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New Coumarins from Some *Citrus* Plants[1)]

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Six new coumarins, 6-formylumbelliferone (**1**), hassanon (**2**), 5-hydroxyseselin (**4**), *cis*-grandmarin (**6**, *cis*), *trans*-grandmarin isovalerate (**8**, *trans*), and kinocoumarin (**9**), were isolated from roots and root barks of some *Citrus* plants, and their structures were determined by means of spectral and chemical studies.

Keywords——*Citrus*; Rutaceae; coumarin; hassanon; grandmarin; kinocoumarin; seselin; umbelliferone; isovalerate

Introduction

In our phytochemical studies of *Citrus* plants,[1)] we examined the constituents of the roots and root barks of some *Citrus* plants; *C. medica* (common name: etrog citron), *C. natsudaidai* (natsudaidai), and *C. sinensis* (valencia orange), and those of several hybrid seedlings resulting from crosses of *C. tamurana* (hyuga-natsu) × *C. kinokuni* (hirakishu) and *C. hassaku* (hassaku) × *C. grandis* (hirato-buntan). We describe here the structural determination of six new coumarins isolated from these *Citrus* plants.

Results and Discussion

The acetone extracts of the roots and root barks of each *Citrus* plant were treated by column and preparative thin layer chromatographies (TLC) on silica gel to isolate new coumarins along with many kinds of known coumarins, acridones, and other components.

Structure of 6-Formylumbelliferone (1)

This compound was obtained from Etrog citron as a colorless oil, showed the molecular formula $C_{10}H_6O_4$ as determined from the high-resolution mass spectrum (MS), and gave ultraviolet (UV) spectral data [λ_{max} 228, 254, and 328 nm] typical of the 7-oxygenated coumarin nucleus.[2)] In the proton nuclear magnetic resonance (^{1}H-NMR) spectrum, H-3 and H-4 were observed at δ 6.34 and 7.67 (each 1H, d, J=9.7 Hz) as AB-type signals, respectively. Lower-field singlets at δ 11.41 (exchangeable with D_2O) and 9.92, and infrared (IR) absorption bands at ν_{max} 3500 and 1660 cm^{-1} were ascribed to a hydrogen-bonded hydroxy and a formyl moiety, respectively. The location of the formyl group at C-6 was indicated by the appearance of aromatic protons as two 1H singlets at δ 6.89 and 7.73 due to H-8 and H-5,

respectively, in the ^{1}H-NMR spectrum. From the above data, this coumarin was elucidated as 6-formylumbelliferone (**1**).

Structure of Hassanon (2)

Hassanon was isolated from roots and root barks of several hybrid seedlings resulting from a cross of hassaku × hirato-buntan as colorless prisms, mp 132—134 °C, $C_{14}H_{14}O_4$. This compound was shown to have a 7-methoxy-8-substituted coumarin nucleus by the UV (see Experimental) and ^{1}H-NMR spectra [δ 7.62 (H-4) and 6.24 (H-3) (each 1H, d, J=9.5 Hz), 7.32 (H-5) and 6.83 (H-6) (each 1H, d, J=8.6 Hz), 3.90 (3H, s, OCH_3)]. Other ^{1}H-NMR signals at δ 3.12 (2H, t, J=7.8 Hz), 2.69 (2H, t, J=7.8 Hz), and 2.19 (3H, s) together with characteristic MS fragments at m/z 203 (100%) and 189 produced by loss of $\cdot COCH_3$ and $\cdot CH_2COCH_3$ from the molecular ion, respectively, indicated the structure [$-CH_2CH_2-COCH_3$] for the side chain at C-8. On the basis of these spectral data, the structure of hassanon was confirmed as formula **2**, corresponding to a dihydrogenated derivative of osthenon (**3**).[3,4]

Structure of 5-Hydroxyseselin (4)

