Structural Elucidation of Two New Chromones Isolated from Glasswort (*Salicornia europaea* L.)

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Two chromones isolated from the methanol extract of glasswort (*Salicornia europaea* L.) were elucidated to be 7-hydroxy-6-methoxychromone and 7-O- β -D-glucopyranosyl-6-methoxychromone on the basis of chemical and spectral analyses and synthetic studies. These two are natural products hitherto unknown.

In a previous paper,¹⁾ we have reported that four compounds were isolated from the reddish leaves and stems of glasswort and Compounds I, II and III were determined to be 2'-hydroxy-6,7-methylenedioxyisoflavone, (–)-(2*S*)-2'-hydroxy-6,7-methylenedioxyflavanone and 2',7-dihydroxy-6-methoxyisoflavone, respectively.

This report deals with the structural elucidation of Compound IV and a further Compound V which has now been obtained from this plant.

The molecular formula of Compound IV obtained as white needles was determined to be $C_{10}H_8O_4$ (calcd. for $C_{10}H_8O_4$: 192.0422) by high resolution MS (a molecular ion peak, m/z 192.0417). The NMR spectrum (DMSO- d_6) of this compound showed two doublets at δ 8.10 (1H, $J=6$ Hz) and δ 6.19 (1H, $J=6$ Hz), which were proved to be coupled with each other by the spin-decoupling technique. By considering the chemical shifts and splitting patterns, these two signals were attributable to the protons at C-2 and C-3 of the chromone nucleus or at C-4 and C-3 of the coumarin nucleus. A carbonyl absorption in the IR spectrum (1640 cm^{-1}) coincides well with those of chromones ($1640\sim 1660\text{ cm}^{-1}$) but it is situated in a region lower than those of coumarins ($1720\sim 1740\text{ cm}^{-1}$). Consequently, Compound IV was estimated to be one of the

chromone compounds.

In the NMR spectrum, a singlet at δ 3.85 (3H) evidently indicates the existence of one methoxyl group. As Compound IV gave a positive reaction (grayish blue) by Folin-Ciocalteu reagent, this compound was subjected to methylation and acetylation, and monomethyl (M^+ , m/z 206) and monoacetyl derivatives (M^+ , m/z 234) were respectively obtained. Therefore, the presence of one phenolic hydroxyl group was proved. The binding sites of the two substituents to the chromone nucleus were determined to be situated at C-6 and C-7, because the signals of two aromatic protons were observed as two respective singlets at δ 7.33 (1H, H-5) and δ 6.90 (1H, H-8). The binding site of the hydroxyl group was established by a comparison of the chemical shifts of the protons at C-5 and C-8 in the NMR spectra of the methyl and acetyl derivatives. Signals of the C-5 and C-8 protons of the acetyl derivative appeared in the lower magnetic field by 0.11 and 0.36 ppm, respectively, than those of the methyl derivative. This means that the acetyl group links to the C-7 position. Furthermore, a bathochromic shift was observed in the UV spectrum when sodium acetate was added. These facts support that the hydroxyl group links to the C-7 position and the methoxyl group is bonded to the C-6 position. Thus, Compound IV was

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estimated to be 7-hydroxy-6-methoxychromone. To confirm this estimated structure, we attempted to synthesize this compound. The spectral data of the synthesized compound **5** agreed well with those of the natural Compound IV.

IV: R=H

V: R=β-D-glucose

The molecular formula of Compound V obtained as white powder from the butanol-soluble fraction was determined to be $C_{16}H_{18}O_9$ by the presence of a peak, m/z 355.0994, corresponding to $(M+H)^+$ (calcd. for $C_{16}H_{19}O_9$, 355.1029) in the FD-high resolution MS spectrum. The UV spectrum of this compound showed absorption maxima at 226 (log ϵ 4.11), 246 sh (3.79), 270 sh (3.66) and 317 nm (3.81). In the IR spectrum, a carbonyl absorption was observed at 1633 cm^{-1} . Two respective doublets (1H, $J=6\text{ Hz}$) appeared at δ 8.19 and δ 6.26 in the NMR spectrum. These spectral data were similar to those of Compound IV. Consequently, Compound V was suggested to be one of the chromone compounds. The presence of sugar in Compound V was proved by the anthrone test²⁾ and also the signals at δ 4.4~5.5 and 3.6~3.9 in the NMR spectrum were estimated to be originated from the sugar. The NMR spectrum also showed that a singlet assigned to the protons of the methoxyl group appeared at δ 3.86. The methoxyl group and sugar are estimated to be linked to C-6 and C-7 of the chromone nucleus, because two singlets ascribed to the aromatic protons were observed at δ 7.38 (H-5) and δ 7.28 (H-8).

