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Studies on Rhubarb (Rhei Rhizoma). V.[1] Isolation and Characterization of Chromone and Chromanone Derivatives

YOSHIKI KASHIWADA, GEN-ICHIRO NONAKA, and ITSUO NISHIOKA*

Faculty of Pharmaceutical Sciences, Kyushu University 62, 3-1-1 Maidashi, Higashi-ku, Fukuoka 812, Japan

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Six chromone and chromanone derivatives (I—VI) have been isolated from rhubarb (commercial name: 馬蹄大黄), together with torachrysone 8-*O*-*β*-D-glucopyranoside (VII), kaempferol (VIII) and kaempferol 3-*O*-*α*-L-rhamnoside (IX). The structures of I—VI were established on the basis of chemical and spectroscopic data to be 2,5-dimethyl-7-hydroxychromone (I), 2-methyl-5-acetonyl-7-hydroxychromone (II), 2-methyl-5-carboxymethyl-7-hydroxychromone (III), 2-(2′-hydroxypropyl)-5-methyl-7-hydroxychromone (IV), 2-(2′-hydroxypropyl)-5-methyl-7-hydroxychromone 7-*O*-*β*-D-glucopyranoside (V) and 2-methyl-5-carboxymethyl-7-hydroxychromanone (VI).

Keywords——rhubarb; Polygonaceae; chromone; chromanone; naphthalene derivative; flavonoid

In previous papers, the isolation of a variety of phenolic glycosides, *i.e.*, anthraquinones,[2] naphthalenes,[1] stilbenes,[3] flavanoids,[4] and tannins and related compounds,[5,6] from various rhubarbs has been reported. As a continuation of our studies on rhubarb, we have investigated phenolic constituents of a representative of rhubarb (commercial name: 馬蹄大黄), and have isolated five chromones (I—V), and a chromanone (VI), together with the known naphthalene glucoside (VII) and flavonoids (VIII and IX). This paper deals with the structure elucidation of these compounds.

The isolation of compounds I—IX from the aqueous acetone extracts was achieved by repeated chromatography on Sephadex LH-20, MCI-gel CHP-20P and silica gel using a variety of solvent systems (Chart 1).

Compounds VII, VIII and IX were identified as torachrysone 8-*O*-*β*-D-glucopyranoside, kaempferol and kaempferol 3-*O*-*α*-L-rhamnoside, respectively, by comparisons of their physical and spectral data with those described in the literature.[1,7]

Compound I, colorless needles (acetone), mp 257—258 °C, $C_{11}H_{10}O_3$, was presumed to be a chromone derivative from its ultraviolet (UV) (λ_{max}^{MeOH} nm: 241, 250, 289) and infrared (IR) (ν_{max}^{KBr} cm^{-1}: 1655, 1625, 1560) spectral data.[8,9] The UV spectrum showed no significant bathochromic shift on addition of aluminium chloride, indicating that there was no chelated hydroxyl group in I. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum showed signals of one olefinic (δ 5.96, 1H, s) and two aromatic (δ 6.60, 2H, s) protons, together with two methyl signals (δ 2.28, 2.66) whose chemical shifts were consistent with a 2,5-dimethylchromone.[10,11] Acetylation of I with acetic anhydride and pyridine afforded a monoacetate (Ia), which exhibited two *meta*-coupled aromatic protons (δ 6.81, 7.05, each d, J= 2 Hz) in the ^{1}H-NMR spectrum. From these chemical and spectroscopic findings, I was presumed to be 2,5-dimethyl-7-hydroxychromone, which had previously been obtained by acid hydrolysis of aloenin,[10] and also by synthesis.[11] The identity of I with this compound was established by comparison of the physical and spectral data with those reported in the literature. This is the first report of isolation of I as a natural product.