5-Hydroxyseselin, colorless needles, mp 210—213 °C, $C_{14}H_{12}O_4$ was isolated from roots and root barks of natsudaidai and several hybrid seedlings resulting from a cross of hyuganatsu × hirakishu. The UV and IR bands (see Experimental) and AB-type doublets at δ 6.15 (H-3) and 7.97 (H-4) (J=9.7 Hz) in the ^{1}H-NMR spectrum suggested the presence of a coumarin nucleus having a hydroxy group (ν_{max} 3320 cm^{-1}). The location of the hydroxy group at C-5 was presumed based on the observation of the H-4 proton signal at δ 7.97, at lower field compared with that of coumarin lacking a C-5 oxygen function.[2] Another pair of doublets having a larger coupling constant (J=10 Hz) and a 6H singlet at δ 1.45, together with a singlet due to an aromatic proton at δ 6.17 assignable to H-6, were attributed to angular oriented dimethylpyran ring protons.[2] These data suggested the structure of this coumarin to be formula **4**. 5-Hydroxyseselin (**4**) has been synthesized by Murray and Jorge,[5] and the synthetic material was found to be identical with the natural specimen by comparisons of IR and ^{1}H-NMR spectra. This is the first example of the occurrence of 5-hydroxyseselin (**4**) from natural sources.

Structure of *cis*-Grandmarin (6, *cis*)

cis-Grandmarin, colorless prisms, mp 229—231 °C, $C_{15}H_{16}O_6$, $[\alpha]_D$ +5.41° (chloroform), was obtained from natsudaidai. The UV spectrum (see Experimental) and ^{1}H-NMR signals including a pair of doublets at δ 6.16 (H-3) and 8.00 (H-4) (each 1H, J=9.8 Hz), an isolated singlet at δ 6.24, and a 3H singlet at δ 3.88 (OCH_3) indicated a 5,7-oxygenated coumarin nucleus.[2] Other signals at δ 3.76 (1H, d, J=4.0 Hz) and 3.19 (1H, d, J=5.4 Hz) disappeared with the addition of D_2O, and a double-doublet at δ 5.15 (1H, J=4.0 and 5.4 Hz) and a triplet at δ 3.84 (1H, J=5.4 Hz) changed to two doublets coupled with each other (J=5.4 Hz). The J values (5.4 Hz) of these two doublets and the appearance of two C-methyl singlets having little difference in chemical shift ($\Delta\delta$ 0.05 ppm) suggested the presence of a dimethyldihydropyran ring bearing a *cis*-oriented glycol moiety.[2,6] The above data were in accordance with the structure **6** (*cis*) for *cis*-grandmarin. In confirm this proposition, dihydroxylation of 5-methoxyseselin (**5**) was carried out. Treatment of 5-methoxyseselin (**5**) already isolated from the plant of the same genus, with *m*-chloroperbenzoic acid (*m*CPBA) in ether gave two isomeric dihydroxy derivatives (A and B). In the ^{1}H-NMR spectra (Table I) of these isomers, two protons attached to a carbon bearing a hydroxy group appeared at δ 3.84 and 5.15 (each doublet, J=5.4 Hz, H-3′ and H-4′, respectively) in compound A, and at δ 3.81 and 4.92 (each doublet, J=6.8 Hz, H-3′ and H-4′, respectively) in compound B. Two methyl proton signals were observed at δ 1.46 and 1.41 in the spectrum of A, and at δ 1.52 and 1.31 in

TABLE I. ^{1}H-NMR Data for Grandmarin Derivatives (**6**, **7**, and **8**)

Compd.	H-3	H-4	H-6	H-3′	H-4′	5-OCH_3	2′-$(CH_3)_2$	$OCOCH_3$	Others
6 (*cis*)	6.16 d (9.8)	8.00 d (9.8)	6.24 s	3.84 t (5.4)	5.15 dd (5.4) (4.0)	3.88	1.46 1.41 $\Delta\delta$ 0.05		3.19 (1H, d, 5.4)[a] 3.76 (1H, d, 4.0)[a]
7 (*cis*)	6.14 d (9.8)	7.93 d (9.8)	6.25 s	5.27 d (4.9)	6.46 d (4.9)	3.89	1.45 1.41 $\Delta\delta$ 0.04	2.11 2.10	
6 (*trans*)	6.16 d (9.8)	8.00 d (9.8)	6.23 s	3.81 d (6.8)	4.92 d (6.8)	3.87	1.52 1.31 $\Delta\delta$ 0.21		
7 (*trans*)	6.15 d (9.8)	7.95 d (9.7)	6.26 s	5.26 d (4.2)	6.13 d (4.2)	3.89	1.45 1.36 $\Delta\delta$ 0.09	2.11 2.10	
8 (*trans*)	6.17 d (9.8)	8.00 d (9.8)	6.27 s	5.17 d (3.5)	4.95 d (3.5)	3.89	1.49 1.38 $\Delta\delta$ 0.21		0.94 (6H, d, 6.6) 2.21 (2H, m) 2.09 (1H, m) 3.42 (1H, br)[a]

