Synthesis of a Capillarisin Sulfur-Analogue Possessing Aldose Reductase Inhibitory Activity by Selective Isopropylation

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We describe the synthesis of 2-[(4-hydroxyphenyl)thio]-7-isopropoxy-5,6-dimethoxy-4*H*-chromen-4-one 2 from 3,4,5-trimethoxyphenol 6 *via* the key intermediate, 3-iodo-7-isopropoxy-5,6-dimethoxy-4*H*-chromen-4-one 3. An important feature of this synthetic scheme involves selective alkylation, which can be achieved by two different routes. One route involves the selective isopropylation of a triacetate derivative 4 under basic conditions. The second route employs the selective demethylation of a trimethoxy derivative 5 under acidic conditions followed by isopropylation. The product of these alternative routes, compound 3, is then converted to a capillarisin sulfur analogue 2 in a one-pot reaction *via* the imidazolyl intermediate 22.

Key words capillarisin; selective isopropylation; substitution reaction; aldose reductase inhibitor; 3,4,5-trimethoxyphenol

Capillarisin **1**,[1] a bioactive constituent of *Artemisiae Capillaris Herba*, is an antioxidant,[2] as well as a choleretic[3] and antitumor agent[4] and an inhibitor of aldose reductase (AR).[5] We have synthesized a number of capillarisin analogues and tested their ability to inhibit AR.[6] Among them, the sulfur analogue **2**, which was prepared from capillarisin **1** by a semi-synthetic method (Chart 1), showed excellent *in vitro* activity with an IC_{50} of 3×10^{-8} mol/l against rat lens AR. Therefore compound **2** is an excellent lead structure for an AR inhibitor. 6-Demethoxycapillarisin has been synthesized by two groups,[7,8] but total synthesis of **1** has not been reported. During the development of a drug to treat diabetic complications, we devised a synthetic route to the sulfur analogue **2** from a commercially available compound.

A key feature of this synthesis is the selective construction of the A-ring substituted with trialkoxy groups and introduction of the phenylthio group into the 2-position in its structure. The retrosynthetic analysis of **2** is outlined in Fig. 1. A substitution reaction using 3-iodochromone **3** with 4-hydroxybenzenethiol affords **2**. To selectively arrange the 7-isopropoxy-5,6-dimethoxy groups on the A-ring of **3**, two synthetic routes were investigated. The first route involves the selective isopropylation using a triacetate derivative **4** (route a), and the second route involves selective demethylation of the trimethoxy derivative **5** (route b). Compounds **4** and **5** can be prepared from 3,4,5-trimethoxyphenol **6**. In this paper, we describe the total synthesis of the novel capillarisin derivative **2** by these two methods.

Synthesis of 3 *via* 4 (Route a) The starting material **7**, is commercially available or can easily be prepared from 3,4,5-trimethoxyphenol **6**.[9] Condensation of **7** with *N*,*N*-dimethylformamide dimethyl acetal gave **8** in 91% yield. Cyclyzation[10] of **8** using iodine afforded 3-iodochromone **9** in 84% yield (Chart 2).

To obtain the desired compounds, **14** or **15**, demethylation of compound **9** was carried out under various conditions (Table 1). Demethylation proceeded in the order of the position 5, 6 and 7 using Lewis acids (runs 1—4). Interestingly, the reaction of **9** with sulfuric acid (run 5) occurred selec-

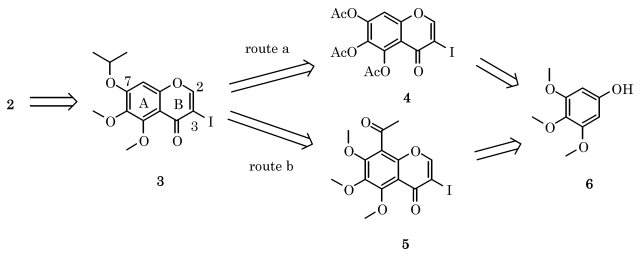


Fig. 1. Retrosynthetic Analysis of **2**

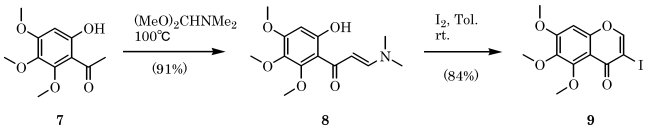
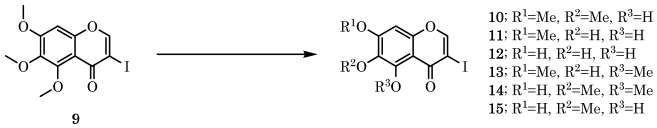