Compound V was subjected to an acid hydrolysis with trifluoroacetic acid. The water-soluble fraction (sugar moiety) obtained from the hydrolyzate was concentrated and examined for sugars by paper chromatography (PC). A spot showing the R_f -value correspond-

ing to D-glucose was observed. After concentration, the chloroform-soluble fraction from the hydrolyzate gave an aglycone compound, whose UV, IR, MS and FT-NMR spectral data and an R_f -value in TLC were proved to be identical with those of Compound IV, i.e., 7-hydroxy-6-methoxychromone.

With β -glucosidase, Compound V could be hydrolyzed to give D-glucose, which was detected by PC. In the NMR spectrum, a signal ascribed to the anomeric proton of β -D-glucose could not be observed because of concealing by the signals of hydroxyl groups, but, after the addition of deuterium oxide, it was detected clearly as a doublet at δ 5.16 ($J=7\text{ Hz}$). These findings indicated that D-glucose was linked to the aglycone by a type of β -bonding.

Consequently, Compound V was elucidated to be 7-O- β -D-glucopyranosyl-6-methoxychromone.

The naturally-occurring 2,3-unsubstituted chromones hitherto isolated and identified are as follows: 5,7-dihydroxychromone from the shells of peanut (*Arachis hypogaea*) (Leguminosae)⁴⁾ and the seeds of *Polygonum persicaria* (Polygonaceae),⁵⁾ leptorumol and its 4-methoxy-D-glucoside (leptorumolin) from *Leptorumohra miqueliana* H. Ito (Aspidiaceae),⁶⁾ 5-hydroxychromone-7-rutinoside from *Mentha longifolia* Hudson (Labiatae),⁷⁾ and 6,7-methylenedioxychromone and 6,7-dimethoxychromone from glasswort (*Salicornia europaea* L.) (Centrospermae).⁸⁾

Therefore, the two chromones described here are new compounds which have never been previously obtained from natural sources.

EXPERIMENTAL

Measurements of melting points and UV, IR, Mass and NMR spectra were carried out in a similar manner to those reported previously.¹⁾ FD-mass spectral data were obtained with a JEOL JMS-01SG-2. FT-NMR spectra were taken at 100 MHz, using a JNM-FX 100 FT NMR spectrometer. Thin-layer chromatography (TLC) was run on silica gel plates (Kiesel gel nach Stahl, Typ 60) with solvent A, $CHCl_3$ -EtOH (9:1, v/v). Paper chromatog-

raphy (PC) was conducted, using Toyo-Roshi paper No. 50 and either solvent B, 1-propanol-ethyl acetate-water (7:1:2, v/v), or solvent C, 2-propanol-water (4:1, v/v). Column chromatography was carried out with silica gel (Wako gel C-200) and activated charcoal (Wako Chemicals Co.).

Isolation of compounds. Reddish leaves and stems of glasswort (fresh weight 52 kg) were extracted with methanol. After removal of the solvent, the concentrate was extracted with ether and then with 1-butanol. The ether-soluble fraction gave Compounds I (81 mg), II (45 mg), III (20 mg) and IV (25 mg) by means of silica gel column chromatography and fractional crystallization.¹⁾ The butanol-soluble fraction was concentrated and chromatographed on a silica gel column employing a CHCl_3 -MeOH mixture as the solvent system. The fraction eluted with CHCl_3 -MeOH (80:20, v/v) was applied to activated charcoal column chromatography and eluted with a water-acetone mixture. The fraction eluted with water-acetone (50:50, v/v) was rechromatographed on a silica gel column, which was then eluted with a chloroform-methanol mixture, monitoring by ultraviolet absorption (356 nm). The fraction eluted with CHCl_3 -MeOH (85:15, v/v) was concentrated and crystallized from the water-acetone mixture to give Compound V (15 mg) as a white powder.

Physicochemical properties of the isolated compounds and their derivatives.