Values are in ppm. *a*) Exchangeable with D_2O. Figures in parentheses are coupling constants in herts (Hz). The $\Delta\delta$ value (ppm) is the difference between the chemical shifts of the two methyl signals.

that of B. The characteristic differences of chemical shift between the two methyl signals, 0.05 ppm in A and 0.21 ppm in B, and the $J_{3'-4'}$ values indicated the relative configuration of A to be *cis* and that of B to be *trans*.[2,6] To confirm this, nuclear Overhauser effect (NOE) experiments were attempted. In the spectrum of A, irradiation of the signal at δ 5.15 (H-4′) gave a 7.7% enhancement of the signal at δ 3.84 (H-3′), and irradiation of the H-3′ signal produced a 5.7% enhancement of the H-4′ signal (*vice versa*). However, in the spectrum of B, no NOE enhancement was observed at any proton signal upon irradiation at δ 4.92 (H-4′) and 3.81 (H-3′). Analogous experiments for **7**, corresponding to the diacetate of **6**, also supported the assignments of the relative configuration of **6** (see Experimental). These results established the relative stereochemistry of the hydroxy groups in **6** as *cis* in A and *trans* in B. Natural *cis*-grandmarin was found to be identical with synthetic A (**6**, *cis*) by direct comparison (IR, ^{1}H-NMR, and MS, and TLC). The absolute stereochemistry of *cis*-grandmarin (**6**, *cis*) remains to be solved.

Structure of *trans*-Grandmarin Isovalerate (8)

trans-Grandmarin isovalerate was isolated from roots and root barks of several hybrid seedlings resulting from a cross of hassaku × hirato-buntan as a colorless oil, $C_{20}H_{24}O_7$, $[\alpha]_D$ +24.1° (chloroform). The UV spectrum showed absorptions similar to those of **6**, and IR bands appeared at ν_{max} 3500, 1730, 1630, 1600 cm^{-1}. The features of the ^{1}H-NMR signals (Table I) of this coumarin resembled those of synthetic **6** (*trans*) described above (see Table I), except for the signals of δ 2.21 (2H, m), 2.09 (1H, m), 0.94 (6H, d, J=6.6 Hz) assignable to the isovaleryl moiety and a doublet due to H-3′, which appeared at δ 3.81 in the spectrum of **6** (*trans*), while that of this coumarin was shifted to lower field by 1.36 ppm, appearing at δ 5.17 (1H, d, J=3.5 Hz). In NOE experiments, irradiation of a methoxy group at δ 3.89 caused a 20% enhancement of the signal at δ 6.27 (H-6). However, on irradiation at δ 4.94 (H-4′) and 5.17 (H-3′), there was no NOE enhancement at any proton signal. These spectral results led us to propose the structure **8** (*trans*) for *trans*-grandmarin isovalerate, except for the absolute stereochemistry.

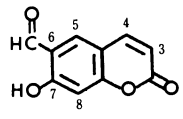
Structure of Kinocoumarin (9)

Kinocoumarin was obtained from roots and root barks of several hybrid seedlings resulting from a cross of hyuga-natsu × hirakishu as a colorless oil, $C_{24}H_{28}O_4$. The UV spectrum (λ_{max} 224, 284, and 336 nm) was similar to those of nordentatin (**10**)[7] and clausarin

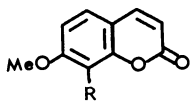
TABLE II. ^{1}H-NMR Data for Kinocoumarin (**9**), Nordentatin (**10**), and Clausarin (**11**)

