(1H, *d*, *J* = 7 Hz, H-3), 6.71 (1H, *d*, *J* = 2 Hz, H-8), 7.01 (1H, *d*, *J* = 2 Hz, H-6), 7.84 (1H, *d*, *J* = 7 Hz, H-2).

5-Methoxy-7-hydroxychromone (**2c**). 5,7-Dihydroxychromone (200 mg), $PhCH_2Cl$ (0.13 ml) and K_2CO_3 (300 mg) in dry Me_2CO (200 ml) were refluxed for 8 hr to give **2e**: colourless needles from EtOAc–petrol, mp 141–142°. ^1H NMR (δ, $CDCl_3$): 5.08 (2H, *s*, $-O\underline{CH_2}Ph$), 6.15 (1H, *d*, *J* = 7 Hz, H-3), 6.4 (2H, *s*, H-6, H-8), 7.35 (5H, *m*, $-OCH_2\underline{Ph}$), 7.67 (1H, *d*, *J* = 7 Hz, H-2), 12.64 (1H, *s*, OH-5). Methylation of **2e** gave **2f**: colourless needles from $CHCl_3$–petrol, mp 170–171°. ^1H NMR (δ, $CDCl_3$): 3.9 (3H, *s*, –OMe), 5.07 (2H, *s*, $-O\underline{CH_2}Ph$), 6.14 (1H, *d*, *J* = 7 Hz, H-3), 6.45 (2H, *m*, H-6, H-8), 7.35 (5H, *m*, $-OCH_2\underline{Ph}$), 7.54 (1H, *d*, *J* = 7 Hz, H-2). Debenzylation of **2f** (100 mg) with HCl (0.5 ml) in HOAc (3 ml) afforded 7-hydroxy-5-methoxychromone (**2c**) which crystallized from EtOAc–petrol as colourless needles (50 mg), mp 218–220°.

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QUERCETIN 3-(6″-CAFFEOYLGALACTOSIDE) FROM *HYDROCOTYLE SIBTHORPIOIDES*

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Key Word Index—*Hydrocotyle sibthorpioides*; Umbelliferae; quercetin 3-galactoside; isorhamnetin; quercetin 3-(6″-caffeoylgalactoside).

Abstract—In addition to quercetin, quercetin 3-galactoside and isorhamnetin, a new caffeoylgalactoside has been isolated from *Hydrocotyle sibthorpioides* and identified by chemical and spectral data as quercetin 3-*O*-β-D-(6″-caffeoylgalactoside).

Hydrocotyle sibthorpioides Lam. (Umbelliferae) is a common weed in Japan. No flavonoid constituents have been reported from this plant but from another species, *H. wilfordi* Maxim. quercetin 3-galactoside has been isolated [1].

Fractionation of the methanolic extract of whole plants of *H. sibthorpioides* with organic solvents followed by repeated CC on Sephadex LH-20 afforded quercetin, methyl caffeate, quercetin 3-galactoside, and its caffeoyl ester (**1**). The ^1H and ^{13}C NMR chemical shift values of **1** suggested that it is composed of quercetin 3-galactoside and caffeic acid. This was confirmed by a mild hydrolysis [2, 3] of **1** with sodium carbonate, which also afforded quercetin 3-galactoside and caffeic acid. The FD-mass spectrum of **1** showed an ion peak indicating the presence of the ester molecule. In the ^{13}C NMR spectrum of **1**

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Table 1. ^{13}C NMR δ values in DMSO-d_6 solutions