1) **Compound IV.** mp: 231~232°C. High MS m/z : 192.0417 (M^+), Calcd. for $\text{C}_{10}\text{H}_8\text{O}_4$: 192.0422. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 226 (4.20), 233 sh (4.06), 280 (3.76), 317 (3.97); +NaOMe 242 sh, 250 sh, 347; +NaOAc 232 sh, 280, 326. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3450 (OH), 3080, 2970, 2920, 2860, 1640 (C=O), 1625, 1590, 1555. MS m/z : 192 (M^+ , base peak), 191, 177, 163, 162, 149. NMR $\delta_{\text{TMS}}^{\text{DMSO-}d_6}$ ppm: 8.10 (1H, d, $J=6$ Hz, H-2), 7.33 (1H, s, H-5), 6.90 (1H, s, H-8), 6.19 (1H, d, $J=6$ Hz, H-3), 3.85 (3H, s, MeO). Folin-Ciocalteu reagent, grayish blue.

2) **Methyl derivative of Compound IV.** An ethereal solution of diazomethane was added to a solution of Compound IV (8 mg) in a small amount of absolute methanol. After standing overnight, the mixture was concentrated to give the methyl derivative (7 mg) as white needles. mp: 162~163°C (lit.⁹⁾ 163°C). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 228 (4.17), 233 (4.17), 275 (3.68), 316 (3.90). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1640 (C=O). MS m/z : 206 (M^+ , base peak), 205, 191, 177, 176, 175, 163, 137, 135. NMR $\delta_{\text{TMS}}^{\text{CDCl}_3}$ ppm: 7.78 (1H, d, $J=6$ Hz, H-2), 7.52 (1H, s, H-5), 6.84 (1H, s, H-8), 6.29 (1H, d, $J=6$ Hz, H-3), 3.98 (6H, s, two MeO).

3) **Acetyl derivative of Compound IV.** To a solution of Compound IV (7 mg) in dry pyridine (1 ml) was added acetic anhydride (1 ml). After standing overnight, the reaction mixture was poured into ice-cooled water and extracted with chloroform. Upon evaporation of the chloroform, the acetyl derivative was obtained as white needles

(5 mg). mp: 91~92°C. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 226 (4.44), 246 (4.14), 316 (4.01). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1760 (AcO), 1650 (C=O). MS m/z : 234 (M^+), 192 (base peak), 191, 177, 163, 149. NMR $\delta_{\text{TMS}}^{\text{CDCl}_3}$ ppm: 7.81 (1H, d, $J=6$ Hz, H-2), 7.63 (1H, s, H-5), 7.20 (1H, s, H-8), 6.29 (1H, d, $J=6$ Hz, H-3), 3.90 (3H, s, MeO), 2.34 (3H, s, AcO).

4) **Compound V.** mp: 228~229°C. FD-High MS m/z : 355.0994 ($\text{M}+\text{H})^+$, Calcd. for $\text{C}_{16}\text{H}_{19}\text{O}_9$: 355.1029. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 226 (4.11), 246 sh (3.79), 270 sh (3.66), 317 (3.81). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3000~3650 (OH), 2930, 1633 (C=O), 1595, 1515. FD-MS m/z : 393 ($\text{M}+\text{K})^+$, 377 ($\text{M}+\text{Na})^+$, 355 ($\text{M}+\text{H})^+$ (base peak), 354 (M^+), 191 ($\text{M}^+ - \text{C}_6\text{H}_{11}\text{O}_5$). NMR $\delta_{\text{TMS}}^{\text{DMSO-}d_6}$ ppm: 8.19 (1H, d, $J=6$ Hz, H-2), 7.38 (1H, s, H-5), 7.28 (1H, s, H-8), 6.26 (1H, d, $J=6$ Hz, H-3), 4.4~5.5 (5H, m, OH-sugar and H-1'), 3.86 (3H, s, MeO), 3.6~3.9 (6H, m, H-2', 3', 4', 5', 6'). NMR $\delta_{\text{TMS}}^{\text{DMSO-}d_6 + \text{D}_2\text{O}}$ ppm: 5.16 (1H, d, $J=7$ Hz, H-1'). Anthrone-sulfuric acid reaction,²⁾ greenish blue.

5) **Acetyl derivative of Compound V.** To a solution of Compound V (7 mg) in dry pyridine (1 ml) was added acetic anhydride (1 ml). After standing overnight, the reaction mixture was poured into ice-cooled water and extracted with chloroform. Upon evaporation of the chloroform, the residue was recrystallized from ethanol to give the acetyl derivative (6 mg) as white needles. mp: 135~136°C. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 227 (4.20), 244 sh (3.93), 270 sh (3.68), 316 (3.90). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2950, 1775 (AcO), 1655 (C=O), 1630, 1510. MS m/z : 331, 271, 193, 192, 191, 169 (base peak), 163, 145, 109, 103. FD-MS m/z : 522 (M^+ , base peak), 331, 191. NMR $\delta_{\text{TMS}}^{\text{CDCl}_3}$ ppm: 7.80 (1H, d, $J=6$ Hz, H-2), 7.57 (1H, s, H-5), 7.18 (1H, s, H-8), 6.30 (1H, d, $J=6$ Hz, H-3), 5.1~5.4 (4H, m, H-1', 2', 3', 4'), 4.23 (2H, m, H-6'), 3.91 (3H, s, MeO), 3.79~3.96 (1H, m, H-5'), 2.10 (3H, s, AcO), 2.08 (3H, s, AcO), 2.06 (3H, s, AcO), 2.05 (3H, s, AcO).

