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# Anthraquinone and Stilbene Derivatives from the Cultivated Korean Rhubarb Rhizomes

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The studies were carried out to evaluate the constituents in the rhizomes of the cultivated Korean Rhubarb (Polygonaceae). From the acetone fraction of methanol extract Compound I (1,8-dihydroxy-3-methyl anthraquinone, chrysophanic acid), Compound II (chrysophanol-8-O-β-D-glucopyranoside), Compound III (emodin-8-O-β-D-glucopyranoside) and Compound IV (aloe -emodin-8-O-β-D-glucopyranoside), and from the ether fraction Compound V (1,8-dihydroxy-3-methyl-6-methoxy anthraquinone, physcion) and Compound VI (1,6,8-trihydroxy-3-methyl anthraquinone, emodin), and also from the n-buthanol fraction Compound VII (rhapontigenin-3-O-β-D-glucopyranoside, rhaponticin) and Compound VIII (piceatannol-3'-O-β-D-glucopyranoside), were isolated and identified on the basis of their physico-chemical and spectroscopic evidences (UV, IR, $^{1}$H-NMR, $^{13}$C-NMR, EI-MS), respectively.

**Key words :** Cultivated Korean Rhubarb, Polygonaceae, 1,8-dihydroxy-3-methyl anthraquinone (chrysophanic acid), Chrysophanol-8-O-β-D-glucopyranoside

## INTRODUCTION

Rhubarb is very common plant drug for stomachic bitter, laxative and purgative with secondary astringent action in indigestion, analgesic, anti-bloodstagnancy, etc. (Yook, 1992).

Recent intensive studies on the constituents of rhubarb (Rhei Rhizoma) have revealed the occurrence of anthraquinone derivatives (Tsukida *et al.*, 1954, Uchibayashi *et al.*, 1961, Okabe *et al.*, 1973, Oshio *et al.*, 1974, 1978, Holzschuh *et al.*, 1982, Khetwal *et al.*, 1988, Rawat *et al.*, 1989, Miyamoto *et al.*, 1967, 1972 and Yamagishi *et al.*, 1987) and stilbene glycosides (Yaki *et al.*, 1971 and Kashiwada *et al.*, 1984a, 1984b, 1988)

Previously, we reported that flavonoids and anthraquinones from polar solvents fraction of MeOH fraction from Korean Rhubarb Leaves were isolated (Ham *et al.*, 1994a, 1994b).

But so far, taxonomical or phytochemical studies on the Korean Cultivated Rhubarb Rhizomes have not been conducted.

This paper describes the isolation and charaterization of the six anthraquinones and two stilbene glycosides from the rhizomes of the cultivated Korean Rhubarb Rhizomes and also chrysophanol-8-O-β-D-glucopyranoside, rhapontigenin-3-O-β-D-glucopyranoside (rhaponticin) and piceatannol-3'-O-β-D-glucopyranoside occur in the large amount (5.26, 0.16 and 0.24%).

According to the results, it is identified that the plant origin of the cultivated Korean Rhubarb is *Rheum undulatum* in the viewpoint of chmotaxonomical classification.

