Five New Pyranocoumarins from Some *Citrus* Plants[1)]

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Five new pyranocoumarins, named *cis*-5-methoxydecursidinol (1), *trans*-5-methoxydecursidinol (2), *cis*-hassanin (4), *trans*-hassanin (5), and hassanidin (7), were isolated from the roots of some *Citrus* plants and their structures were elucidated by spectroscopic methods and chemical derivation from known coumarins.

Keywords coumarin; 5-methoxydecursidinol; hassanin; hassanidin; *Citrus*; Rutaceae

As a continuation of our work on the constituents of *Citrus* plants,[2)] we investigated the components of the roots of *Citrus hassaku* TANAKA, *C. funadoko* HORT. *ex* Y. TANAKA, Swingle Citrumelo[3)] (*Poncirus trifoliata* × *C. paradisi*) and several hybrid seedlings resulting from a cross of Pummelo [*C. grandis* (L.) OSBECK] ev. May Pummelo[4)] × Marsh grapefruit (*C. paradisi* MACF.) and isolated five new pyranocoumarins together with known coumarins and acridone alkaloids. In this paper, we wish to report the structure elucidation of these five new coumarins.

Results and Discussion

The acetone extracts of the roots of each *Citrus* plant were subjected to column, centrifugal preparative thin-layer and preparative thin-layer chromatographies on silica gel to isolate new coumarins along with many known coumarins and acridone alkaloids.[5)]

cis-5-Methoxydecursidinol (1) was isolated from *C. funadoko* as a colorless oil, $[\alpha]_D$ $-30.0°$ ($CHCl_3$), and showed the molecular formula $C_{15}H_{16}O_6$ (M^+, *m/z* 292.0948, Calcd 292.0947) in the high-resolution mass spectrum (HR-MS). The infrared (IR) (1720, 1620 cm^{-1}) and ultraviolet (UV) (250, 260, and 326 nm) spectra showed typical absorptions of coumarins.[6)] The proton nuclear magnetic resonance (^{1}H-NMR) spectrum indicated the presence of three aromatic protons [δ 7.82, 6.24 (each 1H, d, J=9.8 Hz) and 6.62 (1H, s)], one methoxy group (δ 4.00) and a *gem*-dimethyl group [δ 1.50, 1.35 (each 3H, s)]. On addition of deuterium oxide (D_2O), the remaining signals at δ 5.07 (1H, d, J=4.9 Hz), 3.85 (2H, br s), 3.04 (1H, br s) changed to two doublets at δ 5.07 and 3.85 (each 1H, J=4.9 Hz). These data suggested the presence of a 2,2-dimethyl-3,4-dihydroxychromane ring. The linear pyranocoumarin structure was assigned on the basis of a nuclear Overhauser effect (NOE) experiment. Irradiation of the methoxy signal at δ 4.00 induced 5% and 4% increments of the signals at δ 7.82 (H-4) and 5.07 (H-4′), respectively. From the above results, the structure of this compound was supposed to be **1**, except for the stereochemistry of C-3′ and C-4′.

