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Phytochemical Studies on *Reynoutriae Radix* ("Hǔ-Zhàng")

Hyung-Joon Chi and Hyun-Soo Kim

Natural Products Research Institute, Seoul National University, Seoul 110, Korea

Abstract—Anthraquinones, physcion (I), mp 204~205° and emodin (II), mp 254~255°, and emodin-8-O-β-D-glucoside (IV), mp 191~192° together with β-sitosterol glucoside (III), mp 280~282° were isolated from the roots of *Polygonum ellipticum* Migo and *P. sachalinense* Fr. Schm. (Polygonaceae). Stilbene derivatives, 3, 5, 4′-trihydroxystibene (V), mp 258~260° and 3, 5, 4′-trihydroxystilbene-3-O-β-D-glucoside (VI), mp 142~144° were also isolated

Keywords—*Polygonum ellipticum* · *P. sachalinense* · Polygonaceae · physcion · emodin · emodin-8-O-β-D-glucoside · β-sitosterol glucoside · 3, 5, 4′-trihydroxystilbene · 3, 5, 4′-trihydroxystilbene-3-O-β-D-glucoside.

"Ho-zhang",(虎杖), Korean name of *Reynoutriae Radix*, which consisted of three species of genus Polygonum[1], namely *P. ellipticum* Migo (=*Reynoutria elliptica*), *P. sachalinense* Fr. Schm. and *P. cuspidatum* Sieb. et Zucc. The polygonaceous plants which are perennial herbs are distributed in Korea. The root of the plants has been used as laxative, diuretic[2], and for the treatment of suppurative dermatitis, gonorrhoea and favus in the oriental medicine. Most of "Hǔ-zhàng" in Korean market are the rhizomes of *P. sachalinense*. And the rhizome of *P. cuspidatum* can be found only in limited quantity in Korean market. *P. ellipticum* is a species transplanted from the Chinese continent and is not usually collected for the medicinal use.

The rhizomes of *P. ellipticum* Migo, *P. sachalinense* Fr. Schm. and *P. cuspidatum* Sieb. et Zucc. are classified into two types; erect rhizome type (*P. ellipticum* and *P. sachalinense*) (Fig. 1 and Fig. 2) and horizontal type (*P. cuspidatum*)

Fig. 1. Sketch of the leaves and rhizomes of *P. ellipticum* Migo

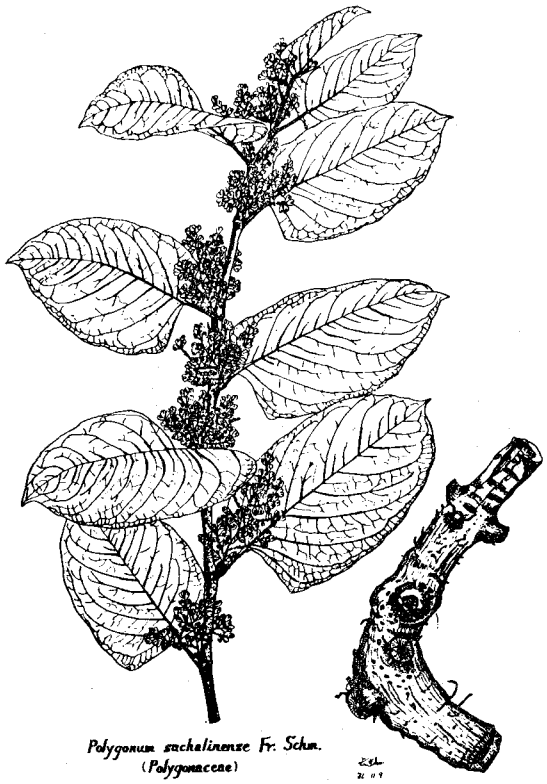


Fig. 2. Sketch of the leaves and rhizomes of *P. sachalinense* Fr. Schm.

(Fig. 3). It is suggested that the name of Reynoutriae Radix should be corrected to Reynoutriae Rhizoma=Polygoni Rhizoma. The shapes of blades are also characteristic for each species. *P. cuspidatum* is acuminate in apex blade and truncate in base of blade (Fig. 3). On the other hand, the shape of blade of *P. ellipticum* is elliptical with smaller size than that of *P. sachalinense* which is rounded in base of blade (Fig. 1 and Fig. 2).

As a part of the study for the comparison of the three species in their components, the authors attempted to isolate the anthraquinones[3,4] and stilbene derivatives[5] from the roots of *P. ellipticum* and those of *P. sachalinense*. Previous workers reported the isolation of the anthraquinones and stilbene derivatives from the roots of *P. cuspidatum*[6].