Chart 2. Synthesis of **9**

Table 1. Demethylation of **9**



Run	Reagent	Solv.	Temp.	Time	Products (Yield)
1	BCl_3	CH_2Cl_2	rt.	20 h	**10** (82%), **11** (18%)
2	BCl_3	CH_2Cl_2	−78 °C	10 min	**10** (90%)
3	$TiCl_4$	Tol., CH_2Cl_2	rt.	20 h	**10** (46%), **11** (21%)
4	$AlCl_3$	Tol.	100 °C	6 h	**12** (94%)
5	H_2SO_4		80 °C	2 h	**13** (96%)
6	LiI	Dioxane	Reflux	20 h	**10** (100%)

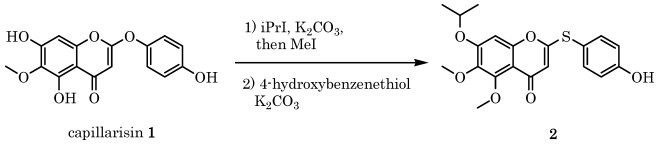


Chart 1. Conversion of Capillarisin **1** to Sulfur-Analogue **2**

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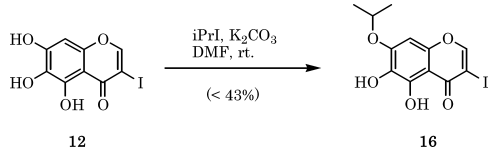

Chart 3. Isopropylation of **12**

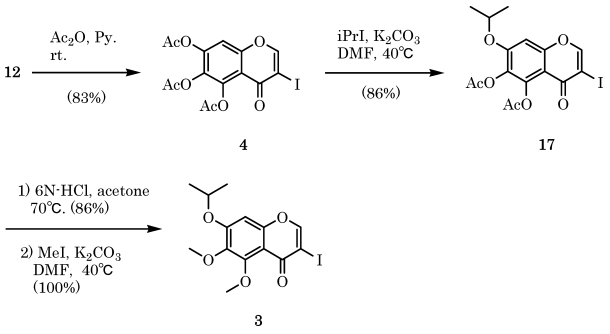

Chart 4. Synthesis of Key Intermediate **3** *via* **4**

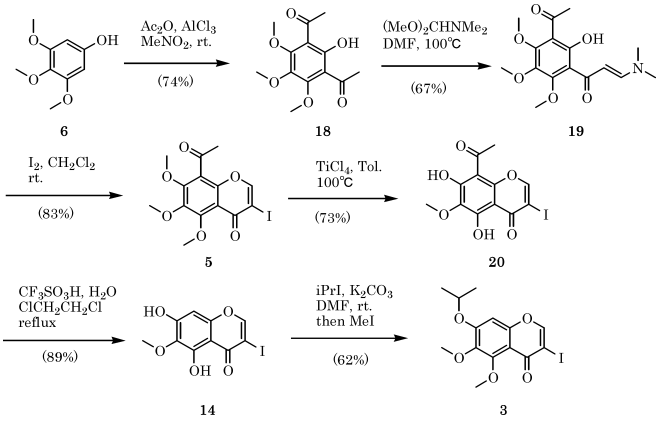

Chart 5. Alternative Synthetic Method of Key Intermediate **3**

tively at the 6-position to afford **13** in 96% yield. Additionally, compound **10** was exclusively obtained after treatment with lithium iodide (run 6). However, the desired compounds, **14** and **15**, could not be obtained by this method.

We then tried selective isopropylation at the 7-position using the trihydroxy derivative **12** under various conditions (base; K_2CO_3, Cs_2CO_3 or Li_2CO_3: solvent; DMF, MEK, acetone or EtOH). However, the yield (maximum 43%) of desired compound **16** was unsatisfactory (Chart 3). Presumably the reactivity of the 7-hydroxy group was equal to that of the 6-hydroxy group, and the substrate **12** is unstable under basic conditions.