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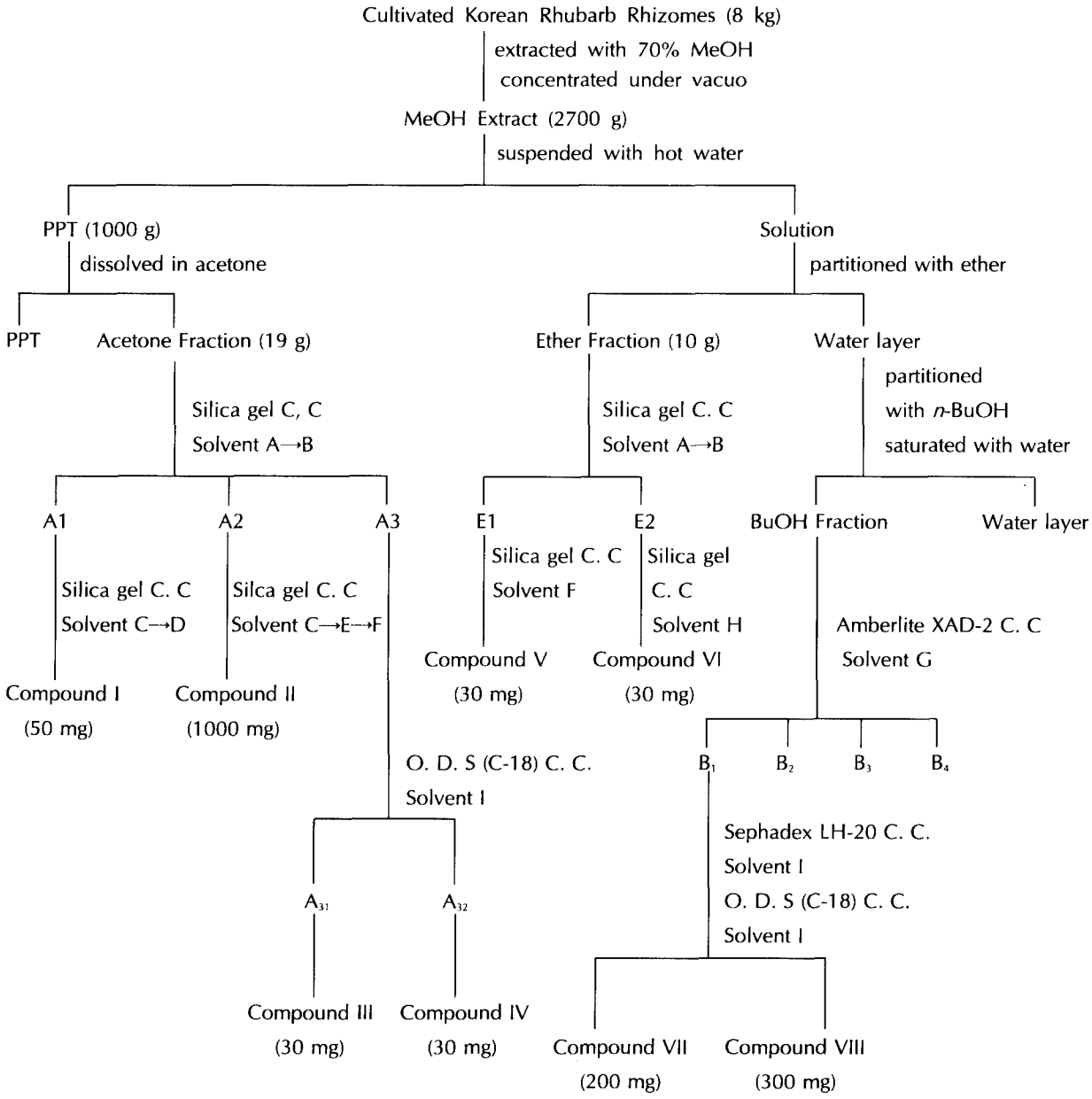
## MATERIALS AND METHODS

### Instruments

Melting points were determined on Electrothermal IA 8100 apparatus and are uncorrected. IR and UV spectra were obtained with a Bruker IFS48, FT-IR and Varian Cary-3 spectrophotometer, respectively. PMR and CMR spectra were measured with a Bruker AM-200, AMX-500 at 200 and 500 MHz with tetramethylsilanes as an internal standard. EI-MS was taken on a GC-MS/MS-DS, TSQ 700 mass spectrometer. GC was carried out to identifyed sugars by the usual manner with a Shimadzu GC-14A.

### Plant Material

Cultivated Korean Rhubarb Rhizomes were collected in May (1991) at Chong Ju of Chung Chong Buk Do. After depositing the voucher specimen at the Department of Pharmacal Botany, College of Pharmacy, Chung-Ang University, we used for ex-




**Scheme I.** Extraction and Isolation of Constituents from the Cultivated Korean Rhubarb Rhizomes

Solvent A: $CHCl_3$:MeOH:$H_2O$=80:25:2.5 Solvent B: $CHCl_3$:MeOH:$H_2O$=60:35:8 Solvent C: EtOAc:MeOH:$H_2O$=90:5:5
Solvent D: Hexane:EtOAc=7:1 Solvent E: EtOAc:MeOH:$H_2O$=100:13.5:10 Solvent F: Hexane:EtOAc=2:1
Solvent G: MeOH:$H_2O$=10%→100% Solvent H: Benzene:EtOAc=1:5 Solvent I: MeOH:$H_2O$=30:70

periment after crushed and air-dried.

## Extraction and isolation

The dried material (8.0 kg) was extracted with hot MeOH (70%). The MeOH extract was suspended in hot $H_2O$ and partitioned with ether and *n*-BuOH, succesively and $H_2O$ insoluble precipitate was extracted with acetone to obtain acetone soluble fraction (19 g).

19 g of the acetone soluble fraction was subjected to chromatography on silica gel with solvents ($CHCl_3$-MeOH-$H_2O$, 80 : 25 : 2.5 and EtOAc-MeOH-$H_2O$, 90 : 5 : 5, homogenous) to give three fractions designated as A1-A3 in order of elution. Further silica gel chromatography of fr. A1 and A2 with EtOAc-MeOH-$H_2O$ (100 : 13.5 : 10) afforded Compound I (50 mg) and Compound II (1000 mg). Fr.A3 was chromatographed on ODS-gel, Waters (70% MeOH) to give Compound III and Compound IV.