trans-5-Methoxydecursidinol (2) was isolated as colorless prisms from *C. funadoko*, mp 170—172 °C, $[\alpha]_D$ $-2.2°$ (MeOH); from *C. hassaku*, mp 162—165 °C, $[\alpha]_D$ $-49.9°$ ($CHCl_3$); and from several hybrid seedlings resulting from a cross of Pummelo ev. May Pummelo × Marsh grapefruit, mp 198—201 °C, $[\alpha]_D$ $-4.7°$ ($CHCl_3$). The molecular formula $C_{15}H_{16}O_6$ was given by HR-MS (M^+, *m/z* 292.0946, Calcd 292.0947). The UV and IR spectra were diagnostic for coumarins.[6)] The ^{1}H-NMR spectrum showed a signal pattern similar to that of **1** except for small differences of chemical shifts. The signals at δ 4.87 (1H, dd, J=4.6, 4.9 Hz), 4.54 (1H, d, J=4.6 Hz), 4.53 (1H, d, J=5.1 Hz), 3.75 (1H, dd, J=5.1, 4.9 Hz) changed to two doublets at δ 4.87 and 3.75 (each 1H, J=4.9 Hz) on addition of D_2O. Comparison of these data with those of **1** suggested isomeric relationships of C-3′ and C-4′ of these two coumarins. From the above data, the structure of this coumarin was assumed to be **2** except for the stereochemistry of C-3′ and C-4′. The stereochemistry of C-3′ and C-4′ of dihydropyranocoumarins have generally been determined by ^{1}H-NMR spectroscopy, based on different chemical shifts[7)] and coupling constants[8)] of H-3′ and H-4′, and the difference of the chemical shifts of the *gem*-dimethyl signals.[8)] In the ^{1}H-NMR spectra of **1** and **2**, although the differences of J-values of H-3′ and H-4′, and chemical shifts of the dimethyl group were not reliable to determine the *cis* and *trans* relationships, the appearance of the H-4′ signal of **2** (δ 4.87) at higher field than that of **1** (δ 5.67) suggested[7)] the *trans* and *cis* isomeric relationships of **2** and **1**, respectively. In an NOE experiment on **1**, irradiation of the signal at δ 3.85 (H-3′) gave a 9% increment of the signal at δ 5.07 (H-4′). When the signal at δ 5.07 was irradiated, an 8% increment was observed at the signal of δ 3.85. On the other hand, **2** showed only 3% increment between the signals at δ 3.75 (H-3′) and 4.87 (H-4′). These results indicated the *cis* and *trans* relationships of H-3′ and H-4′ in **1** and **2**, respectively. To confirm this result, we attempted to synthesize **1** and **2** from xanthoxyletin (**3**). Xanthoxyletin (**3**)[9)] was treated with *meta*-chloroperbenzoic acid (MCPBA) followed by hydrolysis with oxalic acid solution to afford two compounds (A and B). On the other hand, oxidation of **3** with osmium tetroxide gave only compound B, which was assumed to have *cis* configuration. Compound B was identical with a natural sample of **1**, while compound A, assumed to have *trans* configuration, was identical with natural **2** on the basis of comparisons of TLC behavior and IR and NMR

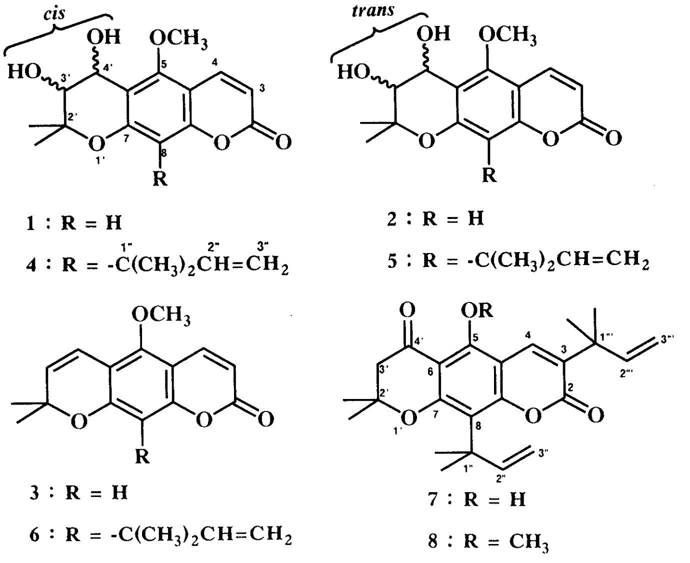

Chart 1

spectra. From the above-mentioned results, *cis*- and *trans*-5-methoxydecursidinols could be represented by the structures **1** and **2**, respectively, except for the absolute stereochemistry.