Assigned position	Compounds			
	Quercetin	Caffeic acid	Quercetin 3-galactoside	Quercetin 3-(6″-caffeoylgalactoside)
C-2	146.7		156.3	156.0
C-3	135.6		133.4	133.4
C-4	175.8		177.4	177.3
C-5	160.6		161.1	161.0
C-6	98.1		98.6	98.6
C-7	163.8		164.0	164.0
C-8	93.3		93.5	93.4
C-9	156.1		156.3	156.1
C-10	102.9		103.9	103.7
C-1′	122.0		121.9	121.7
C-2′	115.0		115.1	115.1
C-3′	145.0		144.7	145.0
C-4′	147.6		148.4	148.3
C-5′	115.5		115.9	115.9
C-6′	120.0		121.0	121.0
C-1″			101.9	101.6
C-2″			71.2	71.0
C-3″			73.2	72.9
C-4″			67.9	68.2
C-5″			75.7	72.9(+2.8)
C-6″			60.1	62.9(−2.8)
C-1		125.7		125.3
C-2		114.5*		113.3*
C-3		145.5		145.4
C-4		148.0		148.2
C-5		115.1*		114.6*
C-6		115.7*		115.6*
C-7		144.5		144.7
C-8		121.1*		121.1*
C-9		167.8		166.3

*These assignments are tentative in each vertical column. For the other assignments: see refs. [6, 7].

(Table 1) the down-field shift (60.1→62.9 ppm) of a triplet carbon (C-6″) along with the up-field shift (75.7→72.9 ppm) of a neighbouring carbon (C-5″) of galactose indicated [4, 5] that the caffeic acid is attached at C-6″ of the galactose. Therefore, the structure of the new ester was deduced as quercetin 3-*O*-(6″-caffeoylgalactoside). The closely related compound, quercetin 3-*O*-caffeoylglucoside has been reported from caraway [8]. However, **1** appears to be the first example of naturally occurring caffeoylgalactoside. Methyl caffeate, which was isolated with **1** may be a methanolysis product produced from **1** during extraction with methanol.

EXPERIMENTAL

Mps are uncorr. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q instrument. TLC analysis was performed on Kieselgel GF-254 plates using the solvent system; toluene–HCO_2Et–HCO_2H, 5:4:1 (TEFF), EtOAc–H_2O–HOAc, 10:10:1 (EAWA), *n*-BuOH–HOAc–H_2O, 3:1:1 (BAW), and pyridine–EtOAc–HOAc–H_2O, 36:36:7:4 (PEAW).

Extraction of plant materials. Fresh whole plants (10 kg) of *H. sibthorpioides* collected at Nagasaki in May were ground with MeOH and extracted completely. The MeOH extract (298 g) was dissolved in H_2O and partitioned successively with $CHCl_3$, Et_2O, EtOAc, and *n*-BuOH. The Et_2O-soluble fraction after purification through a Sephadex LH-20 column eluted with MeOH gave quercetin and colourless needles from MeOH (220 mg), mp 162–164°, which were identical with an authentic sample of caffeic acid methyl ester (mmp, IR and ^1H NMR).

The EtOAc-soluble part (4.16 g) was similarly purified through a column of Sephadex LH-20 to give quercetin 3-galactoside and **1**. Quercetin 3-galactoside: yellow needles from MeOH (330 mg), mp 230–232°, $[\alpha]_D^{30}$ −68.4° (*c*, 0.10, pyridine), UV λ_{max}^{EtOH} nm (ϵ): 260 (23800), 367 (19700), IR ν_{max}^{KBr} cm^{-1}: 3300, 1650, 1605, 1500, 1360, 1200, ^1H NMR δ (CD_3OD): 3.4–5.0 (sugar protons), 5.16 (1H, *d*, J = 7.2 Hz, anomeric), 6.19 (1H, *d*, J = 1.8 Hz, H-6), 6.39 (1H, *d*, J = 1.8 Hz, H-8), 6.84 (1H, *d*, J = 8.1 Hz, H-5′), 7.57 (1H, *dd*, J = 2.7 and 8.1 Hz, H-6′), 7.82 (1H, *d*, J = 2.7 Hz, H-2′). Found: C, 51.93; H, 4.62. $C_{21}H_{20}O_{12} \cdot H_2O$ requires C, 52.28; H, 4.60%. It was identical with an authentic sample of quercetin 3-galactoside [TLC (EAWA), mmp, and acid hydrolysis].