6) **Acid hydrolysis products of compound V.** Compound V (3 mg) was dissolved in aqueous 10% trifluoroacetic acid (1 ml), and the solution was refluxed in a sealed tube for 1 hr. After the tube had been opened, the trifluoroacetic acid was evaporated and the residue was dissolved in water. The aqueous solution was extracted with chloroform. The chloroform layer was concentrated to give a white powder (1.5 mg, aglycone of Compound V). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 227, 233 sh, 279, 317. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1640 (C=O), 1625. MS m/z : 192 (M^+ , base peak), 191, 177, 163, 162, 149. FT-NMR $\delta_{\text{TMS}}^{\text{DMSO-}d_6}$ ppm: 8.13 (1H, d, $J=6$ Hz, H-2), 7.35 (1H, s, H-5), 6.93 (1H, s, H-8), 6.21 (1H, d, $J=6$ Hz, H-3), 3.86 (3H, s, MeO). TLC: R_f 0.55 in solvent A (7-hydroxy-6-methoxychromone 0.55).

On the other hand, the aqueous layer was used for the identification of sugar on PC. Sugar spots were detected with silver nitrate reagent³⁾ PC: R_f 0.36 in solvent B (D-glucose 0.36) and 0.46 in solvent C (D-glucose 0.46).

7) **Enzymatic hydrolysis products of Compound V.** Compound V (2 mg) was digested with β -glucosidase (2 mg) in a 0.2 M acetate buffer solution (1 ml, pH 5.5) at 37°C for 24 hr. To the mixture was added a small amount

of water, and the aqueous solution was extracted with chloroform. After removal of the chloroform, the residue was used for comparison with an authentic sample on TLC. TLC: *R_f* 0.55 in solvent A. The aqueous layer was used for the identification of sugar on PC. PC: *R_f* 0.35 in solvent B and 0.46 in solvent C.

Synthesis of 7-hydroxy-6-methoxychromone (5)

1) *4-Benzylloxy-2-hydroxyacetophenone (1)*. After re-acetophenone (10 g) had been dissolved in dry acetone (50 ml), the solution was refluxed with benzyl chloride (15 ml) and anhydrous potassium carbonate (10 g) for 3 hr. The mixture was cooled and treated with aqueous 10% hydrochloric acid. The solution was extracted with chloroform. Upon evaporation of the chloroform, the residue was chromatographed on a silica gel column. The eluate of benzene was concentrated to give **1** (5.2 g, 32.8%) as colorless plates. mp: 99~100°C (lit.¹⁰ 103~104°C). Found: C, 74.40; H, 5.85. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82%. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 227 (4.07), 274 (4.24), 314 (3.89). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1630 (C=O). MS *m/z*: 242 (M^+), 227, 91 (base peak). NMR $\delta_{\text{TMS}}^{\text{acetone-d}_6}$ ppm: 12.45 (1H, s, OH), 7.59 (1H, d, *J*=8 Hz, H-6), 7.09~7.29 (5H, m, phenyl proton), 6.25~6.43 (2H, m, H-3, 5), 4.99 (2H, s, CH_2), 2.35 (3H, s, AcO).

2) *4-Benzylloxy-2,5-dihydroxyacetophenone (2)*. After **1** (4 g) had been dissolved in pyridine (80 ml) and aqueous 6% sodium hydroxide (80 ml), to this solution thus obtained was added dropwise aqueous 8.4% potassium persulfate (100 ml) during 3 hr at 10°C. After standing for 24 hr, the reaction mixture was acidified with 6*N* hydrochloric acid and the precipitate was filtered off. The filtrate was treated with sodium sulfite (8 g) and conc. hydrochloric acid (100 ml) and kept on a boiling water bath for 30 min. On cooling, the golden yellow needles crystallized in the reaction mixture were collected and washed with water, and then chromatographed on a silica gel column. The eluate of chloroform was concentrated to give **2** (1.1 g, 25.8%) as pale yellow needles. mp: 162~163°C (lit.¹⁰ 159~160°C). Found: C, 69.71; H, 5.48. Calcd. for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46%. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 240 (4.15), 277 (4.04), 350 (3.84). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1645 (C=O). MS *m/z*: 258 (M^+), 167, 91 (base peak). NMR $\delta_{\text{TMS}}^{\text{acetone-d}_6}$ ppm: 12.39 (1H, s, OH-2), 7.60 (1H, s, OH-5), 7.32~7.56 (5H, m, phenyl proton), 7.25 (1H, s, H-6), 6.56 (1H, s, H-3), 5.24 (2H, s, CH_2), 2.52 (3H, s, AcO).