The MeOH extracts of the root of *P. ellipticum* and that of *P. sachalinense* were fractionated according to the procedures shown in scheme 1. Ether soluble portion was subjected to silica gel column chromatography to give I and II. Subsequent chromatography over polyamide afforded V. Ether insoluble portion was dissolved in hot MeOH and filtered. The filtrate was chromatographed over silica gel to yield III, IV and VI. I, II and IV showed positive results in Bornträger test.

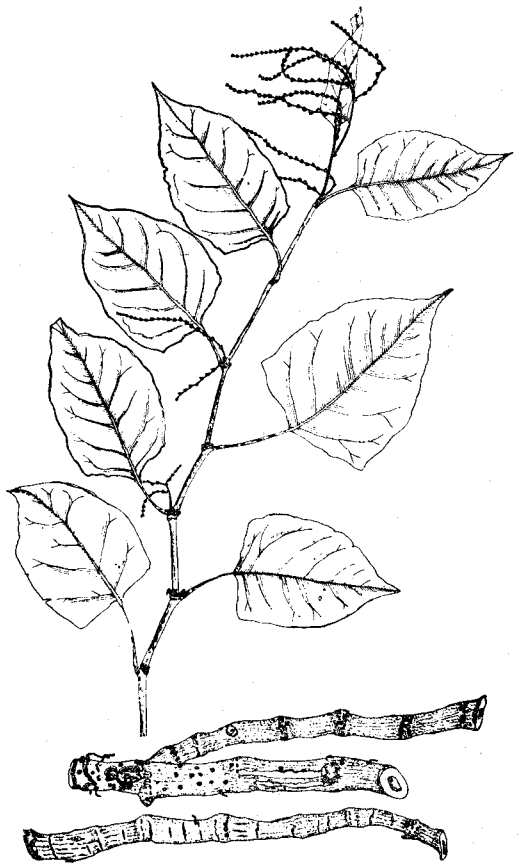
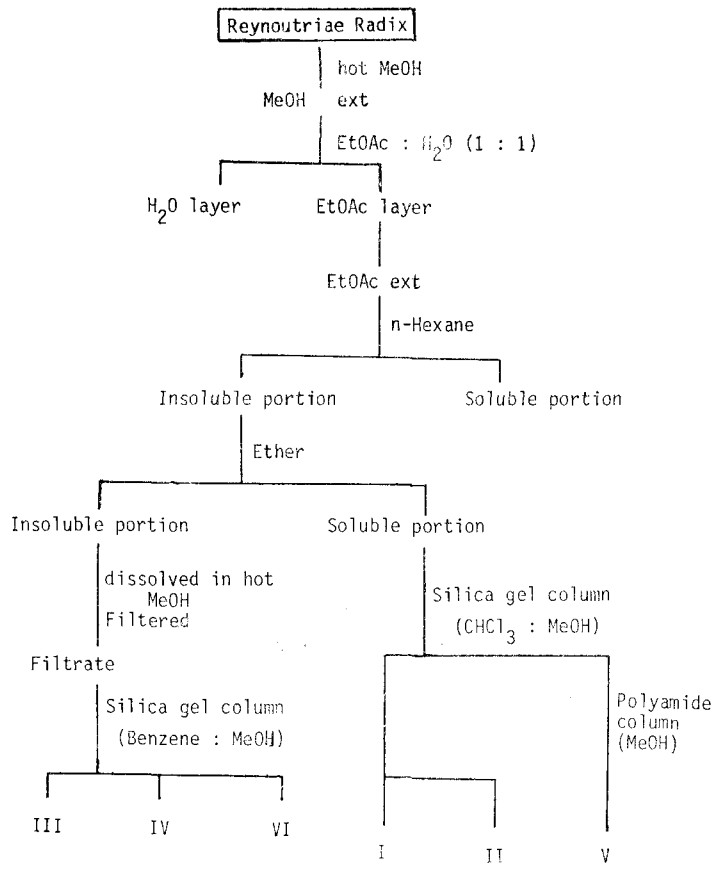


Fig. 3. Sketch of the leaves and rhizomes of *P. cuspidatum* Sieb. et Zucc.

Physcion (I), mp 204~205°, yellow needles (MeOH-$CHCl_3$), ir, νmax (KBr) 1680 (chelated C=O), 1600, 1480 (aromatic ring) cm^{-1}; uv, λ max (MeOH) 224, 265, 289, 436 nm; H^1-nmr, ($CDCl_3$) δ 2.45 (3H, s, Ar-CH_3), 3.95 (3H, s,



Scheme 1. Extraction and isolation of the compounds.