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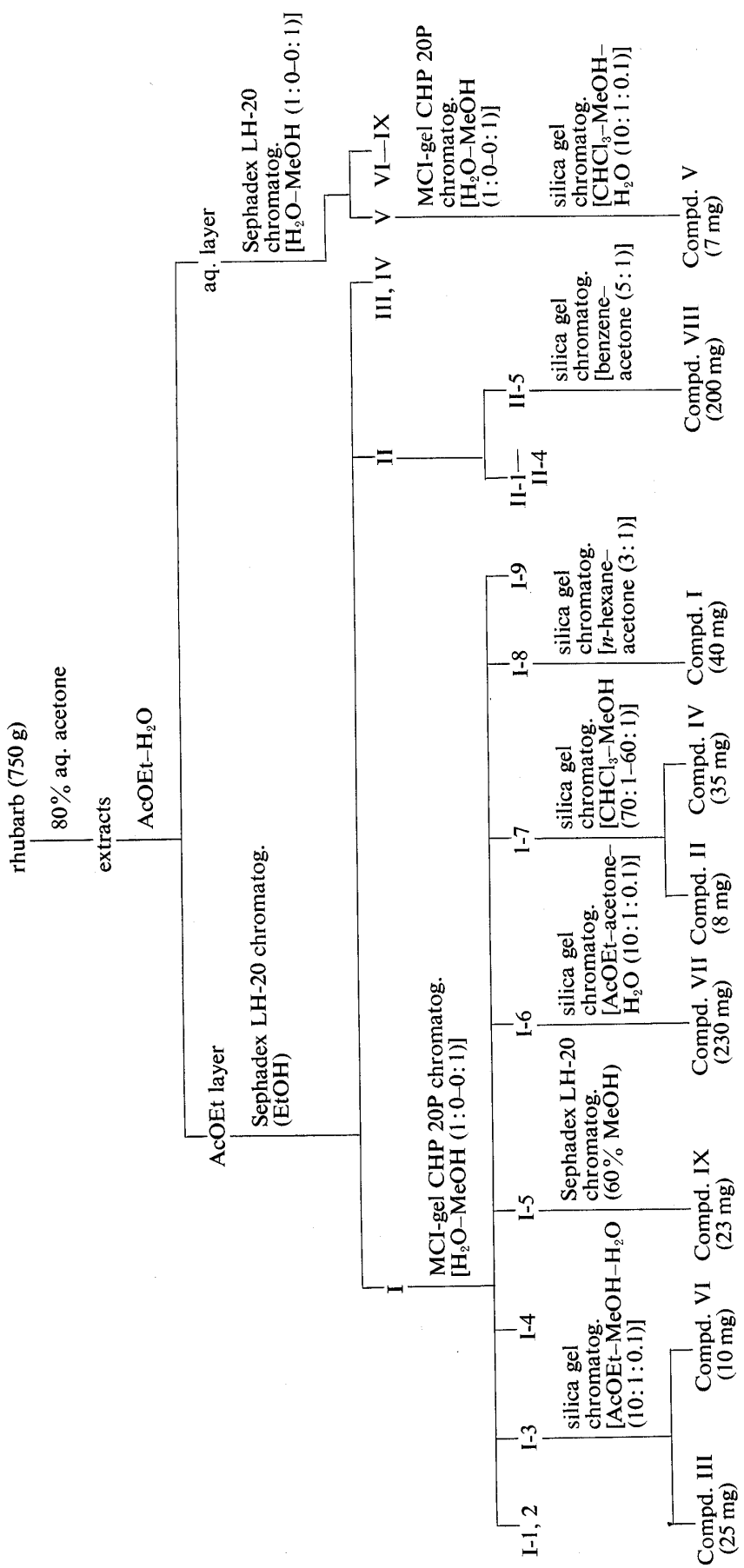

Chart 1

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Compound II, colorless needles (*n*-hexane–AcOEt), mp 214—216 °C, showed UV absorptions (λ_{max}^{MeOH} nm: 243, 250, 291) similar to those of I, indicating the presence of a chromone skeleton. The electron impact-mass spectrum (EI-MS) of II exhibited a molecular ion peak at *m/z* 232, and a base peak at *m/z* 190 formed by the loss of an acetyl group, while the ^{1}H-NMR spectrum showed the presence of acetyl (δ 2.18, 3H, s) and methylene (δ 4.11, 2H, s) functions, in addition to a methyl (δ2.29, 3H, s), an olefinic (δ 5.95, 1H, s) and two *meta*-coupled aromatic (δ 6.58, 6.71, each d, J=2 Hz) signals. The facts that the chemical shift of the methyl group was close to that of C-2 methyl in I, and that the C-5 methyl signal was not observed in II suggested that an acetonyl side chain was located at the C-5 position. Based on these data, the structure of II was considered to be 2-methyl-5-acetonyl-7-hydroxychromone. This was confirmed by comparison of its spectral data with those of a sample[12] isolated previously from flowers of *Cassia siamea*.

Compound III, colorless needles (dil. MeOH), mp 263.5—265 °C, $C_{12}H_{10}O_5$, gave a UV spectrum similar to those of I and II. The ^{1}H-NMR spectrum of III closely resembled that of II, except for the absence of the signal due to an acetyl methyl. The presence of a carboxylic acid function was deduced from the IR (1710 cm^{-1}) and carbon-13 nuclear magnetic resonance (^{13}C-NMR) (δ 172.0) spectra, and also from analysis of the EI-MS, which exhibited a prominent peak at *m/z* 190 formed by the loss of CO_2 from the molecular ion at *m/z* 234. This was further supported by derivatization of III on treatment with diazomethane to give a dimethylate, colorless needles (*n*-hexane–benzene), mp 149—150 °C, which exhibited in the ^{1}H-NMR spectrum a carbomethoxyl signal (δ 3.72), together with an aromatic methoxyl signal (δ 3.88). On the basis of these observations, the structure of III was concluded to be 2-methyl-5-carboxymethyl-7-hydroxychromone.