cis-Hassanin (**4**) was obtained as a colorless oil from *C. hassaku*, $[\alpha]_D$ +45.4° ($CHCl_3$) and Swingle Citrumelo, $[\alpha]_D$ ±0° ($CHCl_3$). The HR-MS showed a molecular ion at *m/z* 360.1572 indicating the molecular formula $C_{20}H_{24}O_6$. The UV and IR spectra were indicative of the presence of a coumarin skeleton. The ^{1}H-NMR spectrum showed signals assignable to H-4 and H-3 [δ 7.83 (1H, d, $J=9.7$ Hz), 6.22 (1H, d, $J=9.7$ Hz)], a 1,1-dimethylallyl group [δ 6.25 (1H, dd, $J=17.6$, 10.5 Hz), 4.90 (1H, dd, $J=17.6$, 1.0 Hz), 4.86 (1H, dd, $J=10.5$, 1.0 Hz), 1.66 (6H, s)], and a methoxy group [δ 3.96 (3H, s)]. Two doublets at δ 5.06 and 3.78 (each 1H, d, $J=4.9$ Hz) and two deuterium-exchangeable broad singlets at δ 3.8 and 3.0 indicated the presence of *vic*-hydroxyl groups on the dihydrochromane ring. In the NOE experiments, irradiation of the signal of the methoxy group (δ 3.96) induced 4% and 5% increments on the signals at δ 7.83 (H-4) and 5.06 (H-4'). The results showed the linear pyranocoumarin structure of **4**. The relative stereochemistry of C-3' and C-4' was assumed to be *cis* on the basis of the relatively small coupling constants of H-3' and H-4' and small differences of chemical shifts of the *gem*-dimethyl groups (0.09 ppm).[8] Further information was obtained by NOE experiments. When the signal at δ 3.78 (H-3') was irradiated, a 7% increment was observed on the signal at δ 5.06 (H-4'). On the other hand, irradiation of the signal at δ 5.06 (H-4') caused 7% and 4% increments of the signals of H-3' (δ 3.78) and the methoxy group (δ 3.96), respectively. From the above data, the structure of *cis*-hassanin was concluded to be **4**, except for the absolute stereochemistry.

trans-Hassanin (**5**) was isolated as a colorless oil from *C. hassaku*, $[\alpha]_D$ +18.2° ($CHCl_3$) and Swingle Citrumelo, $[\alpha]_D$ −8.5° ($CHCl_3$). The molecular formula $C_{20}H_{24}O_6$ was given by HR-MS (M^+, *m/z* 360. 1569, Calcd 360.1573). The ^{1}H-NMR spectrum resembled that of *cis*-hassanin (**4**), except for the differences of the signals at δ 4.83 (1H, d, $J=7.1$ Hz), 3.74 (1H, d, $J=7.1$ Hz), 1.51, 1.26 (each 3H, s),

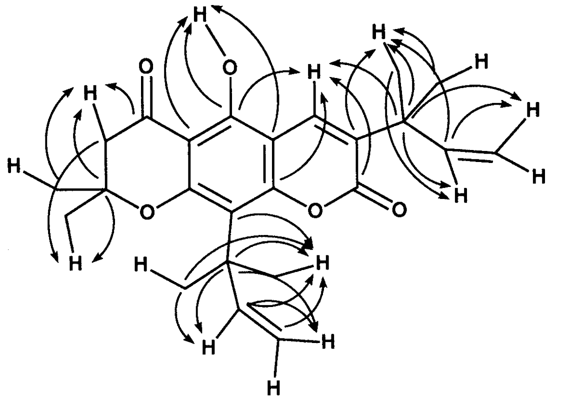

Fig. 1. C–H Correlations in the HMBC Spectrum of Hassanidin (**7**)