OCH_3), 6.72 (1H, d, J_{meta}=2.5 Hz, H-7), 7.10 (1H, sbr, H-2), 7.40 (1H, d, J_{meta}=2.5 Hz, H-5), 7.65 (1H, sbr, H-4).

Emodin (II), mp 254~255°, yellow needles (MeOH), ir, νmax (KBr) 3500~3200(OH), 1630 (C=O), 1470 (aromatic ring) cm^{-1}; UV, λmax (MeOH) 220, 255, 291, 444 nm; H^1-nmr, ($CDCl_3$) δ 2.40(3H, s, Ar-CH_3), 6.57 (1H, d, J_{meta}=2.5 Hz, H-7), 7.02 (1H, sbr, H-2), 7.17 (1H, d, J_{meta}=2.5 Hz, H-5), 7.40 (1H, sbr, H-4), 11.94 (1H, s, OH), 12.01 (1H, s, OH).

Emodin-8-O-β-D-glucoside (IV), mp 191~192°, yellow needles (MeOH), gave positive reaction in Molish test and showed absorption bands at 3400(OH), 1630 (C=O), 1600, 1470 (aromatic ring), 1100~1000 (glycosidic) cm^{-1} in its IR spectrum; uv, λmax (MeOH) 221.5, 285, 433.5 nm. Acetylation of IV with acetic anhydride and pyridine at room temperature overnight gave acetate as yellow needles, mp 206~208°, ir, νmax (KBr) 1745, 1220 (acetate) cm^{-1}, H^1-nmr, ($CDCl_3$) δ 2.05 (6H, s, 2× acetyl), 2.08 (3H, s, acetyl), 2.12 (3H, s, acetyl), 2.32(3H, s, CH_3-Ar), 2.47 (3H, s, AcO-Ar), 2.52 (3H, AcO-Ar), 4.27 (2H, sbr, H-5′, 6′), 0.5~5.5 (4H, m, H-1′, 2′, 3′, 4′), 7.25 (1H, sbr, H-2), 7.30 (1H, d, J_{meta}=2 Hz, H-7), 7.78 (1H, d, J_{meta} =2 Hz, H-1), 7.99 (1H, sbr, H-4). IV was hydrolyzed by refluxing with 5% H_2SO_4 for 2hr. After cooling, the reaction mixture was filtered to give emodin (TLC, mmp). The filtrate was neutralized with $BaCO_3$, conce-

ntrated in vacuo and identified as glucose by TLC. IV was also hydrolyzed by β-glucosidase at 37°C for 2 hr to give emodin and glucose (TLC, mmp). I, II and IV were identified as physcion, emodin and emodin-8-O-β-D-glucoside by direct comparison with authentic samples (TLC, mmp) and these spectral data.

β-Sitosterol glucoside (III), mp 280~282°, colorless needles ($CHCl_3$), showed positive results in Liebermann-Burchard test and Molish test and was identified by direct comparison with authentic samples (TLC, mmp). III was hydrolzed by 5% H_2SO_4 to give sterol mixture and glucose, identified by direct comparison with authentic samples (TLC, mmp).

V and VI emitted strong blue fluorescence under an ultra violet lamp (365 nm) and showed blue coloration with $FeCl_3$ reagent. V, mp 258~260°, ir, νmax (KBr) 3280 (OH), 1600, 1580, 1510 (aromatic), 960 (trans CH=CH) cm^{-1}; uv, λmax (EtOH) 210, 218, 238, 306, 320 nm; uv, λmax (EtOH+NaOH) 235, 318, 344 nm. The uv spectrum with the absorption maxima at 306 and 320 nm and the IR spectrum with the band at 960 cm^{-1} suggested that V should contain a trans stilbene moiety. The NMR spectrum of V[7] exhibited nine proton signals in the olefinic proton region, among which a pair of doublet signals at 6.74 and 6.98 ppm were assigned to trans olefinic protons as shown by the coupling constant (J=16 Hz) and A_2B_2-type quartet signal at 6.73 and 7.38 ppm (J=9 Hz) represented the presence of *p*-substituted benzene ring. The AX_2-type signals appeared at 6.12 (1H, t, J=2 Hz) and 6.38 (2H, d, J=2 Hz) ppm were assignable to the protons on the 1, 3, 5-trisubstituted benzene ring. MS spectrum of V showed molecular ion peak at m/z 228. Methylation[5] of V with ethereal dizomethane afforded a trimethylether, mp 55~56°, colorless needles, which showed molecular ion peak at m/z 270[8]. V on acetylation with acetic anhydride and pyridine in water bath for 3 hr gave a triacetate, mp 108~112°, colorless needles, H^1-nmr, ($CDCl_3$) δ 2.30 (9H, s, OAc ×3), 6.83 (1H, t, J=2 Hz, H-4), 7.08, 7.49 (2H, each, d, J=9.0 Hz), 7.20~7.30 (4H, aromatic H, CH=CH); ms, m/z 354 (M^+), 313, 312, 270, 229, 228, 227, 211, 199, 181. From these spectral data, the structure of V was determined to be 3, 5, 4′-trihydroxystilbene (resveratrol).

