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A NEW CHALCONE GLUCOSIDE FROM *GNAPHALIUM MULTICEPS*

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Key Word Index—*Gnaphalium multiceps* Compositae, 4,2 4-trihydroxy-6-methoxychalcone 4-glucoside naringenin 5-methyl ether

One of the flavonoid components of *Gnaphalium multiceps*, Wall, Compositae, has been reported to be luteolin-4′-glucoside [1] This paper reports an isolation of another flavonoid (**1**) [2] from the flowers, and its structure elucidation as 4,2′,4′-trihydroxy-6′-methoxychalcone 4′-glucoside

RESULTS

The new compound (**1**) is a noncrystalline yellow solid, $C_{22}H_{24}O_{10}$, m p 169 5–172 5°, which is suggested to be a chalcone glucoside from its UV spectrum [λ_{max}^{MeOH} 365 nm (ϵ 24 600)] and its behavior toward acid hydrolysis which gave glucose and a flavanone, (**2**), $C_{16}H_{14}O_5$, m p 258–261°

The structure of **2** was determined as naringenin 5-methyl ether by the following observations The coloration with Mg and HCl (purple) and the UV spectrum [λ_{max}^{MeOH} 283 (ϵ 14 200) and 320 nm (inf)] is consistent with a flavanone skeleton The NMR spectrum shows a presence of a methoxy (δ 3 83) and two hydroxy groups (δ 9 74 and 10 73 D_2O exchangeable), which are located at C-5,7 and 4′ positions as proved by formation of naringenin trimethyl ether [3] on methylation of **2**

As two naringenin monomethyl ethers are already known (sakuranetin and isosakuranetin) compound (**2**) can only be the 5-methyl ether The abnormally low carbonyl absorption at 1620 cm^{-1} (KBr) of **2** which shifts to 1670 cm^{-1} when measured in DMSO is accounted for by intermolecular association with the C-7 hydroxy group [4]

Mahesh *et al* [5] reported naringenin 5-methyl ether diacetate to have m p 138–139° which is much lower than that of the diacetate of **2**, m p 172 5–174 An attempt was made, therefore, to prepare the latter from naringenin Methylation of naringenin 7,4′-diacetate [5] with dimethyl sulfate and K_2CO_3 in boiling acetone followed by PLC of the product gave the methyl ether, m p 171 5–173 identical with **2** diacetate, together with 4,4′-diacetoxy-2′,6′-dimethoxychalcone, m p 145–146

[1] ARITOMI M SHIMOJO M and MAZAKI T (1964) *Yakugaku Zasshi* **84**, 895
[2] HOSOKAWA S and SASAKI S (1968) *Res Rep Ichinoseki Tech Coll* **2**, 80
[3] KAUFMANN F and LAM J (1967) *Acta Chem Scand* **21**, 311
[4] ICHIKAWA N and TOKOROYAMA T (1966) *Jikkenkagaku Koza* (KOTAKI M ed) Suppl Vol V pp 652 Maruzen Tokyo
[5] MAHESH V B NEELAKANTAN, S and SESHADRI, T R (1956) *J Sci Ind Res* **15B**, 287

The position of the sugar link of **1** was determined as follows The fact that one of its hydroxy proton signals in NMR appears at δ 13 52 suggests the presence of hydrogen bonding to the carbonyl group allows to place one of its free hydroxy groups at C-2′ position Methylation of **1** followed by acid hydrolysis of the product afforded 4′-hydroxy-4,2′,6′-trimethoxychalcone, m p 208–209 5°, the hydroxy group of **1** was thus linked to glucose on ring A from its MS analysis[6] (*m/e* 181, $C_6H_2(OH)(OMe)_2C{\equiv}O^+$ and 133, $C_6H_4(OMe)CH{=}C^+H$) Therefore, the glucoside linkage in **1** is at C-4′ and the structure of **1** is 4,2′,4′-trihydroxy-6′-methoxychalcone 4′-glucoside

EXPERIMENTAL

M ps are uncorrected IR were recorded in KBr pellets unless otherwise mentioned, UV in MeOH, NMR in DMSO-d_6 unless otherwise mentioned with TMS as internal standard, and *s, d, dd, m* and *br* denote singlet, doublet, doublet of doublets, multiplet and broad, respectively