And 10 g of the ether fraction was subjected to chromatography on silica gel with solvents ($CHCl_3$-

**Table I.** $^{13}C$ NMR Spectral data of Compounds I, II, III, IV, V and VI

| Carbon No. | Compound I | Compound II | Compound III | Compound IV | Compound V | Compound VI |
|---|---|---|---|---|---|---|
| 1 | 161.5 | 161.8 | 162.4 | 161.6 | 161.8 | 161.6 |
| 2 | 119.5 | 119.5 | 124.2 | 120.6 | 119.5 | 120.6 |
| 3 | 149.3 | 147.8 | 146.0 | 152.2 | 149.2 | 148.3 |
| 4 | 124.6 | 122.7 | 119.0 | 116.0 | 120.8 | 124.2 |
| 5 | 137.5 | 124.2 | 109.9 | 120.6 | 108.0 | 108.9 |
| 6 | 120.7 | 136.1 | 170.9 | 135.9 | 164.8 | 165.7 |
| 7 | 161.7 | 121.5 | 109.9 | 122.4 | 106.5 | 108.0 |
| 8 | 191.8 | 158.4 | 161.9 | 158.2 | 162.1 | 164.6 |
| 9 | 181.7 | 187.9 | 188.7 | 187.5 | 192.0 | 189.8 |
| 10 | 133.5 | 182.3 | 183.3 | 182.1 | 181.3 | 181.4 |
| 4a | 113.5 | 182.3 | 132.5 | 132.2 | 137.2 | 132.9 |
| 8a | 116.0 | 118.5 | 115.1 | 115.4 | 113.7 | 109.0 |
| 9a | 133.2 | 114.9 | 112.4 | 115.4 | 115.8 | 113.8 |
| 10a | | 134.9 | 136.3 | 131.5 | 133.4 | 135.2 |
| G-1 | | 100.7 | 102.0 | 100.5 | | |
| G-2 | | 73.5 | 73.6 | 73.3 | | |
| G-3 | | 76.7 | 77.6 | 76.5 | | |
| G-4 | | 69.7 | 69.7 | 69.5 | | |
| G-5 | | 77.5 | 77.6 | 77.2 | | |
| G-6 | | 60.8 | 60.8 | 60.6 | | |
| $-CH_3$ | 21.8 | 21.7 | 21.5 | | 21.9 | 21.7 |
| $-OCH_3$ | | | | | 56.3 | |
| $CH_2OH$ | | | | 62.0 | | |

Solvent: Compound I, II, III, IV, VI (DMSO-$d_6$), Compound V ($CDCl_3$)

MeOH-$H_2O$, 80 : 25 : 2.5 → EtOAc-MeOH-$H_2O$, 90 : 5 : 5, homogenous) to give two fractions (E1 & E2). Silica gel chromatography of fr. E1 and E2 with solvents (hexane-EtOAc, 7 : 1 and benzene-EtOAc, 1 : 5) afforded Compound V and Compound VI.

Succesively, 500 g of the *n*-BuOH fraction were chromatographed on non ionic ion-exchange polymer, Amberlite XAD-2 (Sigma, U.S.A.) ($H_2O$-MeOH 1 : 0, 8 : 2, 6 : 4, 4 : 6, 2 : 8 and 0 : 1 successively).

The $H_2O$ elute was composed of large amount of mono and oligo saccharides. 20% MeOH elute was separated by ODS-gel and Sephadex LH-20 column chromatography with 70% MeOH to give Compound VII and Compound VIII (Scheme I).

**Compound I:** m. p. 196-197°, Anal. Calcd. for $C_{15}H_{10}O_4$; C, 70.85, H, 4.00, Found: C, 70.83, H, 3.96, IR $\upsilon_{max}^{KBr}cm^{-1}$; 1676 (free C=O), 1626 (chelated C=O), 1560, 1540, 1456 (aromatic C=C), UV $\lambda_{max}$ nm (log ε) EtOH: 225 (4.1), 256 (2.1), 277 (1.1), 287 (1.2), 429 (1.2), EI Mass (m/z); 254 [$M^+$], 226 [$M^+$-CO], 197 , 169, 152, $^1$H-NMR DMSO-$d_6$, δ ppm: 11.78 (2H, s, OH), 7.68 (1H, d, J=8.0 Hz, H-5), 7.57 (1H, m, H-6), 7.39 (1H, s, H-4), 7.26 (1H, d, J=8.0 Hz, H-7), 7.07 (1H, s, H-2), 2.32 (3H, s, $CH_3$), $^{13}$C-NMR DMSO-$d_6$, δ ppm (Table I).