Comp.	H-3	H-4	H-3′	H-4′	8-Dimethylallyl				3 (or 3′)-Dimethylallyl				2′-$(CH_3)_2$
9	6.16 d (9.8)	7.99 d (9.8)	—	6.38 s	6.30 dd (10.7) (17.3)	4.93 d (17.3)	4.87 d (10.7)	1.64 s	5.39 dd (10.7) (17.3)	5.11 d (17.3)	5.08 d (10.7)	1.50[a] s	1.37[a] s
10	6.14 d (9.8)	8.04 d (9.8)	5.68 d (10.0)	6.54 d (10.0)	6.27 dd (10.7) (17.5)	4.91 d (17.5)	4.85 d (10.7)	1.64 s					1.44 s
11	—	7.82 s	5.68 d (10.0)	6.47 d (10.0)	6.29 dd (10.5) (17.4)	4.93 d (17.4)	4.85 d (10.5)	1.64 s	6.17 dd (10.4) (17.2)	5.08 d (17.2)	5.07 d (10.4)	1.47[a] s	1.43[a] s

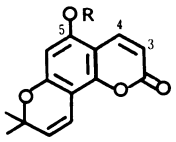
Values are in ppm. Figures in parentheses are coupling constants in hertz (Hz). *a*) Assignments may be interchanged.



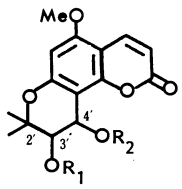
1



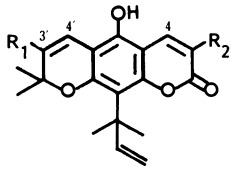
2: R = $-CH_2CH_2COCH_3$
3: R = $-CH=CHCOCH_3$ (*E*)



4: R = H
5: R = CH_3



6: $R_1 = R_2 = H$
7: $R_1 = R_2 = Ac$
8: $R_1 = -COCH_2CH(CH_3)_2$, $R_2 = H$



9: $R_1 = -C(CH_3)_2CH=CH_2$, $R_2 = H$
10: $R_1 = R_2 = H$
11: $R_1 = H$, $R_2 = -C(CH_3)_2CH=CH_2$

Fig. 1

(**11**).[8] The ^{1}H-NMR spectrum showed a D_2O-exchangeable 1H broad singlet at δ 5.26, an 1H singlet at δ 6.38, AB-type doublets at δ 7.99 and 6.16 (each 1H, J = 9.8 Hz, H-4 and H-3, respectively), and a 6H-singlet at δ 1.50 (2 × CH_3). In addition to these signals, the appearance of two ABX-type signals (see Table II) accompanied with four tertiary methyl singlets at δ 1.64 and 1.50 (or 1.37) (each 6H, s) indicated the presence of two 1,1-dimethylallyl moieties. From a comparison (see Table II) of these signal patterns with those of nordentatin (**10**) and clausarin (**11**), 1,1-dimethylallyl moieties were concluded to be located at C-8 and C-3′ in the kinocoumarin molecule. On the basis of these data, kinocoumarin can be represented by the formula **9**.

Experimental

All melting points were measured on a micromelting point hot-stage apparatus (Yanagimoto). ^{1}H-NMR spectra were recorded on a GX-270 (JEOL) or GX-400 (JEOL) spectrometer, and ^{13}C-NMR spectra on a GX-400 (JEOL)

spectrometer, in $CDCl_3$, unless otherwise stated. Chemical shifts are shown in δ values (ppm) with tetramethylsilane (TMS) as an internal reference. Electron impact MS (EI-MS) were taken with an M-52 (Hitachi) spectrometer having a direct inlet system, and high-resolution MS with an M-80 (Hitachi) spectrometer. UV spectra were determined in methanol and IR spectra were recorded in $CHCl_3$.

Extraction and Separation——The roots and root barks of *Citrus* plants grown in the orchard of Okitsu Branch, Fruit Tree Research Station, Ministry of Agriculture, Forestry, and Fisheries, Shimizu, Shizuoka were used as materials.