Gnaphalin (**1**) Fresh flowers (10 6 kg) of the plant was extracted with MeOH, the soln was evaporated to 0 3 of its vol, which on continuous extraction with light petrol in order to remove sticky material afforded a yellow solid (9 1 g) The product, which showed 2 spots on TLC (Silica gel G, CH_2Cl_2–MeOH, 86 5 13 5) was chromatographed on Silica gel and the column was eluted (CH_2Cl_2–Me_2CO–MeOH, 63 30 7) to give a yellow material which was precipitated from EtOH to give a noncrystalline yellow solid (1 4 g), m p 169 5–172 5°, λ_{max} 365 nm (ϵ 24 600) ν_{max} 3380, 1625 cm^{-1}, δ 4 02 *s* (3H), 3 6 *m*, 5 3 *m*, 6 43 *br s* (2H), 7 06 *d* (*J* 9Hz, 2H), 7 80 *d* (*J* 9Hz, 2H), 7 81 *s* (2H), 10 35 *s* (1H, D_2O exchangeable) and 13 52 *s* (1H, D_2O exchangeable) (Found C, 58 63, H, 5 38 Calc for $C_{22}H_{24}O_{10}$ C, 58 92, H, 5 40%)

Hydrolysis of **1** A solution of **1** (600 mg), H_2SO_4 (2 6 g) and H_2O (30 ml) in EtOH (80 ml) was heated for 4 hr under reflux The soln was evaporated to 0 25 of its vol, cooled and crystals appeared were collected, recrystallized from EtOH to give colorless needles of **2** (180 mg), m p 258–261°, λ_{max} 283 (ϵ 14 200) and 320 nm (inf), ν_{max} 1620, ν_{max}^{DMSO} 1670 cm^{-1}, δ 2 3–3 4 (2H), 3 83 *s* (3H), 5 45 *dd* (*J* 12, 4Hz), 6 10 *d* (*J* 3Hz, 1H), 6 20 *d* (*J* 3Hz, 1H), 6 91 *d* (*J* 9Hz, 2H), 7 41 *d* (*J* 9Hz, 2H), 9 74 *s* (1H, D_2O exchangeable) and 10 73 *s* (1H, D_2O exchangeable) (Found C, 66 80, H, 4 92 Calc for $C_{16}H_{14}O_5$ C, 67 12, H, 4 93%) The mother liquor from which **2** was collected was treated with $BaCO_3$, ppt was removed and the soln was evaporated to dryness The residual oil on purification by PLC (Silica gel G, Me_2CO–H_2O–MeOH–$CHCl_3$, 15 1 2 2) gave glucose (120 mg) identified as its pentaacetate m p 128–130° (m p m m p and IR)

Methylation of **2** A solution of **2** (200 mg), Me_2SO_4 (1 2 ml) and K_2CO_3 (2 g) in Me_2CO (25 ml) was heated under reflux for 8 hr The usual work-up gave yellow oil (197 mg), which on PLC separation (Silica gel G, CH_2Cl_2–Me_2CO, 19 1) afforded two fractions One of them by recrystallization (EtOH–H_2O) afforded colorless prisms (61 mg), m p 123–123 5°, which was identical with naringenin trimethyl ether as established by direct comparison with an authentic specimen (m p, m m p and IR) The other fraction was recrystallized (EtOH) to give yellow prisms (66 mg), m p 112° Its MS, UV and NMR spectra are consistent with a structure of 2′-hydroxy-4,4′,6′-trimethoxychalcone [7]

2 *Diacetate* The flavanone (**2**) (300 mg) was acetylated with Ac_2O (3 ml) and C_5H_5N (5 ml), and the product was recrystallized (EtOH) to give colorless needles (230 mg), **2** diacetate, m p 172 5–174°, λ_{max} 273 (ϵ 9800) and 320 nm (inf), ν_{max} 1743 and 1682 cm^{-1}, δ^{CDCl_3} 2 25 *s* (6H), 2 70 *dd* (*J* 16, 5Hz, 1H), 3 02 *dd* (*J* 16, 11Hz, 1H) 5 42 *dd* (*J* 11, 5Hz, 1H), 6 31 *d* (*J* 2Hz, 1H), 6 44 *d* (*J* 2Hz, 1H), 7 10 *d* (*J* 8Hz, 1H), 7 44 *d* (*J* 8Hz, 1H) (Found C, 64 66, H, 5 28 Calc For $C_{20}H_{18}O_7$ C, 64 86, H, 4 90%)