**Compound II:** m. p. 259-260°. Anal. Calcd. for $C_{21}H_{20}O_9$: C, 60.56, H, 4.84 Found: C, 60.58 , H, 4.86, IR $\upsilon_{max}^{KBr}cm^{-1}$; 3385 (OH), 2920 (C-H), 1671 (free C=O), 1632 (chelated C=O), 1594, 1448 (aromatic C=C), 1076 (sugar C-O), UV $\lambda_{max}$ nm (logε) EtOH: 221 (4.4), 258 (3.1), 283 (1.5), 412 (1.0), EI Mass (m/z): 416[$M^+$], 254[M-Glc$^+$], 226[$M^+$-(Glc+CO)], 198 [$M^+$-(Glc+2CO)], 152, $^1$H-NMR DMSO-$d_6$, δ ppm: 12.97 (1H, s, OH), 7.87 (1H, d, J=6.4 Hz, H-5), 7.72 (1H, m, H-6), 7.53 (1H, d, J=6.4 Hz, H-7), 7.39 (1H, s, H-4), 7.21 (1H, s, H-2), 5.17 (1H, d, J=9.0 Hz, anomeric H), 2.43 (3H, s, CH3), $^{13}$C-NMR: DMSO-$d_6$, δ ppm (Table I).

**Compound III:** m. p. 190-191°, Anal. Calcd. for $C_{21}H_{20}O_{10}$: C, 58.32, H, 4.66, Found: C, 58.35, H, 4.67, IR $\upsilon_{max}^{KBr}cm^{-1}$; 3410 (OH), 1629 (chelated C=O), 1596, 1509, 1478 (aromatic C=C), 1072, 1046 (sugar C-O), UV $\lambda_{max}$ nm (log ε) EtOH: 221 (4.16), 285 (2.4), 417 (0.8), EI Mass (m/z): 432 [$M^+$], 270 [$M^+$-Glc], $^1$H-NMR DMSO-$d_6$, δ ppm: 7.41 (1H, s, H-4), 7.10 (1H, brs, H-5), 7.03 (1H, s, H-2), 6.70 (1H, brs, H-7), 4.90 (1H, d, J=7.0Hz, anomeric H), 2.38 (3H, s, CH3), $^{13}$C-NMR DMSO-$d_6$, δ ppm (Table II).

**Compound IV:** m. p. 237-238°, Anal. Calcd. for $C_{21}H_{20}O_{10}$: C, 58.32, H, 4.66, Found: C, 58.34, H, 4.68, IR $\upsilon_{max}^{KBr}cm^{-1}$: 3348 (OH), 2928 (C-H), 1732 (free C=O), 1641 (chelated C=O), 1077 (sugar C-O), 1584, 1447 (aromatic C=C), UV $\lambda_{max}$ nm (log ε) MeOH: 222 (4.25), 253 (3.2), 283 (1.4), 408 (1.0), EI Mass (m/z): 432[$M^+$], 414[$M^+$-$H_2O$], 270[$M^+$-Glc], 242 [$M^+$- (Glc+CO)], $^1$H-NMR DMSO-$d_6$, δ ppm: 7.88 (1H, dd, J=2.0, 8.0 Hz, H-5), 7.86 (1H, t, J=8.0 Hz, H-6), 7.70 (1H, dd, J=2.0, 8.0 Hz, H-7), 7.65 (1H, s, H-4), 7.27 (1H, s, H-2), 5.15 (1H, d, J=7.7 Hz, anomeric H), 4.60 (2H, s, $CH_2OH$), $^{13}$C-NMR DMSO-$d_6$, δ ppm (Table I).

**Compound V:** m. p. 207-208°, Anal. Calcd. for $C_{16}H_{12}O_5$: C, 67.59, H, 4.26 Found: C, 67.61 ; H, 4.28.

**Table II.** $^{13}C$ NMR Spectral Data of Compound VII and VIII (DMSO-$d_6$)

| Carbon No. | Compound VII | Compound VIII |
|---|---|---|
| 1 | 139.3 | 139.6 |
| 2 | 105.4 | 104.8 |
| 3 | 158.5 | 158.7 |
| 4 | 103.0 | 102.7 |
| 5 | 159.0 | 158.7 |
| 6 | 107.4 | 104.8 |
| 1' | 130.2 | 129.3 |
| 2' | 113.1 | 116.3 |
| 3' | 146.7 | 146.9 |
| 4' | 148.0 | 145.9 |
| 5' | 112.3 | 114.5 |
| 6' | 118.7 | 122.5 |
| α | 126.3 | 126.7 |
| β | 128.7 | 128.2 |
| G-1 | 100.8 | 102.2 |
| G-2 | 73.5 | 73.7 |
| G-3 | 77.3 | 77.7 |
| G-4 | 69.9 | 70.4 |
| G-5 | 76.9 | 76.2 |
| G-6 | 60.9 | 61.2 |
| -$OCH_3$ | 55.8 | |