which were assignable to protons on carbons bearing hydroxyl groups and *gem*-dimethyl groups. In the NOE experiments, irradiation of the methoxy signal at δ 3.95 caused 4% and 5% increments of the signals at δ 7.83 (H-4) and δ 4.83 (H-4'). The result indicated the presence of a linear pyranocoumarin skeleton. The relatively large coupling constants ($J=7.1$ Hz) and large difference of chemical shifts of the dimethyl groups (0.25 ppm) indicated the *trans* relationship of the two hydroxyl groups.[8] Thus, the structure of *trans*-hassanin was assigned as **5**, except for the absolute stereochemistry. To confirm the relative stereochemistry of *cis*- and *trans*-hassanins, we attempted to synthesize these compounds from dentatin (**6**).[10] Oxidation of dentatin (**6**) by MCPBA afforded two compounds (C and D). In the NOE experiments, irradiation of the signal of H-4' of compound C caused increments on the signals of H-3' and the methoxy group (each 12% and 2%), indicating the *cis* relationship of the diol group. On the other hand, in the NOE experiments on compound D, irradiation of the signal of H-4' induced an increment only on the signal of the methoxy group (5%) and not in that of H-3', suggesting the *trans* relationship of the two hydroxyl groups. Comparisons of the natural compounds with the synthetic compounds confirmed the structures of *cis*- and *trans*-hassanins to be **4** and **5**, respectively, leaving the absolute stereochemistry undetermined.

Hassanidin (**7**) was isolated from *C. hassaku* as colorless cubes, mp 109–110 °C, and the molecular formula $C_{24}H_{28}O_5$ was obtained from HR-MS (M^+, *m/z* 396.1934, Calcd 396.1937). The UV [λ_{max} 226 (sh), 290, 332 nm] and IR (3400, 1720, 1630 cm^{-1}) spectra showed the presence of a 5,7-dioxygenated coumarin skeleton. The ^{1}H-NMR spectrum showed signals due to one chelated hydroxyl group (δ 13.00), H-4 of the coumarin nucleus (δ 7.89, s), and two 1,1-dimethylallyl groups [δ 6.23 (1H, dd, $J=10.7$, 17.6 Hz), 6.16 (1H, dd, $J=10.7$, 17.6 Hz), 5.10 (1H, dd, $J=17.6$, 1.0 Hz), 5.09 (1H, dd, $J=10.7$, 1.0 Hz), 4.93 (1H, dd, $J=17.6$, 1.0 Hz), 4.88 (1H, dd, $J=10.7$, 1.0 Hz), 1.48, 1.47 (each 6H, s)]. The remaining signal at δ 2.74 (2H, s) was assumed to be due to methylene protons adjacent to a carbonyl group. To confirm the linear structure, hassanidin was transformed to the methyl ether (**8**) by treatment with diazomethane. In the NOE experiments on **8**, irradiation of the methoxy signal at δ 3.90 caused a 16% increment of the H-4 signal at δ 7.85 (s). This result indicated the location of the O-methyl group to be at C-5. Therefore, the hydrogen-bonded carbonyl group was revealed to be located at the 4′ position, confirming the linear pyranocoumarin skeleton. The structure of hassanidin was further supported by ^1H–^{13}C long-range couplings in the heteronuclear multiple bond connectivity (HMBC) experiments shown in Fig. 1. From the above results, the structure of hassanidin was represented as **7**.

Many kinds of dihydropyranocoumarins have been reported,[11] but most of the compounds were of ester type. The four new coumarins possessing a free vicinal hydroxyl group presented in this paper are rare examples from natural sources. Further examination of the constituents of these plants is in progress.

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-360 polarimeter. IR spectra were taken with a Shimadzu IR-435 spectrometer and UV spectra were measured on a Shimadzu UV-160A spectrometer. NMR spectra were recorded on a JEOL 200FX or JEOL GSX 500 spectrometer and chemical shifts are given on the δ (ppm) scale with tetramethylsilane (TMS) as an internal standard. For column chromatography, Wakogel 60 was used. Preparative thin-layer chromatography (PTLC) was carried out on precoated Merck Kieselgel 60 plates.