Compound IV, colorless needles (AcOEt–MeOH), mp 187.5—189 °C, $[\alpha]_D$ +38.4° (MeOH), $C_{13}H_{14}O_4$, was concluded to possess a chromone skeleton on the basis of the UV absorption bands (λ_{max}^{MeOH} nm: 243, 250, 289). The ^{1}H-NMR spectrum of IV exhibited signals

Table I. ^{13}C-NMR Spectral Data (δ Value)[a]

	I	III	IV	V	VI
C_2	163.9	164.1	164.9	165.2	73.2
C_3	116.4	117.8	116.4	116.8	44.6
C_4	178.4	177.7	178.9	178.1	191.2
C_5	141.5	137.8	141.5	141.1	139.5
C_6	110.5	110.3	111.4	111.6	114.0
C_7	160.6[b]	160.8[b]	160.6[b]	159.8[b]	164.0[b]
C_8	100.4	101.3	100.4	99.7	101.6
C_9	159.1[b]	158.8[b]	159.1[b]	158.7[b]	162.6[b]
C_{10}	114.1	114.2	114.4	116.1	111.9
C_2–CH_3	19.2	19.3			20.4
C_5–CH_3	22.3		22.3	22.2	
$C_{1'}$		40.2	42.7	42.8	40.5
$C_{2'}$		172.0	64.0	63.9	172.1
$C_{2'}$–CH_3			23.2	23.3	
$C_{1''}$				101.4	
$C_{2''}$				73.0	
$C_{3''}$				77.0	
$C_{4''}$				69.4	
$C_{5''}$				76.3	
$C_{6''}$				60.5	

a) Spectra were measured at 25.05 MHz in DMSO-d_6.
b) Assignments with the superscript *b*) may be interchanged in each column.

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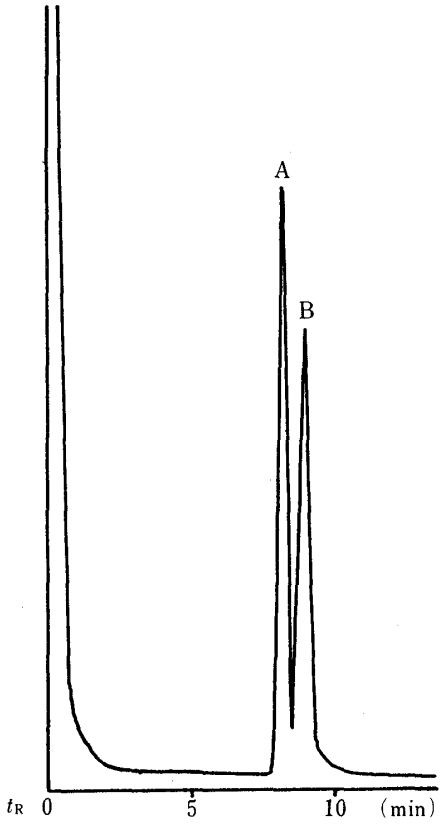

Fig. 1. Gas-Liquid Chromatogram of Diastereoisomers

A: Amide formed by reaction of (*R*)-α-phenylethylamine and (−)-(*R*)-α-phenylbutyric acid.
B: Amide formed by reaction of (*R*)-α-phenylethylamine and (+)-(*S*)-α-phenylbutyric acid.

due to a secondary methyl (δ 1.15, 3H, $J=7$ Hz), an allyl methylene (δ 2.58, 2H, d, $J=7$ Hz) and a carbinol methine (δ 4.02, m). It also showed an olefinic (δ 5.97, 1H, s), two aromatic (δ 6.61, 2H, s) and a methyl (δ 2.66, 3H, s) signals, which were similar to those observed in I. The observation that the chemical shift of singlet methyl was in good accord with that of the C-5 methyl in I suggested the location of the methyl group at the C-5 position. In the ^{13}C-NMR spectrum, signals attributable to a secondary methyl group (δ 23.2, q), a hydroxy-bearing carbon (δ 64.0, d) and a methylene (δ 42.7, t) were observed, while other signals were quite similar to those of I (Table I). These findings suggested that IV contains a 2-hydroxypropyl side chain at the C-2 position. Further support for this was provided by analysis of the EI-MS, which showed a molecular ion peak at *m/z* 234 (44 mass units more than that of I), and the base peak at *m/z* 190 formed by fission of the side chain. The absolute configuration of the hydroxy-bearing methine carbon (C-2′) was determined by application of the modified Horeau method[13] to the monomethylate (IVa). It was first acylated with phenyl-α-butyric anhydride in dry pyridine, and the excess (−)-*R*- and (+)-*S*-α-phenylbutyric anhydride was treated with (*R*)-α-phenylethylamine to form a mixture of two diastereoisomers whose relative ratio was estimated by gas liquid chromatographic analysis. The chromatogram is shown in Fig. 1; from this the absolute configuration at the C-2′ position could be determined to be *S*. Based on these results, the structure of this compound was determined to be IV.