IR $\upsilon_{max}^{KBr}cm^{-1}$: 3430 (OH), 2925 (C-H), 1684 (free C=O), 1625 (chelated C=O), 1559, 1540, 1506 (aromatic C=C), UV $\lambda_{max}$ nm (log ε) EtOH: 223 (4.3), 253 (2.0), 286 (2.0), 437 (1.4), EI Mass (m/z): 284 [$M^+$], 256 [$M^+$-CO], 228 [$M^+$-2CO], 213, 185, $^1$H-NMR $CDCl_3$, δ ppm: 12.30 (1H, s, OH), 12.10 (1H, s, OH), 7.60 (1H, s, H-4), 7.33 (1H, d, J=2.2 Hz, H-5), 7.06 (1H, s, H-2), 6.66 (1H, d, J=2.2 Hz, H-7), 3.93 (3H, s, $CH_3$), 2.44 (3H, s, $CH_3$), $^{13}$C-NMR $CDCl_3$, δ ppm (Table I).

**Compound VI:** m. p. 264-265°, Anal. Calcd. for $C_{15}H_{10}O_5$: C, 66.65, H, 3.73, Found : C, 66.68, H, 3.75, IR $\upsilon_{max}^{KBr}cm^{-1}$: 3430 (OH), 2930 (C-H), 1684 (free C=O), 1633 (chelated C=O), 1559, 1540, 1480 (aromatic C=C), UV $\lambda_{max}$ nm (log ε) EtOH: 220 (4.6), 252 (2.6), 266 (2.5), 290 (2.6), 440 (1.4), EI Mass (m/z): 270 [$M^+$], 242 [$M^+$-CO], 214 [$M^+$-2CO], 185, 168, $^1$H-NMR DMSO-$d_6$, δ ppm: 12.03 (1H, s, OH), 11.96 (1H, s, OH), 7.42 (1H, s, H-4), 7.10 (1H, s, H-2), 7.06 (1H, d, J=2.3 Hz, H-5), 6.54 (1H, d, J=2.3 Hz, H-7), 2.38 (3H, s, $CH_3$). $^{13}$C-NMR DMSO-$d_6$, δ ppm (Table I).

**Compound VII:** m. p. 246-248°, $[\alpha]_D$ -56.3° (c=0.88, in acetone: $H_2O$=1 : 1), Anal. Calcd. for $C_{21}H_{24}O_9$: C, 59.98, H, 5.76, Found: C, 59.96, H, 5.73, IR $\upsilon_{max}^{KBr}cm^{-1}$: 3482, 3341 (OH), 1612, 1583, 1513 (aromatic C=C), UV $\lambda_{max}$ nm (log δ) EtOH: 220 (4.5), 302 (4.2), 324 (5.0), EI Mass (m/z): 420[$M^+$], 258[$M^+$-Glc], 225, 197, $^1$H-NMR DMSO-$d_6$, δ ppm: 9.45 (1H, s, OH), 8.98 (1H, s, OH), 6.91, 6.83 (each $^1$H, d, J=16.0 Hz, olefinic H), 7.02 (1H, brs, H-2'), 6.95-6.79 (2H, m, H-5', 6'), 6.74 (1H, s, H-6), 6.58 (1H, s, H-2), 6.34 (1H, s, H-4), 4.80 (1H, d, J=6.5 Hz, anomeric H), 3.78 (3H, s, $OCH_3$). $^{13}$C-NMR DMSO-$d_6$, δ ppm (Table II).

**Compound VIII:** m. p. 229-230°, $[\alpha]_D$ -40.4° (c=0.56, in MeOH), Anal. Calcd. for $C_{20}H_{22}O_9$: C, 59.09 , H, 5.46 Found: C, 59.06, H, 5.43, IR $\upsilon_{max}^{KBr}cm^{-1}$: 3373 (OH), 2916 (C-H), 1594, 1515 (aromatic C=C), UV $\lambda_{max}$ nm (log ε): 217 (4.4), 302 (4.0), 320 (4.2), EI Mass (m/z): 406[$M^+$], 244[$M^+$-Glc], $^1$H-NMR DMSO-d 6, δ ppm: 9.20 (2H, s, OH), 8.70 (1H, s, OH), 7.44 (1H, d, J=2.0 Hz, H-2'), 7.06 (1H, dd, J=2.0, 8.0 Hz, H-6'), 6.91, 6.83 (each 1H, d, J=16.0 Hz, olefinic H), 6.79 (1H, d, J=8.0 Hz, H-5'), 6.39, 6.38 (each 1H, d, J=2.0 Hz, H-2,6), 6.12 (1H, d, J=2.0 Hz, H-4), 4.74 (1H, d, J=7.4 Hz, anomeric H), $^{13}$C-NMR DMSO-$d_6$, δ ppm (Table II).