We judged that direct isopropylation of **12** is difficult, and therefore adopted a selective alkylation methodology using methyl gallate.[11] Compound **12** was converted to the triacetate **4** in 83% yield, and then reacted with 2-iodopropane in the presence of potassium carbonate. As expected, the 7-acetoxy group *para* to the carbonyl group reacted selectively to give the desired compound **17** in 86% yield. Hydrolysis of **17** followed by methylation afforded the key intermediate **3** in 86% yield (Chart 4).

Synthesis of 3 *via* 5 (Route b) Since selective demethylation of **9** failed (Table 1), conversion of **9** to **3** was achieved

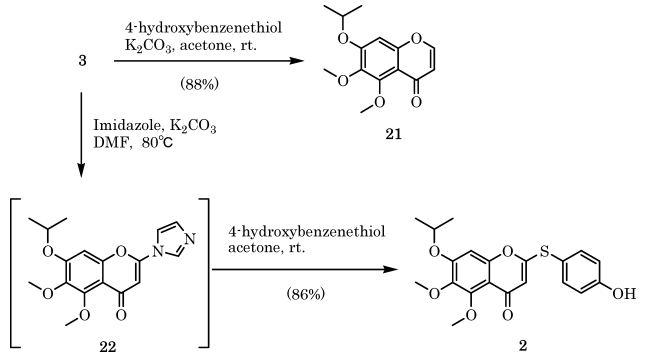

Chart 6. One-Pot Conversion of **3** to **2**

in 5 steps (route a). Thus we planned an alternative route involving the selective demethylation at the 7-position *via* intermediate **5**, possessing a carbonyl function at the 8-position.

Friedel–Crafts reaction of 3,4,5-trimethoxyphenol **6** using acetic anhydride and aluminum chloride in nitromethane afforded the diacetyl derivative **18** in 74% yield. Condensation of **18** with *N*,*N*-dimethylformamide dimethyl acetal (1 eq) followed by treatment with iodine gave **5**. Demethylation of **5** using titanium tetrachloride as Lewis acid proceeded selectively to afford the 5,7-dihydroxy-6-methoxy derivative **20** as expected. The acetyl group of **20** was then removed by reaction with trifluoromethanesulfonic acid[12] to afford **14** in 89% yield. Isopropylation at the 7-position followed by methylation at the 5-position of **14** gave compound **3** in 62% yield (Chart 5).

Preparation of 2 from 3 The conversion of **3** to **2** is outlined in Chart 6. A direct substitution reaction of the 3-iodo-derivative **3** with 4-hydroxybenzenethiol gave only the reduced product **21** in 88% yield. It was reported that 3-iodochromone reacted with imidazole to give 2-(1-imidazolyl)chromone.[13] Treatment of **3** with imidazole in the presence of potassium carbonate in DMF gave the imidazolyl derivative **22**, which without isolation then underwent a substitution reaction with 4-hydroxybenzenethiol to give **2** in 86% yield. These two steps could proceed either in a one-pot reaction or step-by-step.

Conclusion

We have developed two synthetic routes for the preparation of the key intermediate **3** in the synthesis of a capillarisin-analogue **2**. Both reaction schemes use readily available starting reagents. One route employs the selective isopropylation of **4**, whereas the second route involves the selective demethylation of **5**. Compound **2** was prepared from **3** in a one-pot reaction *via* the imidazoyl derivative **22**.

Experimental

Melting points were measured by the use of a Yanaco micro melting point apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a JEOL FX-200 (200 MHz) using tetramethylsilane as an internal standard. Infrared spectra were recorded using a Hitachi 270-30 spectrophotometer. Mass spectra were recorded on a JEOL DX-300 spectrometer. Elemental analyses were performed on a Heraus CHN-O-Rapid.

(*E*)-3-(Dimethylamino)-6′-hydroxy-2′,3′,4′-trimethoxyacrylophenone (8) A mixture of 6′-hydroxy-2′,3′,4′-trimethoxyacetophenone (607 mg, 2.69 mmol) and *N*,*N*-dimethylformamide dimethyl acetal (0.534 ml, 4.03 mmol) was stirred at 100 °C for 2 h. The reaction mixture was purified by flash chromatography on silica gel (hexane/EtOAc=1/1) to give the title

compound (691.1 mg, 91%). Recrystallization from EtOAc–hexane afforded yellow crystals: mp 113—114 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.96 (3H, br s), 3.18 (3H, br s), 3.81 (3H, s), 3.86 (3H, s), 3.87 (3H, s), 6.25 (1H, s), 6.33 (1H, d, J=12.4 Hz), 7.95 (1H, d, J=12.4 Hz), 14.84 (1H, s). IR (KBr) cm^{-1}: 1616, 1528. EI-MS m/z: 281 (M^+). *Anal.* Calcd for $C_{14}H_{19}NO_5$: C, 59.78; H, 6.81; N, 4.98. Found: C, 59.71; H, 6.96; N, 5.09.