Compound V, colorless needles ($CHCl_3$–MeOH), mp 191—193 °C, $[\alpha]_D$ −4.3° (MeOH), $C_{19}H_{24}O_9 \cdot H_2O$, exhibited, in the field desorption mass spectrum (FD-MS), peaks at *m/z* 397 and 419 due to $[M+H]^+$ and $[M+Na]^+$, respectively, together with a prominent peak at *m/z* 163 suggestive of the presence of a hexosyl moiety. Enzymatic hydrolysis of V with crude hesperidinase yielded, together with glucose, an aglycone, colorless needles (AcOEt–MeOH), mp 186—187 °C, which was identified as IV. The position of the glucosyl moiety in V was determined as follows. In the ^{1}H-NMR spectrum of V, a doublet signal due to an anomeric

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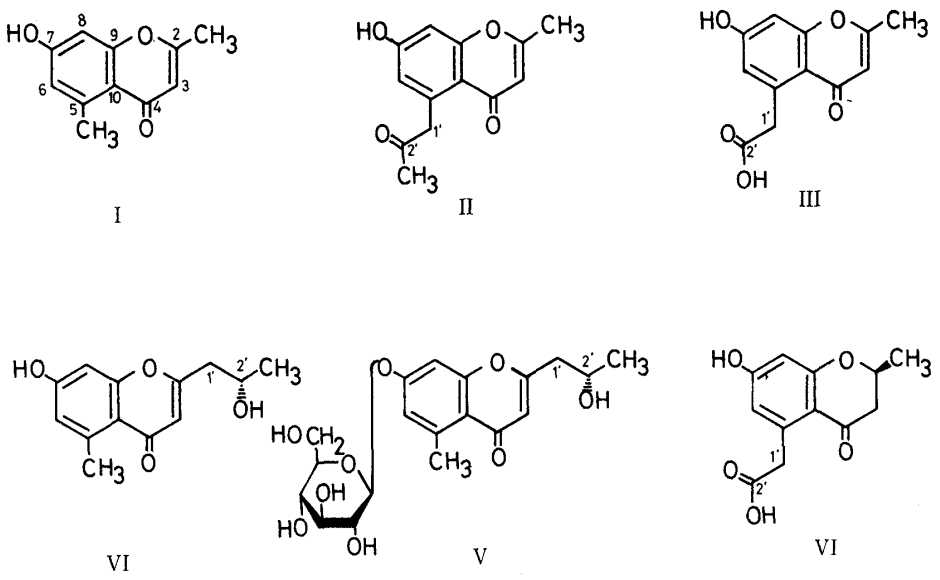

Fig. 2

proton was observed at δ 5.05 ($J=7$ Hz), and its chemical shift suggested that the glucosyl residue was bound to the aromatic hydroxyl group. Furthermore, in the ^{13}C-NMR spectrum, the signal of the C-2′ carbon was observed at δ 63.9, close to the chemical shift of IV (δ 64.0), while the signal of the C-8 carbon appeared at higher field (δ 99.7) than that of IV (δ 100.4). These observations indicated that the glucosyl residue was linked to the C-7 hydroxyl group. The configuration at the anomeric center was determined to be β on the basis of the coupling constant (d, $J=7$ Hz) of the anomeric proton in the ^{1}H-NMR spectrum of V. Thus, the structure of this compound was concluded to be V.

Compound VI, colorless needles (dil. MeOH), mp 205—207 °C, $[\alpha]_D$ −9.1° (MeOH), $C_{12}H_{12}O_5 \cdot 1/2H_2O$, possessed twelve carbon atoms including four aliphatic carbons, as shown by ^{13}C-NMR analysis (Table I). The appearance of a carbonyl carbon signal (δ 191.2) at lower field than those in I—IV was consistent with a chromanone structure. A signal appearing at a position (δ 172.1) analogous to that observed in III (δ 172.0) was assignable to a carboxylic acid carbon. The ^{1}H-NMR spectrum exhibited, in addition to *meta*-coupled aromatic signals (δ 6.24, 6.30, each d, $J=2$ Hz), signals due to a methine with an oxygen function (δ 4.50, m) and a methylene (δ 2.54, m), and these were shown by spin-decoupling experiments to be coupled with each other. The spectrum also revealed the presence of a secondary methyl group (δ 1.37, d, $J=6$ Hz) and a benzylic methylene (δ 3.80 s), the latter being considered to be next to the carboxyl group from the similarity of the chemical shift to that of III. Since the spin-decoupling experiments showed coupling between the methyl and methine signals, the methyl group could be placed at the C-2 position in the chromanone skeleton. The absolute configuration of the asymmetric center (C-2) was confirmed by comparison of its circular dichroism (CD) curve with those of similar 2-methyl chromanone derivatives[14] of known absolute stereochemistry. Compound VI showed several CD bands ($[\Phi]_{219}-14.16\times10^3$, $[\Phi]_{303}+9.78\times10^3$, $[\Phi]_{332}-7.75\times10^3$), the latter two of which were assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions, respectively, the signs being consistent with *S*-configuration. On the basis of these findings, the structure of this compound was determined as VI.