Methylation of naringenin 4′,7-diacetate [5] Naringenin 4′,7-diacetate (1 1 g) was methylated as described above and PLC separation (Silica gel G, CH_2Cl_2–Me_2CO, 19 1) of the product followed by recrystallization (EtOH) afforded two products colorless prisms (62 mg) m p 171 5–173° which was identical with **2** diacetate (m p, m m p TLC and IR) and yellow needles (122 mg) m p 145–146 , which was characterized as 4,4′-diacetoxy-2′,6′-dimethoxychalcone from the following data λ_{max}222 (inf) and 300 nm (ϵ 13 700), ν_{max}1676 cm^{-1}, *m/e* 384 (M^+), δ^{CDCl_3} 2 31 *s* (3H), 2 33 *s* (3H), 3 80 *s* (3H), 6 47 *s* (2H) and 6 8–7 8 *m* (6H) (Found C 65 33, H, 5 21 Calc for $C_{21}H_{20}O_7$ C, 65 61, H, 5 24%)

Formation of 4′-hydroxy-4 2′,6′-trimethoxychalcone from **1** **1** (400 mg) was methylated as described above and PLC separation (Silica gel G, CH_2Cl_2–MeOH, 9 1) of the product afforded orange crystalline material (144 mg) The product was then hydrolyzed with 5% H_2SO_4 (5 8 ml) and EtOH (1 6 ml) by heating under reflux for 4 hr, crystals appeared on cooling were collected and recrystallized (EtOH) to give yellow prisms (11 mg), 4′-hydroxy-4,2′,6′-trimethoxychalcone, m p 208–209 5°, λ_{max} 228 (inf) and 325 nm (ϵ 19 900), ν_{max} 1640 cm^{-1}, *m/e* 314 (M^+), 181 and 133, δ 3 65 *s* (6H), 3 77 *s* (3H), 6 13 *s* (2H), 6 78 *d* (*J* 16Hz, 1H), 7 16 *d* (*J* 16Hz, 1H), 6 93 *d* (*J* 9Hz, 2H) and 7 60 *d* (*J* 9Hz, 2H) (Found C, 68 33, H, 5 88 Calc for $C_{18}H_{18}O_5$ C, 68 78, C, 5 77%)

[6] SASAKI, S, ITAGAKI, Y, KUROKAWA, T, WATANABE, E and AOYAMA, T (1965) *Shitsuryo Bunseki* **14**, 82

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FURANOEREMOPHILAN-14β,6α-OLIDE FROM *LIGULARIA* SPECIES

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Plant Ligularia fauriei (Fr) Koidz (Compositae) *Source* Rikuchu-Nakano, Iwate prefecture, Japan Voucher specimen is deposited in the Herbarium of National Science Museum, Tokyo (TNS 265532)

Plant L angusta (Nakai) Kitam (Compositae) *Source* Botanic Garden of the University of Tokyo, Tokyo, Japan Voucher specimen is kept in the Herbarium of National Science Museum, Tokyo (TNS 281712) *Previous work* On sister species *L hodgsonii* (furanoeremophilan-14β 6α-olide) [1]

Present work Dried roots (900 g) of *L fauriei* was extracted with hot C_6H_6 and the residue obtained after removal of the solvent was chromatographed on silica gel Elution with light petrol - Et_2O (20 1) gave a crystalline compound which was recrystallized from Et_2O to afford 5 40 g of furanoeremophilan-14β,6α-olide,[1] m p 145 146 (corr), $C_{15}H_{18}O_3$ (M^+ at *m/e* 246) $[\alpha]_D$ − 47 (dioxane) UV λ_{max}^{EtOH} 216 nm (ϵ 7200) IR (Nujol) 1770 1635 1562, 1086 cm^{-1} PMR ($CDCl_3$) δ 1 25 (3H, s tert-Me), δ 2 01 (3H *d J* 1 Hz, –CH=C–Me), δ ~2 3 (2H *m* –CH–CH_2–furan) δ 5 07 (1 H *br* s –O–CH–) δ 7 03 ppm (1H, *m* –O–CH=C–Me), identical (m p , m m p IR $[\alpha]_D$, UV PMR and MS) with the authentic sample [1]

The Et_2O extract of the dried roots (34 g) of *L angusta* was sublimed at 200 under reduced pressure (1 mmHg) and the material sublimed was chromatographed on silica gel Treatment as described above gave 47 mg of furanoeremophilan-14β 6α-olide [1]

[1] ISHIZAKI Y , TANAHASHI, Y , TAKAHASHI T and TORI, K (1969) *Chem Commun* 551