**Acid hydrolysis of Compound II, III, IV, VII and VIII:** Compound II, III, IV, VII and VIII (each 30 mg) were hydrolyzed by acid using the method described in general procedure.

The reaction mixture was diluted with $H_2O$ and extracted with $CHCl_3$. then $CHCl_3$ part thus obtained was washed with $H_2O$ and concentrated to give aglycone. The water layer was neutralized with mixed bed resin TMD-8 column and concentrated to give sugars. This aglycones and sugars were identified by direct comparison with authentic samples.

## RESULTS AND DISCUSSION

The acetone and ether and *n*-buthanol fraction of the methanol extract from cultivated Korean Rhubarb Rhizomes was chromatographed on silica gel, O.D.S (C-18) gel, Sephadex LH-20 gel and Amberlite XAD-2, successively. Six compounds (compound I, II, III, IV, V, VI) were identified as anthraquinone derivatives and the remaining two compounds (compound VII, VIII) were identified as stilbene derivatives.

Compound I was obtained as a yellow needles, IR spectrum of compound I gave 1676 (free C=O), 1626 (chelated C=O), 1559, 1540, 1477 and 1456 (aromatic C=C)$cm^{-1}$ and UV spectrum of 225, 256, 277, 287 and 429 (sh.)nm, suggesting it to be an anthraquinone derivative (Thomson *et al.*, 1971).

In the EI-MS spectrum of Compound I molecular ion and fragment ion appeared at m/z 254 [$M^+$], 226 [$M^+$-CO], 197, 169 and 152. $^1$H-NMR spectrum (DMSO-$d_6$) showed two doublet signals at δ 7.68, 7.26 (each 1H, J=8.0 Hz, H-5, H-7), two singlet signals at δ 7.39, 7.07 (each 1H, H-4, H-2) and a multiplet signal at δ 7.57 (1H, H-6) on aromatic ring, and also the signals at δ 11.78 (2H,s) and δ 2.32 (3H,s) were assigned to chelated hydroxy signal and aromatic methyl proton, respectively. $^{13}$C-NMR spectrum (DMSO-$d_6$) showed a carbonyl signal at δ 191.8 and δ 181.7, and a C-1 and C-8 carbon signal at δ 161.5 and δ 161.7, respectively.

The identification was confirmed by $^{13}$C-NMR, $^1$H-

NMR and EI-MS and by comparison of the reported data (Kato *et al.*, 1987, Tamano *et al.*, 1982).

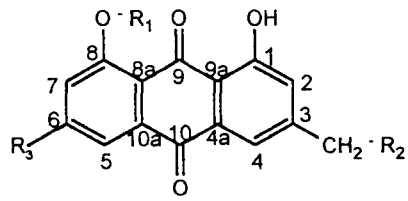
In the results, Compound I was identified 1,8-dihydroxy-3-methyl anthraquinone (chrysophanic acid).

Compound II was obtained as a yellow needles. IR spectrum of Compound II gave 3385 (OH), 2920 (C-H), 1671 (free C=O), 1632 (chelated C=O), 1594, 1448 (aromatic C=C), and UV spectrum of 221, 258, 283, 412 (sh.)nm, suggesting it to be an anthraquinone derivative.

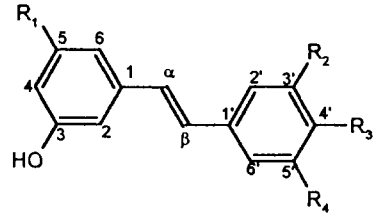
In the EI-MS spectrum of Compound II molecular ion and fragment ion appeared at m/z 416 [$M^+$] and 254 [$M^+$-Glc]. $^1$H-NMR spectrum (DMSO-$d_6$) showed two doublet signals at δ 7.87, 7.53 (each 1H, J=6.4 Hz, H-5, H-7), two singlet signals δ 7.39, 7.21 (each 1H, H-4, H-2), a multiplet signal at δ 7.72 (1H, H-6) on aromatic ring and the anomeric proton signal at δ 5.17 (J=9.0 Hz) supported our assignment for the β-configuration, and also the signals at δ 12.97 (1H, s) and δ 2.43 (3H, s) were assigned to chelated hydroxy signal and aromatic methyl proton.

$^{13}$C-NMR spectrum (DMSO-$d_6$) showed a aromatic methyl signal at δ 21.7 and carbon signals of sugar moiety were found at δ 100.7, δ 77.5, δ 76.7, δ 73.5, δ 69.7 and δ 60.8, respectively.