Compounds I—VI appear to be the first examples of chromone and chromanone derivatives isolated from rhubarb.

A possible biogenetic scheme for phenolic constituents occurring in rhubarbs is shown in Chart 2. The isolation of a chromanone and chromones which might be derived *via* a C_{12} or

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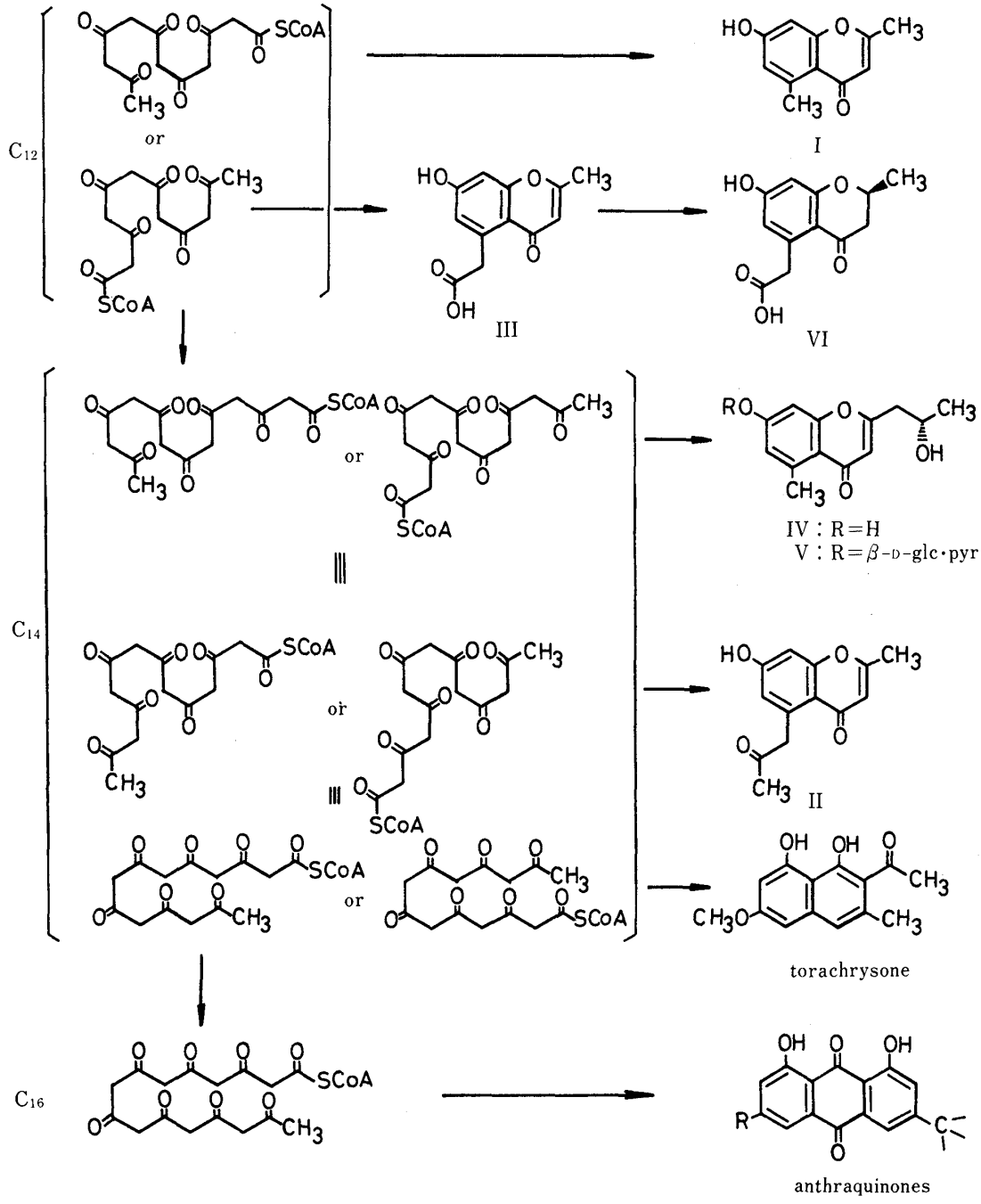

Chart 2. Possible Scheme for the Biogenesis of Phenolic Constituents in Rhubarb

C_{14} polyketide intermediate suggests the presence of complicated metabolic pathways in rhubarbs.