VI, mp 142~144°, $[\alpha]_D^{25}$ −66.6° (C=0.3, aqueous MeOH), pale yellow needles, gave positive result in Molish test, ir, ν max (KBr) 3350 (OH), 1610, 1580, 1510 (aromatic), 1100~1000 (glycosidic), 960 (trans CH=CH) cm^{-1}; uv, λmax (EtOH) 236, 309, 322 nm; uv, λmax (EtOH+NaOH) 245, 322, 347.5 nm. The uv spectrum suggested the presence of a highly conjugated system (λmax (MeOH) 309, 322 nm); ms, m/z 390 (M^+). Acid hydrolysis of VI by refluxing with 5% H_2SO_4 for 3 hr yielded V, mp 256°, ms, m/z 228 (M^+) and glucose, which were identified by direct comparison with authentic samples (TLC). Treatment of VI with etheral diazomethane gave a dimethylether, mp 167°, ms, m/z 418 (M^+). Acetylation of VI with acetic anhydride and pyridine in water bath for 3 hr afforded hexaacetate, mp 156~158°, ir, ν max (KBr) 1750, 1220 (acetate). The NMR spectrum of acetate of VI[9] exhibited two phenolic acetyl signals and four acetyl signals of glucose moiety in the region of 2.30 and 2.04~2.06 ppm, respectively. H^1-nmr, ($CDCl_3$) δ 2.04~2.06 (12H, s, OAc, sugar moiety), 2.30 (6H, s, 2 ×phenolic OAc), 3.72~5.32 (7H, sugar H), 6.66 (1H, t, J=2 Hz H-4), 6.97 (2H, d, J=2.0 Hz, H-2, 6), 6.96-7.01 (2H, CH=CH), 7.18, 7.48 (2H, each, d, J=9 Hz, aromatic); ms, m/z 642 (M^+). Thus the structure of VI was characterized to be 3, 5, 4′-trihydroxystilbene-3-O-β-D-glucoside (piceid)[6-a].

In conclusion, the anthraquinones (I,II and IV) and stilbene derivatives (V and VI) were isolated

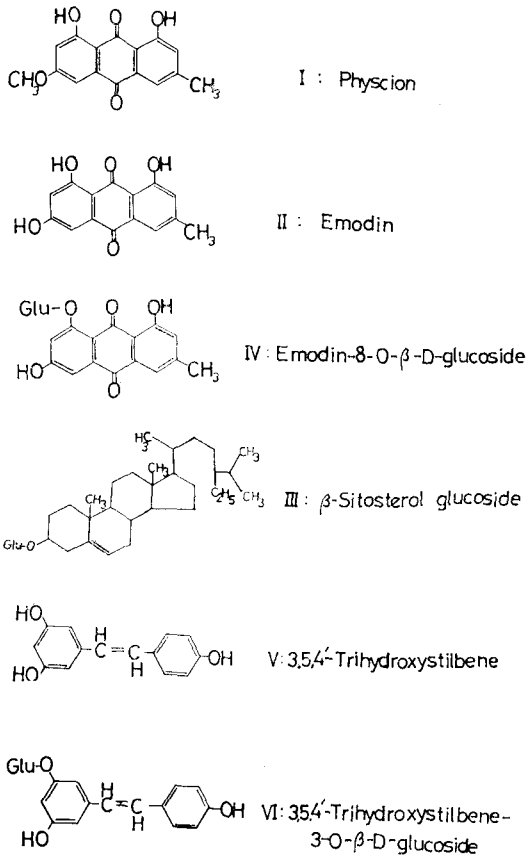


Fig. 4. The anthraquinones and stilbene derivatives from the roots of *P. ellipticum* and *P. sachalinense*.

from the roots of *P. ellipticum* and *P. sachalinense* (Fig. 4). Identical anthraquinones and stilbene derivatives were already reported to be isolated from the root of *P. cuspidatum*. Therefore, it was suggested that the roots of *P. ellipticum*, *P. sachalinense* and *P. cuspidatum* could be used altogether as a source of *Reynoutriae* Radix.

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