생 약 학 회 지
Kor. J. Pharmacog.
13(1): 7~9 (1982)

Anthraquinones from the Leaves of *Polygonum sachalinense*

Sam-Sik Kang and Won-Sick Woo
Natural Products Research Institute, Seoul National University

왕호장 잎의 안트라퀴논

강 삼 식·우 원 식
서울대학교 생약연구소

From the leaves of *Polygonum sachalinense* Fr. Schm. (Polygonaceae) physcion (I) mp 205~6°, emodin (II) mp 248~50°, physcion-8-0-β-glucoside (III) mp 245~6° and emodin-8-0-β-glucoside (IV) mp 186~8° were isolated.

The presence of phenolic acids[1], flavonoids[2-6], anthocyanins[7] and anthraquinones[6,8] has been known in the leaves of *Polygonum sachalinense*. Hower, Tsukida, *et. al.*[9] reported that anthraquinones were not detected by paper chromatography. Our reinvestigation of phytochemical work on this plant part resulted in the isolation of physcion and emodin and their glucosides.

The MeOH extract of dried leaves was fractionated into $CHCl_3$-, ethylacetate-, BuOH- and H_2O-soluble fractions. From the $CHCl_3$ soluble fraction two anthraquinones (I and II) were isolated and identified as physcion (I) and emodin (II) by direct comparison (mmp, IR and TLC) with authentic samples, respectively.

The other two compounds (III and IV) isolated from ethylacetate soluble fraction showed characteristic positive color test for hydroxyanthraquinone and on acid hydrolysis, gave physcion (I) and emodin (II) respectively together with glucose.

The attachment of the glucose moiety at 8-position in both compounds was established by UV, NMR spectra[10-12] and methylation followed by hydrolysis liberating 1, 6-di-0-methyl emodin, mp 195~6°. The NMR spectra of both glucoside acetates showed that glucose is in the pyranose form with β-configuration[13,14].

On the basis of these results, the structure of compound III and IV was suggested as physcion-8-0-β-glucoside and emodin-8-0-β-glucoside, respectively and confirmed by comparison with authentic samples.

This is the first report of the occurrence of physcion and its glucoside in this plant.

Experimental

The mps were taken on a Mitamura-Riken apparatus and are uncorrected. The UV spectra were runned on a Shimadzu model MPS-50L recording spectrophotometer and the IR spectra were determined in KBr pellets on a Beckman model IR-20A spectrophotometer. The NMR spectra were recorded on a Nicolet 297 Fourier Transformated T-60 spectrometer with TMS as internal standard.

Extraction and isolation of anthraquinones: The MeOH extract of *P. sachalinense*

leaves was fractionated into $CHCl_3$-, ethylacetate-, BuOH- and H_2O-soluble fractions. The $CHCl_3$ and ethylacetate soluble fractions were subjected to SiO_2 column chromatography eluting with $CHCl_3$-hexane (gradient) and $CHCl_3$-MeOH-H_2O (13:7:2, lower phase), respectively. Compounds I and II were obtained from $CHCl_3$ fraction and compounds III and IV were from ethylacetate fraction. Compounds I and II were crystallized from MeOH-$CHCl_3$ to yield orange needles, mp 205~6° and 248~50°, respectively. Both were confirmed by direct comparison with authentic physcion and emodin, respectively (mmp, IR and TLC). Compounds III and IV were crystallized from MeOH to yield orange needles and showed posititive result in Bronträger test.

Compound III (10mg): mp 245~6°; UV λ_{max}^{EtOH} nm(log ε) 224(4.47), 272(4.37), 283(sh, 4.34), 301(sh, 4.10), 433(3.87); IR ν_{max}^{KBr} cm^{-1} 3400(OH), 1672(free C=O), 1633 (chelated C=O), 1100~1000(glycosidic).

Compound IV (15mg): mp 186~8°; UV λ_{max}^{EtOH} nm(log ε) 224(4.47), 273(4.28), 288 (4.30), 304(sh, 4.19), 432(3.91); IR ν_{max}^{KBr} cm^{-1} 3400(OH), 1660(free C=O), 1630(chelated C=O), 1100~1000 (glycosidic).

Acid hydrolysis of glucosides: Compounds III and IV (4mg each) were refluxed with 5% H_2SO_4 for 1hr respectively. After cooling, the reaction mixture was filtered. Physcion, mp 205~7°, was obtained from compound III and emodin, mp 249~51°, from compound IV. The filtrate was neutralized with $BaCO_3$, concentrated in vacuo respectively and identified as glucose in both cases by TLC (precoated cellulose, pyridine-ethylacetate-HOAc-H_2O=36 : 36 : 7:21, Rf=0.46).

Acetylation of glucosides: Compounds III (5mg) and IV (8mg) were refluxed with Ac_2O/pyridine (0.5ml each) for 3hr, respectively. The reaction mixture was followed by the usual work-up and subjected to spectroscopy.

Compound III acetate: IR ν_{max}^{KBr} cm^{-1} 1760, 1220(acetate); NMR($CDCl_3$)δ 2.05(6H, s, 2× acetyl), 2.10(3H, s, acetyl), 2.11(3H, s, acetyl), 2.45(3H, s, C_3-CH_3), 2.52(3H, s, acetyl), 3.96(3H, s, OCH_3), 3.96(1H, m, H-5′), 4.20(2H, q-like, H-6′), 5.0~5.5(4H, m, H-1′, 2′, 3′, 4′), 6.95(1H, d, J=2Hz, H-7), 7.22(1H, bs, H-2), 7.52(1H, d, J=2Hz, H-5), 7.95(1H, bs, H-4).

Compound IV acetate: IR ν_{max}^{KBr} cm^{-1} 1745, 1220(acetate); NMR($CDCl_3$)δ 2.05(3H, s, acetyl), 2.09(9H, s, 3×acetyl), 2.34(3H, s, C_3-CH_3), 2.52(6H, s, 2×acetyl), 3.92(1H, m, H-5′), 4.26(2H, bs, H-6′), 5.0~5.5(4H, m, H-1′, 2′, 3′, 4′), 7.25(1H, bs, H-2), 7.30 (1H, d, J=2Hz, H-7), 7.78(1H, d, J=2Hz, H-5), 7.99(1H, bs, H-4).

Methylation of glucosides followed by acid hydrolysis: To compound III and IV (10mg each) in acetone (30ml), dimethylsulfate (1ml) and K_2CO_3 (100mg) were added, separately and refluxed for 5hr. The reaction mixture was filtered, concentrated in vacuo and poured onto crushed ice. The precipitate was refluxed with 5% H_2SO_4 for 1hr in 20ml of 50% dioxane, diluted with H_2O and extracted with ether. The ether extract was subjected to SiO_2 column chromatography eluting with benzene-ether (4:1) to give orange stout crystals, mp 195~6°. It was identified as 1,6-di-0-methyl emodin by direct comparison with authentic sample (mmp, TLC and IR).

Acknowledgement: We are indebted to Dr. I. Nishioka, Kyushu University, Japan, for his generous gift of samples of glucosides of physcion and emodin and 1,6-di-0-methyl emodin.

〈Recieved April 9, 1982〉

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