3) *4-Benzylloxy-2-hydroxy-5-methoxyacetophenone (3)*. The compound **2** (1.3 g) was refluxed with dimethyl sulfate (0.5 ml), dry acetone (60 ml) and anhydrous potassium carbonate (3 g) for 8 hr. After cooling, the reaction mixture was treated with aqueous 10% hydrochloric acid and extracted with chloroform. Upon evaporation of the chloroform, the residue was chromatographed on a silica gel column. The eluate of the chloroform was concentrated to give **3** (875 mg, 63.8%) as pale yellow needles. mp: 127~128°C (lit.¹⁰ 128~129°C). Found: C, 70.76; H, 6.08. Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92%. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm

(log ϵ): 236 (4.13), 276 (4.07), 340 (3.81). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1630 (C=O). MS *m/z*: 272 (M^+), 91 (base peak). NMR $\delta_{\text{TMS}}^{\text{acetone-d}_6}$ ppm: 12.54 (1H, s, OH), 7.32~7.56 (6H, m, H-6 and phenyl proton), 6.57 (1H, s, H-3), 5.22 (2H, s, CH_2), 3.82 (3H, s, MeO), 2.57 (3H, s, AcO).

4) *7-Benzylloxy-2-hydroxy-6-methoxychromanone (4)*. To a solution of **3** (300 mg) in ethyl formate (4 ml) was added in steps pulverized sodium (200 mg) while chilling with ice-cooled water. The reaction mixture was allowed to stand for 20 min and refluxed for 10 min. After standing at room temperature for 24 hr, it yielded yellow solids, which were carefully, in limited amounts, added to ice-cooled water with stirring. The aqueous mixture thus obtained was washed three times with an adequate amount of ether, and then acidified with acetic acid to deposit the precipitates. The precipitates collected by filtration were chromatographed on a silica gel column. The eluate of the chloroform-ethanol mixture (19:1) was concentrated to give **4** (198 mg, 59.8%) as yellow needles. mp: 174~175°C. Found: C, 68.12; H, 5.36. Calcd. for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37%. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 236 (4.20), 273 (4.08), 334 (3.87). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1643 (C=O). MS *m/z*: 300 (M^+), 282, 93 (base peak). NMR $\delta_{\text{TMS}}^{\text{acetone-d}_6}$ ppm: 7.3~7.6 (5H, m, phenyl proton), 7.22 (1H, s, H-5), 6.60 (1H, s, H-8), 6.40~6.48 (1H, d, *J*=6 Hz, OH), 5.72~5.90 (1H, m, H-2), 5.20 (2H, s, CH_2), 3.80 (3H, s, MeO), 2.68~2.90 (2H, m, H-3).

5) *7-Hydroxy-6-methoxychromone (5)*. A solution of **4** (127 mg) in a conc. hydrochloric acid-acetic acid mixture (1:1, v/v, 2 ml) was heated at 65°C for 2 hr. The reaction mixture was evaporated to dryness and the residue was chromatographed on a silica gel column. The eluate with chloroform was concentrated to give **5** (72 mg, 88.5%) as colorless needles. mp: 233°C. Found: C, 62.48; H, 4.38. Calcd. for $C_{10}H_8O_4$: C, 62.50; H, 4.20. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 226 (4.12), 233 sh (4.10), 279 (3.67), 316 (3.90). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1640 (C=O). MS *m/z*: 192 (M^+ , base peak), 191, 177, 163, 149. NMR $\delta_{\text{TMS}}^{\text{DMSO-d}_6}$ ppm: 8.12 (1H, d, *J*=6 Hz, H-2), 7.34 (1H, s, H-5), 6.92 (1H, s, H-8), 6.21 (1H, d, *J*=6 Hz, H-3), 3.87 (3H, s, MeO).

This synthesized chromone was identical with the natural product Compound IV and aglycone of Compound V in its spectral data.

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