Experimental

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 digital polarimeter. IR spectra were obtained with a JASCO DS-301 spectrometer. EI- and FD-MS were obtained with JEOL D-300 and JEOL DX-300 spectrometers, respectively. ^{1}H- and ^{13}C-NMR spectra were taken with JEOL PS-100 and FX-100 spectrometers, respectively, using tetramethylsilane as an internal standard, and chemical shifts are given in δ (ppm). CD data were obtained with a JASCO J-20 machine. Column chromatography was carried out with Sephadex LH-20 (25—100 μ, Pharmacia Fine Chemical Co., Ltd.), MCI-gel CHP-20P (75—150 μ, Mitsubishi Chemical Industries, Ltd.) and Kieselgel 60 (70—230 mesh, Merck). Thin-

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layer chromatography (TLC) was conducted on precoated Kieselgel 60 F_{254} plates (0.20 mm, Merck) and precoated Avicel SF cellulose plates (Funakoshi), and spots were located by ultraviolet illumination, and by spraying 10% H_2SO_4 (for phenolics) and aniline-hydrogen phthalate (for sugars) reagents.

Isolation of Compounds I—IX——The pulverized rhubarb (馬蹄大黄750 g) was extracted three times with 80% aqueous acetone at room temperature. The acetone was removed by evaporation under reduced pressure (*ca.* 40 °C), and the aqueous solution was shaken three times with AcOEt. The AcOEt layer (40 g), after removal of the solvent by evaporation, was chromatographed over Sephadex LH-20 using EtOH–H_2O (1 : 0—3 : 2) to afford four fractions (fractions I—IV). Fractions I (23.8 g) and II (8 g) were rechromatographed over MCI-gel CHP-20P using H_2O–MeOH (1 : 0–0 : 1) to give nine (I-1—I-9) and five (II-1—II-5) fractions, respectively. Each fraction was repeatedly chromatographed over silica gel (solvent: AcOEt–MeOH–H_2O, AcOEt–acetone–H_2O, $CHCl_3$–MeOH, benzene–acetone) and Sephadex LH-20 (solvent: 60% MeOH) to afford compounds I (40 mg), II (8 mg), III (25 mg), IV (35 mg), VI (10 mg), VII (230 mg), VIII (200 mg) and IX (23 mg). The aqueous layer (115 g), after removal of the solvent by evaporation, was chromatographed over Sephadex LH-20 using H_2O–MeOH (1 : 0–0 : 1) to give five fractions (fractions V—IX). Fraction V was repeatedly chromatographed over MCI-gel CHP-20P (solvent: H_2O–MeOH) and silica gel (solvent: $CHCl_3$–MeOH–H_2O) to afford compound V (7 mg).

Compound I——Colorless needles (acetone), mp 257—258 °C, *Anal.* Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.21; H, 5.37. UV λ_{max}^{MeOH} nm (log ε): 241 (4.47), 250 (4.50), 289 (4.28). $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 241 (4.46), 250 (4.49), 289 (4.26). IR ν_{max}^{KBr} cm^{-1}: 1655, 1625, 1560. EI-MS (*m/z*): 190 (M^+), 175, 161, 150, 122. ^{1}H-NMR (DMSO-d_6): 2.28 (3H, s, 2-CH_3), 2.66 (3H, s, 5-CH_3), 5.96 (1H, s, 3-H), 6.60 (2H, s, 6, 8-H), 10.42 (1H, OH, disappeared on addition of D_2O). ^{13}C-NMR: Table I.

Acetylation of I——I (6 mg) was treated with Ac_2O (0.5 ml) and pyridine (0.5 ml) at room temperature for 3.5 h, and the reaction mixture was worked up as usual to give colorless needles (Ia, 4 mg) (*n*-hexane–AcOEt), mp 110—111 °C, EI-MS (*m/z*): 232 (M^+), 190, 182, 162, 161. ^{1}H-NMR ($CDCl_3$): 2.31 (3H, s, 2-CH_3), 2.33 (3H, s, $OCOCH_3$), 2.83 (3H, s, 5-CH_3), 6.06 (1H, s, 3-H), 6.81, 7.05 (each 1H, d, J=2 Hz, 6, 8-H).

Compound II——Colorless needles (*n*-hexane–AcOEt), mp 214—216 °C, UV λ_{max}^{MeOH} nm (log ε): 243 (4.32), 250 (4.34), 291 (4.21). $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 243 (4.34), 250 (4.37), 291 (4.21). IR ν_{max}^{KBr} cm^{-1}: 1715, 1645, 1625, 1570. EI-MS (*m/z*): 232 (M^+), 217, 215, 190, 161, 150, 122. High resolution MS: Found 232.073. Calcd for $C_{13}H_{12}O_4$: 232.074. ^{1}H-NMR (DMSO-d_6): 2.18 (3H, s, 2′-CH_3), 2.29 (3H, s, 2-CH_3), 4.11 (2H, s, 1′-H_2), 5.95 (1H, s, 3-H), 6.58, 6.71 (each 1H, d, J=2 Hz, 6, 8H).