3-Iodo-5,6,7-trimethoxy-4*H*-chromen-4-one (9) A mixture of **8** (1.897 g, 6.75 mmol) and iodine (3.40 g, 13.4 mmol) in toluene (19 ml) was stirred at room temperature for 1.5 h. The reaction mixture was quenched with $Na_2S_2O_3$ aq and extracted with EtOAc. The organic phase was dried over Na_2SO_4, concentrated and then recrystallized from EtOAc–hexane to give the title compound (1.871 g, 77%). The filtrate of the recrystallization was purified by flash chromatography on silica gel (CH_2Cl_2/EtOAc=10/1) to give the title compound (177 mg, 7%): mp 183—184 °C. ^{1}H-NMR ($CDCl_3$) δ: 3.90 (3H, s), 3.95 (3H, s), 3.97 (3H, s), 6.68 (1H, s), 8.13 (1H, s). IR (KBr) cm^{-1}: 1628, 1612. EI-MS m/z : 362 (M^+). *Anal.* Calcd for $C_{12}H_{11}IO_5$: C, 39.80; H, 3.06. Found: C, 39.95; H, 3.19.

5,6,7-Trihydroxy-3-iodo-4*H*-chromen-4-one (12) To a suspension of **9** (497.9 mg, 1.38 mmol) in toluene (10 ml) was added $AlCl_3$ (915 mg, 6.88 mmol) at room temperature. The mixture was then heated and stirred at 100 °C for 6 h. After cooling, the reaction mixture was poured into 3 N-HCl, and stirred at room temperature for 1 h. The reaction mixture was extracted with EtOAc, dried over Na_2SO_4 and concentrated. The residue was washed with CH_2Cl_2 to give the title compound (415.6 mg, 94%): mp 227—229 °C. ^{1}H-NMR (DMSO-d_6) δ: 6.50 (1H, s), 8.65 (1H, s), 12.11 (1H, s). IR (KBr) cm^{-1}: 3472, 3420, 1650, 1612. EI-MS m/z: 320 (M^+). *Anal.* Calcd for $C_9H_5IO_5$: C, 33.78; H, 1.57. Found: C, 33.75; H, 1.72.

5,6,7-Triacetoxy-3-iodo-4*H*-chromen-4-one (4) To a solution of **12** (1.02 g, 3.19 mmol) in pyridine (5 ml) was added acetic anhydride (1.51 ml, 15.95 mmol), and the mixture was stirred at room temperature for 4 h. The reaction mixture was poured into 3 N-HCl, and the resulting solid was filtered, washed with H_2O, and dried *in vacuo* to give the title compound (1.18 g, 83%). Recrystallization from EtOAc–hexane afforded colorless crystals: mp 200—202 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.33 (3H, s), 2.34 (3H, s), 2.45 (3H, s), 7.40 (1H, s), 8.21 (1H, s). IR (KBr) cm^{-1}: 1774, 1646, 1626. EI-MS m/z: 446 (M^+). HR-EI-MS m/z: 445.9482 (Calcd for $C_{15}H_{11}IO_8$: 445.9499).

5,6-Diacetoxy-3-iodo-7-isopropoxy-4*H*-chromen-4-one (17) A mixture of **4** (928 mg, 2.08 mmol), 2-iodopropane (0.416 ml, 4.16 mmol), and K_2CO_3 (861 mg, 6.24 mmol) in DMF (4.6 ml) was stirred at 40 °C for 6 h. H_2O was added to the mixture, and the mixture was extracted with EtOAc, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel (hexane/EtOAc=2/1) to give the title compound (795.5 mg, 86%). Recrystallization from EtOAc–hexane afforded colorless crystals: mp 138—139 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.39 (6H, d, J=6.1 Hz), 2.32 (3H, s), 2.44 (3H, s), 4.64 (1H, septet, J=6.1 Hz), 6.79 (1H, s), 8.14 (1H, s). IR (KBr) cm^{-1}: 1762, 1626. EI-MS m/z: 446 (M^+). *Anal.* Calcd for $C_{16}H_{15}IO_7$: C, 43.07; H, 3.39. Found: C, 43.08; H, 3.51.