Carbon signals in compound II were assigned in comparison to the reported data I (Rawat *et al.*, 1989)




| | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| Compound I | H | H | H |
| Compound II | Glc | H | H |
| Compound III | Glc | H | OH |
| Compound IV | Glc | OH | H |
| Compound V | H | H | $OCH_3$ |
| Compound VI | H | H | OH |




| | $R_1$ | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|
| Compound VII | O-Glc | OH | $OCH_3$ | H |
| Compound VIII | OH | H | OH | O-Glc |

for compound II and C-8 carbon signal in compound II was shifted upfield and C-7 and C-8a carbon signal downfield, and on acid hydrolysis, compound II gave chrysophanic acid and glucose.

In the results, compound II were identified as chrysophanol-8-O-β-D-glucopyranoside. Compound III was obtained as a orange needles. IR spectrum of Compound III gave 3410 (OH), 1629 (chelated C=O), 1596, 1509, 1478 (aromatic C=C), 1072 and 1046 (sugar C-O), and UV spectrum 221, 285 and 417 (sh.) nm , suggesting it to be an anthraquinone derivative.

In the EI-MS spectrum of Compound III molecular ion and fragment ion appeared at m/z 432 [$M^+$] and 270 [$M^+$-Glc]. $^1$H-NMR spectrum (DMSO-$d_6$) showed two singlet signal at δ 7.41, 7.03 (each 1H, H-4, H-2) and two singlet signals at δ 7.10, 6.70 (each 1H, H-5, H-7) on aromatic ring and the anomeric proton signal δ 4.90 at (J=7.0 Hz) supported our assignment for the β-configuration.

$^{13}$C-NMR spectrum (DMSO-$d_6$) showed an aromatic methyl signal at δ 21.5 and carbon signals of sugar moiety were found at δ 102.0, δ 77.6, δ 76.3, δ 73.6, δ 69.7 and δ 60.8, respectively. Carbon signals in compound III were assigned in comparison to the reported data for compound VI and C-8 carbon signal in compound III was shifted upfield and C-7 and C-8a carbon signal downfield.

On the acid hydrolysis, Compound III gave emodin (Compernolle *et al.*, 1987) and glucose by authentic samples, correspond to these of Compound III is identified as the homologous structure; 8-O-glucopyranoside of emodin.

Compound IV was obtained as a yellow needdles. IR spectrum of Compound IV gave 3348 (OH), 2928 (C-H), 1641 (chelated C=O), 1077 (sugar C-O), 1584 and 1447 (aromatic C=C)$cm^{-1}$, and UV spectrum 222, 253, 283, 408 (sh.)nm, suggesting it to be an anthraquinone derivative.

In the EI-MS spectrum of Compound IV molecular ion appeared at m/z 432 [$M^+$] and other important fragment ion at m/z 270 [$M^+$-Glc] for aglycone moiety. $^1$H-NMR spectrum (DMSO-$d_6$) showed two double doublet signals at δ 7.88, 7.70 (1H, J=2, 8 Hz, H-5, H-7), a triplet signal at δ 7.86 (1H, J=8.0 Hz, H-6), two singlet signals δ 7.65, 7.27 (1H, H-4, H-2), on aromatic ring and also the anomeric proton signal at δ 5.15 (J=7.7 Hz) supported our assignment for the β-configuration.

$^{13}$C-NMR spectrum (DMSO-$d_6$) showed a $CH_2OH$ signal at δ 62.0 and carbon signals of sugar moiety were found at δ 100.5, δ 73.3, δ 76.5, δ 69.5, δ 77.2 and δ 60.6, respectively. On the acid hydrolysis, Compound IV gave aloe-emodin and glucose. $^1$H-$^{13}$C long range cosy spectrum observed an anomeric proton signal at δ 5.15 and H-6 proton signal at δ 7.86

was encountered C-8 carbon signal at δ 158.2. Thus compound IV were identified as 8-O-glucopyranosides of aloe-emodin (Okabe *et al.*, 1973, Compernolle *et al.*, 1987). In the results, Compound IV was aloe-emodin-8-O-β-D-gluco pyranoside.

Compound V was obtained a orange needdles, IR spectrum of Compound V gave 3430 (OH), 2925 (C-H), 1684 (free C=O), 1625 (chelated C=O), 1559, 1540 and 1506 (aromatic C=C)$cm^{-1}$ and UV spectrum 223; 253, 286 and 437 (sh.)nm , suggesting it to be an anthraquinone derivatives.

In the EI-MS spectrum of Compound V molecular ion and fragment ion appeared at m/z 284 [$M^+$], 256 [$M^+$-CO] and 228 [$M^+$-2CO]. The $^1$H-NMR spectrum ($CDCl_3$) showed two singlet signal at δ 7.60, 7.06 (1H, H-4, H-2) and two doublet signal at δ 7.33, 6.66 (1H, J=2.2Hz, H-5, H-7) on aromatic ring. The signals at δ 3.93 and δ2.44 were assigned to methoxyl signal (3H, s) and aromatic methyl signal (3H,s), respectively.