Extraction and Isolation The roots of *Citrus hassaku* TANAKA were collected at Innoshima, Hiroshima. The roots of *C. funadoko* HORT. *ex* TANAKA, Swingle Citrumelo, and several hybrid seedlings resulting from a cross of Pummelo [*C. grandis* (L.) OSBECK] cv. May Pummelo × Marsh grapefruit (*C. paradisi* MACF.) were cultivated and collected at the orchard of the Okitsu Branch, Fruit Tree Research Station, Ministry of Agriculture, Forestry, and Fisheries, Okitsu, Shizuoka. The dried roots were extracted with acetone. The acetone extract was chromatographed on silica gel using solvent systems: hexane, benzene, ethyl acetate, CH_2Cl_2 and methanol successively. Each eluate was further subjected to PTLC using solvent systems of isopropyl ether, acetone–hexane, chloroform–acetone, benzene–hexane and benzene–ethyl acetate. Details of the procedures of separation and characterization of known components will be reported elsewhere.

***cis*-5-Methoxydecursidinol (1)** Colorless oil. Content: 0.0000158% in the roots of *C. funadoko*, $[\alpha]_D$ $-30.0°$ ($c=0.003$, $CHCl_3$). HR-MS Calcd for $C_{15}H_{16}O_6$: 292.0947. Found: 292.0948. EI-MS *m/z*: 292 (M^+), 274, 246, 222, 221 (base peak), 205. UV λ_{max}^{MeOH} nm: 250, 260, 326. IR ($CHCl_3$): 3500, 1720, 1620 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 7.82 (1H, d, $J=9.8$ Hz, H-4), 6.62 (1H, s, H-8), 6.24 (1H, d, $J=9.8$ Hz, H-3), 5.07 (1H, d, $J=4.9$ Hz, H-4′), 4.00 (3H, s), 3.85 (2H, br s, H-3′, OH), 3.04 (1H, br s, OH), 1.50, 1.35 (each 3H, s).

***trans*-5-Methoxydecursidinol (2)** Colorless prisms. Content: 0.000114% in the roots of *C. funadoko*, mp 170—172 °C, $[\alpha]_D$ $-2.2°$ ($c=0.04$, MeOH): 0.0000166% in the roots of *C. hassaku*, mp 162—165 °C, $[\alpha]_D$ $-49.9°$ ($c=0.66$, $CHCl_3$); and 0.0000224% in the roots of hybrid seedlings of Pummelo cv. May Pummelo × Marsh grapefruit, mp 198—201 °C, $[\alpha]_D$ $-4.7°$ ($c=0.633$, $CHCl_3$). HR-MS Calcd for $C_{15}H_{16}O_6$: 292.0947. Found: 292.0946. EI-MS *m/z*: 292 (M^+), 274, 246, 243, 222, 221 (base peak), 220, 219, 206, 205, 203, 202. UV λ_{max}^{EtOH} nm (log ε): 223 (sh, 3.95), 247 (4.32), 257 (4.34), 270 (4.42). IR ($CHCl_3$): 3500, 1720, 1620, 1600 cm^{-1}. ^1H-NMR (acetone-d_6) δ: 8.00 (1H, d, $J=9.8$ Hz, H-4), 6.48 (1H, s, H-8), 6.18 (1H, d, $J=9.8$ Hz, H-3), 4.87 (1H, dd, $J=4.6$, 4.9 Hz, H-4′), 4.54 (1H, d, $J=4.6$ Hz, OH), 4.53 (1H, d, $J=5.1$ Hz, OH), 4.03 (3H, s), 3.75 (1H, dd, $J=5.1$, 4.9 Hz, H-3′), 1.47, 1.35 (each 3H, s).