3-Iodo-7-isopropoxy-5,6-dimethoxy-4*H*-chromen-4-one (3) 1) To a solution of **17** (793.8 mg, 1.78 mmol) in acetone (8 ml) was added 6 N-HCl, and the mixture was stirred at 70 °C for 5 h. After adding H_2O the mixture was extracted with EtOAc, dried over Na_2SO_4 and concentrated to give 5,6-hydroxy-3-iodo-7-isopropoxy-4*H*-chromen-4-one (554 mg, 86%). Recrystallization from EtOAc–hexane afforded colorless crystals: mp 151—152 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.45 (6H, d, J=6.1 Hz), 4.70 (1H, septet, J=6.1 Hz), 5.43 (1H, s), 6.50 (1H, s), 8.17 (1H, s), 11.96 (1H, s). IR (KBr) cm^{-1}: 3508, 1660, 1596. EI-MS m/z: 362 (M^+). *Anal.* Calcd for $C_{12}H_{11}IO_5$: C, 39.80; H, 3.06. Found: C, 39.97; H, 3.24.

2) A mixture of the above compound (554 mg, 1.53 mmol), K_2CO_3 (1.47 g, 10.68 mmol) and iodomethane (0.665 ml, 10.68 mmol) in DMF (8 ml) was stirred at 40 °C for 5 h. After adding H_2O the mixture was extracted with EtOAc, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel (hexane/EtOAc=4/1) to give the title compound (597.8 mg, 100%). Recrystallization from EtOAc–hexane afforded colorless crystals: mp 99—100 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.45 (6H, d, J=6.1 Hz), 3.87 (3H, s), 3.96 (3H, s), 4.65 (1H, septet, J=6.1Hz), 6.65 (1H, s), 8.11 (1H, s). IR (KBr) cm^{-1}: 1638, 1608, 1478. EI-MS m/z: 390 (M^+). *Anal.* Calcd for $C_{14}H_{15}IO_5$: C, 43.10; H, 3.88. Found: C, 43.06; H, 3.82.

2,6-Diacethyl-3,4,5-trimethoxyphenol (18) To a solution of 3,4,5-trimethoxyphenol (3.21 g, 16.96 mmol) and acetic anhydride (6.41 ml, 67.84 mmol) in nitromethane (31 ml) was added $AlCl_3$ (6.77 g, 50.88 mmol) at 0 °C. The mixture was then stirred at room temperature for 20 h. 3 N-HCl was added to the reaction mixture, and the mixture was stirred at room temperature for 1 h, extracted with EtOAc, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel (hexane/EtOAc=6/1) to give the title compound (3.35 g, 74%). Recrystallization from hexane afforded colorless crystals: mp 85—86 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.59 (6H, s), 3.79 (3H, s), 4.00 (6H, s), 13.31 (1H, s). EI-MS m/z: 268 (M^+). *Anal.* Calcd for $C_{13}H_{16}O_6$: C, 58.20; H, 6.01. Found: C, 58.18; H, 6.04.

(*E*)-3′-Acetyl-3-(dimethylamino)-2′-hydroxy-4′,5′,6′-trimethoxyacrylophenone (19) A mixture of **18** (3.33 g, 12.4 mmol) and *N*,*N*-dimethylformamide dimethyl acetal (1.65 ml, 12.4 mmol) in DMF (3.3 ml) was stirred at 100 °C for 6 h. The reaction mixture was purified by flash chromatography on silica gel (hexane/EtOAc=1/4) to give the title compound (2.70 g, 67%). Recrystallization from EtOAc–hexane afforded yellow crystals: mp 113—114 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.60 (3H, s), 2.91 (3H, s), 3.12 (3H, s), 3.81 (3H, s), 3.94 (3H, s), 3.97 (3H, s), 5.78 (1H, br d, J=12.4 Hz), 7.65 (1H, br s), 13.96 (1H, br s). EI-MS m/z: 323 (M^+). *Anal.* Calcd for $C_{16}H_{21}NO_6$: C, 59.43; H, 6.55; N, 4.33. Found: C, 59.21; H, 6.53; N, 4.31.