The scientific names along with Japanese common names (in parentheses) of plant materials treated in our studies are listed below:

Citrus medica L. var. *etrog* ENGL. (etrog citron), *C. natsudaidai* HAYATA (natsudaidai); several hybrid seedlings resulting from crosses of *C. hassaku* HORT. *ex.* TANAKA (hassaku), and *C. tamurana* HORT. *ex* TAKAHASHI (hyuganatsu); several hybrid seedlings resulting from crosses of *C. grandis* OSBECK (hirato-buntan), and *C. kinokuni* HORT. *ex.* TANAKA (hirakishu).

The dried roots and root barks of each *Citrus* plant were extracted with acetone. The acetone extract was subjected to silica gel column chromatography. Successive elution with benzene, benzene–isopropyl ether (3 : 1—1 : 3), and benzene–acetone (3 : 1) gave 3—6 fractions. Each fraction was subjected repeatedly to preparative silica gel TLC developed with appropriate combinations of acetone, benzene, hexane, isopropyl ether, and chloroform to yield new coumarins as well as known coumarins, and other components.

Details of the procedures of separation and characterization of known components will be reported elsewhere.

6-Formylumbelliferone (1)——Colorless oil. Content: 0.00035% in the roots and root barks of etrog citron. High-resolution MS: Calcd for $C_{10}H_6O_4$: 190.0266. Found: 190.0270. UV λ_{max} nm: 228, 254, 328. IR ν_{max} cm^{-1}: 3500 (br), 1740, 1660. ^{1}H-NMR δ: 11.41 (1H, s, exchanged with D_2O), 9.92 (1H, s), 7.73 (1H, s), 7.67 (1H, d, J=9.7 Hz), 6.89 (1H, s), 6.34 (1H, d, J=9.7 Hz). MS *m/z* (%): 190 (M^+, 100), 189 (26), 162 (53), 161 (60), 105 (13).

Hassanon (2)——Colorless prisms from EtOAc, mp 132—134 °C. Content: 0.0035% in the roots and root barks of several hybrid seedlings of hassaku × hirato-buntan. High-resolution MS: Calcd for $C_{14}H_{14}O_4$: 246.0891. Found: 246.0903. UV λ_{max} nm: 216 (sh), 256, 321. IR ν_{max} cm^{-1}: 1720, 1610. ^{1}H-NMR (400 MHz) δ: 7.62 (1H, d, J=9.5 Hz), 7.32 (1H, d, J=8.6 Hz), 6.83 (1H, d, J=8.6 Hz), 6.24 (1H, d, J=9.5 Hz), 3.90 (3H, s), 3.12 (2H, t, J=7.8 Hz), 2.69 (2H, t, J=7.8 Hz), 2.19 (3H, s). ^{13}C-NMR (100 MHz) δ: 208.1 (s), 161.2 (s), 160.3 (s), 153.1 (s), 143.7 (d), 126.7 (d), 116.9 (s), 113.1 (d), 112.9 (s), 107.3 (d), 56.0 (q), 42.6 (t), 29.6 (q), 17.3 (t). MS *m/z* (%): 246 (M^+, 21), 203 (100), 189 (17), 131 (19).

5-Hydroxyseselin (4)——Colorless needles from EtOAc, mp 210—213 °C. Content: 0.0046% in roots and root barks of natsudaidai, 0.0015% in hybrid seedlings of hyuga-natsu × hirakishu. High-resolution MS: Calcd for $C_{14}H_{12}O_4$: 244.0734. Found: 244.0734. UV λ_{max} nm: 212 (sh), 226, 283, 292, 311, 325. IR ν_{max} cm^{-1}: (KBr) 3320 (br), 1710, 1650, 1620, 1605. ^{1}H-NMR δ: 7.97 (1H, d, J=9.7 Hz), 6.79 (1H, d, J=10.0 Hz), 6.17 (1H, s), 6.15 (1H, d, J=9.7 Hz), 5.58 (1H, d, J=10.0 Hz), 1.45 (6H, s). ^{1}H-NMR δ: (acetone-d_6) 9.76 (1H, br), 8.03 (1H, d, J=9.7 Hz), 6.70 (1H, d, J=10.0 Hz), 6.28 (1H, s), 6.10 (1H, d, J=9.7 Hz), 5.71 (1H, d, J=10.0 Hz), 1.44 (6H, s). MS *m/z* (%): 244 (M^+, 33), 230 (24), 229 (100), 201 (21), 149 (39).