Synthesis of *cis*- and *trans*-5-Methoxydecursidinols MCPBA (150 mg) was added to a solution of xanthoxyletin (**3**)[12] (75.6 mg) in $CHCl_3$ (10 ml) and allowed to stand in the dark for 48 h. After being diluted with $CHCl_3$, the reaction mixture was washed with 10% $NaHCO_3$ solution, dried over $MgSO_4$ and evaporated to give an oily residue. A solution of oxalic acid (720 mg) in H_2O (50 ml) was added to the residue and the mixture was refluxed for 8 h. After cooling, the product was extracted with CH_2Cl_2 and the organic layer was evaporated to afford an oily residue. The product was subjected to PTLC [solvent; $CHCl_3$–acetone (9 : 1)]. *cis*-5-Methoxydecursidinol (**1**) (13.3 mg) was obtained from the less polar part and *trans*-5-methoxydecursidinol (**2**) (21.7 mg) from the polar part. Xanthoxyletin (**3**) (30 mg) was dissolved in absolute benzene (5 ml) and treated with osmium tetroxide (50 mg) in pyridine (5 ml). After 10 d, a solution of sodium hydrosulfide (2 g) in H_2O (20 ml) was added and the mixture was stirred for 3 h, diluted with H_2O and extracted with $CHCl_3$. The extract was washed with H_2O, dried over $MgSO_4$ and evaporated. The residue was subjected to PTLC [solvent; acetone–benzene (1 : 4)] to afford *cis*-5-methoxydecursidinol (**1**) (4.1 mg).

***cis*-Hassanin (4)** Colorless oil. Content: 0.0000126% in the roots of *C. hassaku*, $[\alpha]_D$ $+45.4°$ ($c=0.0009$, $CHCl_3$); 0.000012% in the roots of Swingle Citrumelo, $[\alpha]_D$ $\pm 0°$ ($c=0.133$, $CHCl_3$). HR-MS Calcd for $C_{20}H_{24}O_6$: 360.1573. Found: 360.1572. EI-MS *m/z*: 360 (M^+), 288, 274, 273 (base peak), 247, 245, 233, 231. UV λ_{max}^{EtOH} nm: 230 (sh), 256, 265, 331. IR ($CHCl_3$): 3400 (br), 1720, 1620, 1595 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 7.83 (1H, d, $J=9.7$ Hz, H-4), 6.25 (1H, dd, $J=17.6$, 10.5 Hz, H-2″), 6.22 (1H, d, $J=9.7$ Hz, H-2), 5.06 (1H, d, $J=4.9$ Hz, H-4′), 4.90 (1H, dd, $J=17.6$, 1.0 Hz, H-3″), 4.86 (1H, dd, $J=10.5$, 1.0 Hz, H-3″), 3.96 (3H, s), 3.8 (1H, br s, OH), 3.78 (1H, d, $J=4.9$ Hz, H-3′), 3.0 (1H, br s, OH), 1.66 (6H, s), 1.45, 1.36 (each 3H, s).

***trans*-Hassanin (5)** Colorless oil. Content: 0.0000116% in the roots of *C. hassaku*, $[\alpha]_D$ $+18.2°$ ($c=0.002$, $CHCl_3$); 0.000023% in the roots of Swingle Citrumelo, $[\alpha]_D$ $-8.5°$ ($c=0.092$, $CHCl_3$). HR-MS Calcd for $C_{20}H_{24}O_6$: 360.1573. Found: 360.1569. EI-MS *m/z*: 360 (M^+), 289, 288, 274, 273 (base peak), 259, 245, 233. UV λ_{max}^{EtOH} nm (log ε): 231 (sh, 4.06), 256 (3.73), 265 (3.76), 332 (4.08). IR ($CHCl_3$): 3450 (br), 1720, 1620, 1600 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 7.83 (1H, d, $J=9.5$ Hz, H-4), 6.24 (1H, dd, $J=17.3$, 10.7 Hz, H-2″), 6.23 (1H, d, $J=9.5$ Hz, H-3), 4.90 (1H, dd, $J=1.2$, 17.3 Hz, H-3″), 4.86 (1H, dd, $J=1.2$, 10.7 Hz, H-3″), 4.83 (1H, d, $J=7.1$ Hz, H-4′), 3.95 (3H, s), 3.84 (1H, br s, OH), 3.74 (1H, d, $J=7.1$ Hz, H-3′), 2.77 (1H, br s, OH), 1.67, 1.63, 1.51, 1.26 (each 3H, s).