8-Acetyl-3-iodo-5,6,7-trimethoxy-4*H*-chromen-4-one (5) A mixture of **19** (1.23 g, 3.81 mmol) and iodine (1.94 g, 7.62 mmol) in CH_2Cl_2 (12 ml) was stirred at room temperature for 2 h. The reaction mixture was quenched with $Na_2S_2O_3$ aq and extracted with EtOAc. The organic phase was dried over Na_2SO_4, concentrated, and purified by flash chromatography on silica gel (hexane/EtOAc=8/3) to give the title compound (1.27 g, 83%). Recrystallization from EtOAc–hexane afforded colorless crystals: mp 139—140 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.56 (3H, s), 3.93 (3H, s), 3.99 (3H, s), 4.05 (3H, s), 8.11 (1H, s). EI-MS m/z: 404 (M^+). *Anal.* Calcd for $C_{14}H_{13}IO_6$: C, 41.61; H, 3.24. Found: C, 41.35; H, 3.16.

8-Acetyl-5,7-dihydroxy-3-iodo-6-methoxy-4*H*-chromen-4-one (20) To a solution of **5** (100 mg, 0.248 mmol) in toluene (2 ml) was added $TiCl_4$ (0.74 ml, 1 M solution in toluene) at room temperature, and the mixture was then stirred at 100 °C for 1 h. After cooling, the reaction mixture was poured into 3 N-HCl and stirred at 80 °C for 0.5 h. The reaction mixture was extracted with EtOAc, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel (CH_2Cl_2/EtOAc=30/1) to give the title compound (68 mg, 73%). Recrystallization from EtOAc afforded colorless crystals: mp 224—226 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.76 (3H, s), 3.93 (3H, s), 8.31 (1H, s), 13.26 (1H, s), 14.54 (1H, s). EI-MS m/z: 376 (M^+). *Anal.* Calcd for $C_{12}H_9IO_6$: C, 38.32; H, 2.41. Found: C, 38.11; H, 2.47.

5,7-Dihydroxy-3-iodo-6-methoxy-4*H*-chromen-4-one (14) To a solution of **20** (222 mg, 0.59 mmol) in 1,2-dichloroethane (4 ml) was added trifluoromethanesulfonic acid (0.2 ml) and H_2O (0.2 ml) at room temperature. The mixture was then refluxed for 20 h. The reaction mixture was extracted with CH_2Cl_2, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel (CH_2Cl_2/EtOAc=30/1) to give the title compound (174.8 mg, 89%). Recrystallization from EtOAc–hexane afforded colorless crystals: mp 175—176 °C. ^{1}H-NMR ($CDCl_3$) δ: 4.03 (3H, s), 6.52 (1H, s), 6.57 (1H, s), 8.14 (1H, s), 12.45 (1H, s). EI-MS m/z: 334 (M^+). *Anal.* Calcd for $C_{10}H_7IO_5$: C, 35.95; H, 2.11. Found: C, 35.91; H, 2.03.

2-[(4-Hydroxyphenyl)thio]-7-isopropoxy-5,6-dimethoxy-4*H*-chromen-4-one (2) A mixture of **3** (225.2 mg, 0.578 mmol), imidazole (79 mg, 1.16 mmol) and K_2CO_3 (798 mg, 5.78 mmol) in DMF (2.3 ml) was stirred at 80 °C for 2 h. After cooling, a solution of 4-hydroxybenzenethiol (146 mg, 1.16 mmol) in acetone (1 ml) was added to the reaction mix, and the mixture was stirred at room temperature for 2 h. The reaction mixture was poured into 3 N-HCl, extracted with CH_2Cl_2, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel (CH_2Cl_2/acetone=10/1) to give the title compound (193 mg, 86%). Recrystallization from EtOH afforded colorless crystals: mp 213—215 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.45 (6H, d, J=6.1 Hz), 3.86 (3H, s), 3.92 (3H, s), 4.65 (1H, septet, J=6.1 Hz), 5.64 (1H, s), 6.70 (1H, s), 6.85 (2H, d, J=8.8 Hz), 7.36 (2H, d, J=8.8 Hz), 9.82 (1H, s). IR (KBr) cm^{-1}: 3230, 1612, 1578. EI-MS m/z: 388 (M^+), 373, 331.

Reference and Notes

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9) Although the acetophenone **7** was a commercially available material, it was synthesized by the following method. Friedel–Crafts reaction of 3,4,5-trimethoxyphenol and acetic anhydride using zinc choride in nitromethane followed by hydrolysis using sodium hydrogencarbonate to give **7** in 91% yield.
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