Compound III——Colorless needles (dil. MeOH), mp 263.5—265 °C, *Anal.* Calcd for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 61.74; H, 4.56. UV λ_{max}^{MeOH} nm (log ε): 242 (4.31), 249 (4.32), 290 (5.05). $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 242 (4.31), 249 (4.34), 290 (4.05). IR ν_{max}^{KBr} cm^{-1}: 1710, 1640, 1620, 1570. EI-MS (*m/z*): 234 (M^+), 218, 190, 176, 150, 122, 120. ^{1}H-NMR (DMSO-d_6): 2.29 (3H, s, 2-CH_3), 4.00 (2H, s, 1′-H_2), 5.98 (1H, s, 3-H), 6.65, 6.72 (each 1H, d, J=2 Hz, 6, 8-H), 10.56 (1H, OH, disappeared on addition of D_2O). ^{13}C-NMR: Table I.

Methylation of III——A solution of III (10 mg) in MeOH was treated with an ethereal solution of CH_2N_2 at room temperature for 3 h. The solvent was evaporated off, and the residue was purified by silica gel chromatography [solvent: benzene–acetone (2 : 1)] to afford colorless needles (IIIa, 5 mg) (*n*-hexane–benzene), mp 149—150 °C, EI-MS (*m/z*): 262 (M^+), 230, 202, 188, 174. High resolution MS: Found 262.085. Calcd for $C_{14}H_{14}O_5$: 262.084. ^{1}H-NMR ($CDCl_3$): 2.30 (3H, s, 2-CH_3), 3.72 (3H, s, $COOCH_3$), 3.88 (3H, s, arom.-OCH_3), 4.15 (2H, s, 1′-H_2), 6.00 (1H, s, 3-H), 6.68, 6.77 (each 1H, d, J=2 Hz, 6, 8-H).

Compound IV——Colorless needles (AcOEt–MeOH), mp 187.5—189 °C, $[\alpha]_D^{21}$ +38.4° (c=0.89, MeOH), *Anal.* Calcd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.47; H, 6.02. UV λ_{max}^{MeOH} nm (log ε): 243 (4.35), 250 (4.37), 289 (4.19). $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 243 (4.35), 250 (4.37), 289 (4.18). CD (c=4.27 × 10^{-3}, MeOH) $[\Phi]^{24}$ × 10^3 (nm): +3.75 (279) (positive max.), 0 (252), +7.96 (219) (positive max.). EI-MS (*m/z*): 234 (M^+), 190, 161, 151, 124, 122. ^{1}H-NMR (DMSO-d_6): 1.15 (3H, d, J=7 Hz, 2′-CH_3), 2.58 (2H, d, J=7 Hz, 1′-H_2), 2.66 (3H, s, 5-CH_3), 4.02 (1H, m, 2′-H), 5.97 (1H, s, 3-H), 6.61 (2H, s, 6, 8-H), 10.51 (1H, OH, disappeared on addition of D_2O). ^{13}C-NMR: Table I.

Methylation of IV——IV (10 mg) was methylated in the same way as described for III. Purification of the product on a silica gel column [solvent: benzene–acetone (3 : 1)] gave colorless plates (*n*-hexane–benzene) (8 mg), mp 119—120 °C, $[\alpha]_D^{19}$ +43.6° (c=0.36, MeOH), EI-MS (*m/z*): 248 (M^+), 204, 165. High resolution MS: Found 248.105. Calcd for $C_{14}H_{16}O_4$: 248.105. ^{1}H-NMR ($CDCl_3$): 1.33 (3H, d, J=6 Hz, 2′-CH_3), 2.67 (2H, d, J=6 Hz, 1′-H_2), 2.74 (3H, s, 5-CH_3), 3.86 (3H, s, arom.-OCH_3), 4.30 (1H, m, 2′-H), 6.08 (1H, s, 3-H), 6.64 (2H, s, 6, 8-H).

Application of the Modified Horeau Method——IVa (5 mg) was treated with phenylbutyric anhydride (6 μl) and dry pyridine (10 μl) at 40 °C for 2 h, then (*R*)-α-phenylethylamine (6 μl) was added to the mixture. After 15 min, the mixture was diluted with AcOEt (200 μl), and analyzed by GLC. The result is shown in Fig. 1. (column, 1.5% OV-17; column temp., 220 °C, flow rate, 50 ml/min).

Compound V——Colorless needles ($CHCl_3$–MeOH), mp 191—193 °C, $[\alpha]_D^{24}$ −4.3° (c=0.21, MeOH), *Anal.* Calcd for $C_{19}H_{24}O_9 \cdot H_2O$: C, 55.06; H, 6.32. Found: C, 55.00; H, 6.29. FD-MS (*m/z*): 419 $(M+Na)^+$, 397 $(M+H)^+$, 379 $(M-OH)^+$, 234 $(M+H-glc.)^+$, 163. ^{1}H-NMR (DMSO-d_6): 1.15 (3H, d, J=6 Hz, 2′-CH_3), 2.67 (2H, d, J=6 Hz, 1′-H_2), 2.70 (3H, s, 5-CH_3), 3.15—4.20 (7H, m, sugar-H and 2′-H), 5.05 (1H, d, J=7 Hz, arom.–H), 6.05 (1H, s, 3-H), 6.83, 6.98 (each 1H, d, J=2 Hz, 6, 8-H). ^{13}C-NMR (DMSO-d_6): Table I.