Synthesis of *cis*- and *trans*-Hassanins Dentatin (**6**)[12] (10 mg) was dissolved in dry benzene (4 ml) and MCPBA (12 mg) was added. The mixture was allowed to stand at room temperature. After 1 h, the organic layer was separated by PTLC [solvent; hexane–acetone (4 : 1) and (2 : 1)] to give **4** (3 mg) and **5** (3 mg). The synthetic samples were shown to be identical with the corresponding natural samples by IR, NMR and TLC comparisons.

Hassanidin (7) Colorless cubes, mp 109—110 °C. Content: 0.0000029% in the roots of *C. hassaku*. HR-MS Calcd for $C_{24}H_{28}O_5$: 396.1937. Found: 396.1934. EI-MS *m/z*: 396 (M^+, base peak), 382, 381, 326, 325, 287, 257. UV λ_{max}^{EtOH} nm: 226 (sh), 290, 332. IR ($CHCl_3$): 3400, 1720, 1630 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 13.00 (1H, s, OH), 7.89 (1H, s, H-4), 6.23 (1H, dd, $J=10.7$, 17.6 Hz, H-2″), 6.16 (1H, dd, $J=10.7$, 17.6 Hz, H-2‴), 5.10 (1H, dd, $J=17.6$, 1.0 Hz, H-3‴), 5.09 (1H, dd, $J=10.7$, 1.0 Hz, H-3‴), 4.93 (1H, dd, $J=17.6$, 1.0 Hz, H-3″), 4.88 (1H, dd, $J=10.7$, 1.0 Hz, H-3″), 2.74 (2H, s, H-3′), 1.63 [6H, s, 1″-$(CH_3)_2$], 1.48 [6H, s, 2′-$(CH_3)_2$], 1.47 [6H, s, 1‴-$(CH_3)_2$]. ^{13}C-NMR ($CDCl_3$) δ: 198.27 (C-4′), 159.69 (C-2), 159.34 (C-7), 158.93 (C-8a), 158.82 (C-5), 149.63 (C-2″), 145.31 (C-2‴), 132.47 (C-4), 129.79 (C-3), 113.87 (C-8), 112.24 (C-3″), 108.31 (C-3‴), 104.00 (C-6), 103.52 (C-4a), 79.77 (C-2′), 47.85 (C-3′), 40.94 (C-1″), 40.30 (C-1‴), 30.88 [1″-$(CH_3)_2$], 26.53 [2′-$(CH_3)_2$], 26.08 [1‴-$(CH_3)_2$].

***O*-Methylhassanidin (8)** Hassanidin (**7**) (6.2 mg) was dissolved in MeOH (10 ml) and methylated with ethereal diazomethane in the usual way. After purification by PTLC using isopropylether, 3.3 mg of *O*-methylhassanidin (**8**) was obtained. Colorless oil. EI-MS *m/z*: 410 (M^+), 395, 355, 339, 311, 299, 217. UV λ_{max}^{EtOH} nm: 234 (sh), 271, 322. IR ($CHCl_3$): 1720, 1680, 1620, 1570 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 7.85 (1H, s, H-4), 6.24 (1H, dd, $J=17.5$, 10.8 Hz, H-2″), 6.16 (1H, dd, $J=17.8$ Hz, 10.4 Hz, H-2‴), 5.10 (1H, dd, $J=1.0$, 17.8 Hz, H-3‴), 5.10 (1H, dd, $J=1.0$, 10.8 Hz, H-3‴), 4.93 (1H, dd, $J=1.0$, 17.5 Hz, H-3″), 4.88 (1H, dd, $J=1.0$, 10.4 Hz, H-3″), 3.90 (3H, s), 2.68 (2H, s, H-3′), 1.66, 1.47, 1.46 (each 6H, s).

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3) A common name is "Taiwan Citrus." This plant is considered to be a hybrid resulting from a cross of *Poncirus trifoliata* (Karatachi) × *C. paradisi* (grapefruit). The scientific name has not been identified.
4) May Pummelo is a hybrid variety resulting from a cross of Hassaku

(*C. hassaku* HORT. *ex* TANAKA) × Hirado Pummelo (*C. grandis* (L.) OSBECK).

5) Isolation and characterization of known compounds will be reported elsewhere.

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