***cis*-Grandmarin (6, *cis*)**——Colorless prisms from ether–hexane, mp 229—231 °C. 0.0040% in roots and root barks of natsudaidai. $[\alpha]_D$ +5.41° (c=0.074, $CHCl_3$), High-resolution MS: Calcd for $C_{15}H_{16}O_6$: 292.0946. Found: 292.0959. UV λ_{max} nm: 208, 224 (sh), 250, 260, 329. IR ν_{max} cm^{-1}: 3400 (br), 1720, 1630, 1600. ^{1}H-NMR δ: see Table I. MS *m/z*: (%): 292 (M^+, 28), 221 (100), 220 (31), 205 (10), 192 (36), 164 (51), 149 (21).

***trans*-Grandmarin Isovalerate (8)**——Colorless oil. Content: 0.0032% in roots and root barks of hybrid seedlings of Hassaku × Hirato-buntan. $[\alpha]_D$ +24.1° (c=0.071, $CHCl_3$). High-resolution MS: Calcd for $C_{20}H_{24}O_7$: 376.1520. Found: 376.1518. UV λ_{max} nm: 209, 222 (sh), 249, 258, 328. IR ν_{max} cm^{-1}: 3500 (br), 1730, 1630, 1600. ^{1}H-NMR δ: see Table I. MS *m/z* (%): 376 (M^+, 1), 274 (8), 259 (100), 221 (17).

Kinocoumarin (9)——Colorless oil. Content: 0.00093% in roots and root barks of hybrid seedlings of hyuganatsu × hirakishu. High-resolution MS: Calcd for $C_{24}H_{28}O_4$: 380.1985. Found: 380.1974. UV λ_{max} nm: 224, 284, 336. IR ν_{max} cm^{-1}: 3300 (br), 1720, 1620, 1600. ^{1}H-NMR δ: see Table II. MS *m/z* (%): 380 (M^+, 25), 365 (100), 311 (25), 297 (10), 243 (9).

Treatment of 5-Methoxyseselin (5) with *m*CPBA——A mixture of 5-methoxyseselin (**5**) (20 mg) and *m*CPBA (20 mg) in CH_2Cl_2 (5 ml) was stirred for 1 h at room temperature. After addition of CH_2Cl_2 (10 ml), the solution was washed with diluted aqueous $NaHCO_3$, dried with anhydrous $MgSO_4$, and then concentrated to dryness. The residue was dissolved in MeOH (5 ml). The solution was stirred with diluted aqueous $NaHCO_3$ overnight, extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, and then concentrated. The residue was subjected to preparative TLC (hexane–acetone, 2 : 1) to give **6** (*cis*) (2.3 mg) and **6** (*trans*) (3.0 mg) as oils. ^{1}H-NMR: see Table I.

Acetylation of 6——A mixture of **6** (*trans*) (2.0 mg), acetic anhydride (2 ml), and pyridine (1 drop) was left overnight at room temperature. The reaction mixture was treated in the usual manner, and the residue was subjected to preparative TLC to give a diacetate (**7**, *trans*) (2 mg). In the ^{1}H-NMR spectrum of **7**, no NOE enhancement was observed on irradiation at δ 5.26 (H-3′) or 6.13 (H-4′).

6 (*cis*) (2.0 mg) was also treated in the same manner to afford **7** (*cis*) (2.0 mg). ^{1}H-NMR: see Table I. On

irradiation at δ 6.46 (H-4′), a 9% NOE enhancement of a signal at δ 5.27 (H-3′) was observed. A 10% increase of the signal at δ 6.46 (H-4′) was seen on irradiation at δ 5.27 (H-3′).

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3) This coumarin has been isolated from leaves of *Murraya exotica* L.,[4] and also obtained from roots and root barks of *Citrus tachibana* TANAKA (tachibana), *C. rugulosa* HORT. *ex.* TANAKA (attani), and several hybrid seedlings resulting from crosses of hyuga-natsu × hirakishu and hassaku × hirato-buntan. Isolation and structural elucidation will be reported elsewhere.
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