 (C)	161.0 (C)	157.3 (C)	157.4 (C)	162.0 (C)	159.8 (C)
6	99.0 (CH)	98.7 (CH)	98.2 (CH)	98.1 (CH)	98.9 (CH)	95.4 (CH)	98.8 (CH)	98.1 (CH)	99.5 (CH)
7	163.7 (C)	164.1 (C)	162.6 (C)	162.6 (C)	164.3 (C)	163.2 (C)	164.2 (C)	165.2 (C)	164.3 (C)
8	93.2 (CH)	93.6 (CH)	104.6 (C)	104.6 (C)	93.7 (CH)	99.5 (CH)	94.6 (CH)	92.6 (CH)	94.5 (CH)
9	156.0 (C)	156.5 (C)	156.2 (C)	156.0 (C)	156.9 (C)	161.2 (C)	161.7 (C)	157.4 (C)	157.3 (C)
10	102.5 (C)	104.1 (C)	104.2 (C)	104.1 (C)	104.0 (C)	105.4 (C)	103.3 (C)	105.6 (C)	105.2 (C)
1'	121.8 (C)	121.3 (C)	121.6 (C)	122.0 (C)	121.3 (C)	120.5 (C)	120.4 (C)	131.5 (C)	121.0 (C)
2'	114.9 (CH)	115.7 (CH)	129.1 (CH)	114.0 (CH)	115.4 (CH)	104.6 (CH)	110.2 (CH)	126.2 (CH)	113.7 (CH)
3'	144.8 (C)	144.8 (C)	115.9 (CH)	145.8 (C)	145.0 (C)	148.3 (C)	150.8 (C)	129.0 (CH)	145.6 (C)
4'	147.7 (C)	148.4 (C)	160.4 (C)	149.7 (C)	148.6 (C)	140.1 (C)	147.9 (C)	131.4 (CH)	149.9 (C)
5'	115.4 (CH)	121.7 (CH)	115.9 (CH)	115.7 (CH)	116.1 (CH)	148.3 (C)	115.8 (CH)	129.0 (CH)	115.8 (CH)
6'	119.6 (CH)	116.5 (CH)	129.1 (CH)	119.4 (CH)	122.4 (CH)	104.6 (CH)	121.8 (CH)	126.2 (CH)	119.3 (CH)
CH_3O						55.6 (CH_3)	56.1 (CH_3)	55.7 (CH_3)	
Sugar		Glu	Rha	Glu	Glu	Gal	Glu		Glu
1		101.2 (CH)	100.8 (CH)	73.8 (CH)	73.4 (CH)	101.9 (CH)	100.8 (CH)		100.1 (CH)
2		74.3 (CH)	70.1 (CH)	70.8 (CH)	70.8 (CH)	71.3 (CH)	73.3 (CH)		73.1 (CH)
3		76.3 (CH)	70.6 (CH)	78.6 (CH)	78.8 (CH)	73.4 (CH)	77.4 (CH)		77.5 (CH)
4		70.1 (CH)	71.9 (CH)	70.5 (CH)	70.7 (CH)	68.1 (CH)	69.8 (CH)		69.7 (CH)
5		75.8 (CH)	68.2 (CH)	81.7 (CH)	82.0 (CH)	75.8 (CH)	76.6 (CH)		76.4 (CH)
6		67.0 (CH_2)	17.5 (CH_3)	61.3 (CH_2)	61.7 (CH_2)	60.3 (CH_2)	60.8 (CH_2)		60.6 (CH_2)



Flavonoid	R_1	R_2	R_3	R_4	R_5	R_6
1	OH	H	OH	OH	OH	H
2	OGlc-(6→1)-Rha	H	OH	OH	OH	H
3	H	Glc	OH	H	OH	H
4	H	Glc	OH	OH	OH	H
5	OGal	H	OH	OH	OH	H
6	H	H	OGlc	OCH_3	OH	OCH_3
7	H	H	OH	OCH_3	OH	H
8	H	H	OCH_3	H	H	H
9	H	H	OGlc	OH	OH	H

chrysoeriol, tectochrysin and luteolin-7-O-glucopyranoside in this genus.