Quercetin 3-O-β-D-(6″-caffeoylgalactoside) (**1**). Yellow needles (200 mg), mp 198–200°, $[\alpha]_D^{30} - 19.5°$ (*c*, 0.12, pyridine), UV λ_{max}^{EtOH} nm (ε): 257 (27300), 340 (27900), IR ν_{max}^{KBr} cm^{-1}: 3360, 1650, 1600, 1500, 1353, 1280, 1195, 1160, 1070, FDMS *m/z*: 627 $[M+H]^+$ (100%), 465 (36), ^1H NMR δ (CD_3OD): 5.13 (1H, *d*, *J* = 7.2 Hz, anomeric), 6.00 (1H, *d*, *J* = 16.2 Hz, =CH–Ph), 6.13 (1H, *d*, *J* = 1.8 Hz, H-6), 6.30 (1H, *d*, *J* = 1.8 Hz, H-8), 6.80 (1H, *d*, *J* = 9 Hz, H-5′), 7.32 (1H, *d*, *J* = 16.2 Hz, CO–CH=), 7.55 (1H, *dd*, *J* = 1.8 and 9 Hz, H-6′), 7.80 (1H, *d*, *J* = 1.8 Hz, H-2′), 6.7–7.0 (3H, *m*, aromatic-H of caffeic acid). Found: C, 52.13; H, 4.42. $C_{30}H_{26}O_{15} \cdot 3.5\,H_2O$ requires C, 52.25; H, 4.82%. **1** (46 mg) was hydrolysed with saturated methanolic Na_2CO_3 (10 ml) at room temp. overnight. The reaction mixture was evaporated *in vacuo* and, after addition of H_2O (5 ml), extracted with EtOAc and then *n*-BuOH. The EtOAc extract gave colourless needles (4.3 mg), mp 220–225°, TLC R_f: 0.82 (TEFF), ^1H NMR δ (DMSO-d_6): 6.21 (1H, *d*, *J* = 16.2 Hz), 6.74–7.06 (3H, *m*), 7.46 (1H, *d*, *J* = 16.2 Hz), identical with caffeic acid. The BuOH extract gave yellow needles (11.4 mg), mp 225–230° of quercetin 3-galactoside [mmp, TLC (EAWA) and NMR].

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KAEMPFEROL 3-SULPHATE IN THE FERN *ADIANTUM CAPILLUS-VENERIS*

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Key Word Index—*Adiantum capillus-veneris*; Adiantaceae; kaempferol 3-sulphate.

Abstract—A new natural product isolated from the fronds of the fern *Adiantum capillus-veneris* has been shown to be kaempferol 3-sulphate by chemical and spectroscopic methods.

Previous work on the phenolic constituents of *Adiantum capillus-veneris* L. has led to the identification of kaempferol 3, 7-diglucoside [1]. Very recently [Imperato, F., unpublished results] four sulphate esters of hydroxycinnamic acid sugar derivatives have been isolated. This paper describes the isolation of kaempferol 3-sulphate from this fern.

This flavonoid (colour reactions: brown to yellow in UV + NH_3) was isolated from an ethanolic extract of fresh fronds of *Adiantum capillus-veneris* by prep. PC. The UV spectral data: λ_{max}^{MeOH} nm: 267, 303 (sh), 347; + NaOAc 275, 303, 378; + NaOAc/H_3BO_3 268, 350; + $AlCl_3$ 278, 304, 349, 396; + $AlCl_3$–HCl 276, 303, 343, 395; + NaOMe 275, 322, 392 (increase in intensity); + $ZrOCl_2$–citric acid 265, 345 are consistent [2] with those of a 3-substituted flavonol with free hydroxyl groups at positions 5, 7 and 4′. The isolated compound was electrophoretically highly mobile (towards anode), strongly suggestive of a sulphate derivative. Total acid hydrolysis, controlled