$^{13}$C-NMR spectrum ($CDCl_3$) showed a carbonyl signal at δ 192.0 and δ 181.3, and a C-1 and C-8 carbon signal at δ 161.8 and δ 161.1, respectively. The identification was confirmed by NMR ($^1$H-, $^{13}$C-), MS and by comparison of the reported data (Kato *et al.*, 1987, Tamano *et al.*, 1982).

In the results, Compound V was 1,8-dihydroxy-3-methyl-6-methoxy anthraquinone (physcion).

Compound VI was obtained a orange needdles. IR spectrum of Compound VI gave 3430 (OH), 2930 (C-H), 1684 (free C=O), 1633 (chelated C=O), 1559, 1540 and 1480 (aromatic C=C)$cm^{-1}$ and UV spectrum 220, 252, 266, 290 and 440 (sh.)nm, suggesting it to be an anthraquinone derivative.

In the EI-MS spectrum of Compound VI molecular ion and fragment ion appeared at m/z 270 [$M^+$], 242 [$M^+$-CO] and 214 [$M^+$-2CO]. The $^1$H-NMR spectrum (DMSO-$d_6$) showed two singlet signal at δ 7.42, 7.10 (1H, H-4, H-2) and two doublet signals at δ 7.06, 6.54 (1H, J=2.3 Hz, H-5, H-7) on aromatic ring and also the signals at δ 12.03, δ 11.96 and δ 2.38 were assigned to chelated hydroxy signal and aromatic methyl proton (3H, s), respectively.

$^{13}$C-NMR spectrum (DMSO-$d_6$) showed a carbonyl signal at δ 189.8 and δ 181.4, and a C-1 and C-8 carbon signal at δ 161.6 and δ 164.6, respectively. The identification was confirmed by these instrumental data (Kato *et al.*, 1987, Tamano *et al.*, 1982) and by comparison of authentic sample.

In the results. Compound VI was 1,6,8-trihydroxy-3-methyl anthraquinone (emodin).

Compound VII was obtained as a colorless needdles. IR spectrum of Compound VI gave 3482, 3341 (OH), 1612, 1583 and 1513 (C=C)$cm^{-1}$ and UV spectrum 220, 302 and 324 (sh.) nm.

In the EI-MS spectrum of Compound VII molecular ion and fragment ion appeared at m/z 420 [$M^+$] and 258 [$M^+$-Glc], suggesting it to be a stilbene derivative.

The $^1$H-NMR spectrum (DMSO-$d_6$) two singlet signals at δ 9.45 and δ 8.98 were assigned to chelated hydroxy signal (1H, s), respectively and two doublet signals at δ 6.91 and δ 6.83 showed trans-olefinic protons (each 1H, d, J=16.0 Hz), and also the anomeric proton signal at δ 4.80 (J=6.5 Hz) supported our assignment for the β-configuration.

$^{13}$C-NMR spectrum (DMSO-$d_6$) showed a methoxyl signal at δ 55.8 and carbon signals of sugar moiety were found at δ 100.8, δ 73.5, δ 77.3, δ 69.9, δ 76.9 and δ 60.9, respectively. On the acid hydrolysis, compound VII gave rhapontigenin and glucose and identificated by comparison of authentic samples (Kashiwada *et al.*, 1984).

On the basis of these data the structure of Compound VII was formulated as rhapontigenin-3-O-β-D-glucopyranoside (rhaponticin).

Compound VIII was obtained as a colorless needdles. IR spectrum of Compound VIII gave 3373 (OH), 2916 (C-H), 1594 and 1515 (C=C)$cm^{-1}$ and UV spectrum 217, 302 and 320 (sh.)nm, suggesting it to be a stilbene derivative.

In the EI-MS spectrum of Compound VIII, molecular ion and fragment ion appeared at m/z 406 [$M^+$] and 244 [$M^+$-Glc], suggesting it to be stilbene derivatives. The $^1$H-NMR spectrum (DMSO-$d_6$) two singlet signals at δ 9.20 and δ 8.70 were assigned to chelated hydroxy signals, respectively and two doublet signals at δ 6.91 and δ 6.83 showed trans-olefinic proton (each 1H, d, J=16.0Hz) and also the anomeric proton signal at δ 4.74 (J=7.4 Hz) supported our assignment for the β-configuration. $^{13}$C-NMR spectrum (DMSO-$d_6$) showed carbon signals of sugar moiety were found at δ 102.2, δ 73.7, δ 77.7, δ 70.4, δ 76.2 and δ 61.2, respectively.

On the acid hydrolysis, Compound VIII gave piceatannol and glucose and identifyed by comparison of reported data (Kashiwada *et al.*, 1984). These data suggest that compound VIII was composed as piceatannol and glucose.

In the results, Compound VIII was piceatannol-3'-O-β-D-glucopyranoside.

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