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Enzymatic Hydrolysis of V——V (5 mg) in H_2O was incubated overnight with crude hesperidinase at 37 °C. The reaction mixture was evaporated under reduced pressure, and the residue was treated with MeOH. The MeOH-soluble portion was subjected to MCI-gel CHP-20P chromatography to afford the aglycone (IV), colorless needles (AcOEt–MeOH), mp 186—187 °C, CD ($c=5.13\times10^{-3}$, MeOH) $[\Phi]^{24}\times10^3$ (nm): +3.90 (279) (positive max.), 0 (252), +8.58 (219) (positive max.). ^{1}H-NMR (DMSO-d_6): 1.14 (3H, d, $J=6$ Hz, 2′-CH_3), 2.65 (3H, s, 5-CH_3), 2.67 (2H, d, $J=6$ Hz, 1′-H_2), 4.02 (1H, m, 2′-H), 5.97 (1H, s, 3-H), 6.62 (2H, s, 6, 8-H), and the sugar which was identified as glucose by comparison of the *Rf* value (0.30) on TLC [solvent: *n*-BuOH–pyridine–H_2O (6:4:3)] with that of authentic sample.

Compound VI——Colorless needles (dil. MeOH), mp 205—207 °C, $[\alpha]_D^{24}$ −9.1° ($c=0.23$, MeOH), *Anal.* Calcd for $C_{12}H_{12}O_5\cdot1/2H_2O$: C, 58.77; H, 5.34. Found: C, 58.98; H, 5.52. EI-MS (*m/z*): 236 (M^+), 192, 190, 176, 166, 150, 122. CD ($c=5.93\times10^{-3}$, MeOH) $[\Phi]^{24}\times10^3$ (nm): −7.75 (332) (negative max.), +9.78 (303) (positive max), −14.16 (219) (negative max.). ^{1}H-NMR (DMSO-d_6): 1.37 (3H, d, $J=6$ Hz, 2-CH_3), 2.54 (2H, m, 3-H_2), 3.80 (2H, s, 1′-H_2), 4.50 (1H, m, 2-H), 6.24, 6.30 (each 1H, d, $J=2$ Hz, 6, 8-H), 10.48 (1H, OH, disappeared on addition of D_2O). ^{13}C-NMR: Table I.

Compound VII——Pale yellow needles (dil. MeOH), mp 151—153 °C, $[\alpha]_D^{19}$ −108.2° ($c=1.10$, MeOH). ^{1}H-NMR (acetone-d_6): 2.28 (3H, s, arom.-CH_3), 2.54 (3H, s, $COCH_3$), 3.40—5.05 (6H, m, sugar-H), 3.86 (3H, s, OCH_3), 5.18 (1H, d, $J=7$ Hz, anom.-H), 6.86, 7.02 (each 1H, d, $J=2$ Hz, 5, 7-H), 7.04 (1H, s, 4-H), 9.64 (1H, OH, disappeared on addition of D_2O).

Compound VIII——Pale yellow needles (MeOH), mp 277—279 °C (dec.). IR ν_{max}^{KBr} cm^{-1}: 3400, 1660, 1615, 1570, 1510. ^{1}H-NMR (acetone-d_6): 6.27, 6.52 (each 1H, d, $J=2$ Hz, 6, 8-H), 7.00, 8.14 (each 2H, d, $J=8$ Hz, 2′, 6′ and 3′, 5′-H), 9.24 (2H, OH, disappeared on addition of D_2O), 12.14 (1H, OH, disappeared on addition of D_2O).

Compound IX——Pale yellow needles (dil. MeOH), mp 179—182 °C, $[\alpha]_D^{19}$ −125.2° ($c=1.03$, MeOH). ^{1}H-NMR (acetone-d_6 + D_2O): 0.89 (3H, d, $J=6$ Hz, 5″-CH_3), 3.24—4.28 (4H, m, sugar-H), 5.50 (1H, br s, anom.-H), 6.27, 6.48 (each 1H, d, $J=2$ Hz, 6, 8-H), 7.03, 7.80 (each 2H, d, $J=8$ Hz, 2′, 6′ and 3′,5′-H). ^{13}C-NMR (acetone-d_6 + D_2O): 17.7 ($C_{5''}$-CH_3), 71.3 ($C_{2'',3''}$), 71.8 ($C_{5''}$), 72.6 ($C_{4''}$), 94.6 (C_8), 99.6 (C_6), 102.7 ($C_{1''}$), 105.4 (C_{10}), 116.3 ($C_{3',5'}$), 122.0 ($C_{1'}$), 131.6 ($C_{2',6'}$), 135.5 (C_3), 157.9 (C_2), 158.5 (C_9), 161.0 ($C_{4'}$), 162.6 (C_5), 165.3 (C_7), 179.0 (C_4).

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