Quercetin (1), yellow needles ($CHCl_3$-MeOH), m.p. 312-314 ºC. UV spectrum (MeOH, λ_{max}, nm): 208 sh, 255, 284, 379 sh; IR spectrum (KBr, ν_{max}, cm^{-1}): 3406 (OH), 1665 (C=O), 1611, 1562, 1522, 1452 (Ar); negative FAB-MS *m/z*: 301 $[M-H]^-$. ^{1}H and ^{13}C NMR (Tables 1 and 2).

Rutin (2), yellow powder ($CHCl_3$-MeOH), m.p. 191-192 ºC. UV spectrum (MeOH, λ_{max}, nm): 207, 259 sh, 261, 356 sh; IR spectrum (KBr, ν_{max}, cm^{-1}): 3422 (OH), 1656 (C=O), 1604, 1567, 1506, 1456 (Ar), 1363 (CH_3), 1064, 1025 (glycosidic bond); negative FAB-MS *m/z*: 609 $[M-H]^-$. ^{1}H and ^{13}C NMR (Tables 1 and 2).

Vitexin (3), yellow crystal (MeOH), m.p. 269-271 ºC. UV (MeOH, λ_{max}, nm): 250, 267 sh, 337 sh; IR spectrum (KBr, ν_{max}, cm^{-1}): 3278 (OH), 1660 (C=O), 1608, 1500 (Ar); negative FAB-MS *m/z*: 431 $[M-H]^-$. ^{1}H and ^{13}C NMR (Tables 1 and 2).

Orientin (4), yellow crystal (MeOH), m.p. 261-263 ºC. UV (MeOH, λ_{max}, nm): 248 sh, 258 sh, 324; IR spectrum (KBr, ν_{max}, cm^{-1}): 3312 (OH), 1658 (C=O), 1612, 1500 (Ar); negative FAB-MS *m/z*: 447 $[M-H]^-$. ^1H and ^{13}C NMR (Tables 1 and 2).

Hyperin (5), pale yellow needles (MeOH), m.p. 235-237 ºC. UV spectrum (MeOH, λ_{max}, nm): 206 sh, 257, 299, 362 sh; IR spectrum (KBr, ν_{max}, cm^{-1}): 3423 (OH), 1661 (C=O), 1604, 1562, 1501, 1463 (Ar); negative FAB-MS *m/z*: 463 $[M-H]^-$. ^1H and ^{13}C NMR (Tables 1 and 2).

Tricin-7-O-β-D-glucopyranoside (6), yellow needles (MeOH), m.p. 186-188 ºC. UV spectrum (MeOH, λ_{max}, nm): 250, 266 sh, 352 sh; IR spectrum (KBr, ν_{max}, cm^{-1}): 3447 (OH), 1650 (C=O), 1607, 1510, 1478 (Ar); negative FAB-MS *m/z*: 491 $[M-H]^-$. ^1H and ^{13}C NMR (Tables 1 and 2).

Chrysoeriol (7), yellow needles, m.p. 323-325 ºC. UV spectrum (MeOH, λ_{max}, nm): 247 sh, 267, 345 sh; IR spectrum (KBr, ν_{max}, cm^{-1}): 3356 (OH), 1652 (C=O), 1626, 1597, 1508 (Ar); negative FAB-MS *m/z*: 299 $[M-H]^-$. ^1H and ^{13}C NMR (Tables 1 and 2).

Tectochrysin (8), pale yellow needles (EtOH), m.p. 162-165 ºC. UV spectrum (MeOH, λ_{max}, nm): 248, 269 sh, 312 sh; IR spectrum (KBr, λ_{max}, cm^{-1}): 3441 (OH), 1620 (C=O), 1615, 1595 (Ar); negative FAB-MS *m/z*: 267 $[M-H]^-$. ^1H and ^{13}C NMR (Tables 1 and 2).

Luteolin-7-O-β-D-glucopyranoside (9), yellow crystal (MeOH), m.p. 252-254 ºC. UV spectrum (MeOH, λ_{max}, nm): 255 sh, 267, 351 sh; IR spectrum (KBr, ν_{max}, cm^{-1}): 3375 (OH), 1665 (C=O), 1560, 1510 (Ar), 1095, 1030 (glycosidic bond); negative FAB-MS *m/z*: 447 $[M-H]^-$. ^1H and ^{13}C NMR (Tables 1 and 2).

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