Acta Chemica Scandinavica, 1998: 52: 1243–1246
Printed in UK all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Huazhongilexone is not 3′,5,5′,7-Tetrahydroxyflavanone. Preparation of 3′,5′-Dimethoxy-5,7-dihydroxyflavanone

Uffe Anthoni,[a] Rosalba Encarnación D.,[b] Per H. Nielsen[a] and Carsten Christophersen[a,*]

[a]Marine Chemistry Section, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark and [b]Departamento de Agronomía, Universidad Autónoma de Baja California Sur, A.P. 19-B, La Paz, B. C. S. 23080, México

Anthoni, U., Encarnación D., R., Nielsen, P. H. and Christophersen, C., 1998. Huazhongilexone is not 3′,5,5′,7-Tetrahydroxyflavanone. Preparation of 3′,5′-Dimethoxy-5,7-dihydroxyflavanone. – Acta Chem. Scand. 52: 1243–1246. © Acta Chemica Scandinavica 1998.

Huazhongilexone, isolated from *Ilex centrochinensis*, was originally assigned the structure 3′,5,5′,7-tetrahydroxyflavanone. The racemic flavanone has been synthezised. Huazhongilexone is different from the synthetic compound and thus must have a different structure. In addition the new (±)-3′,5′-dimethoxy-5,7-dihydroxyflavanone has been prepared and characterized.

Results and discussion

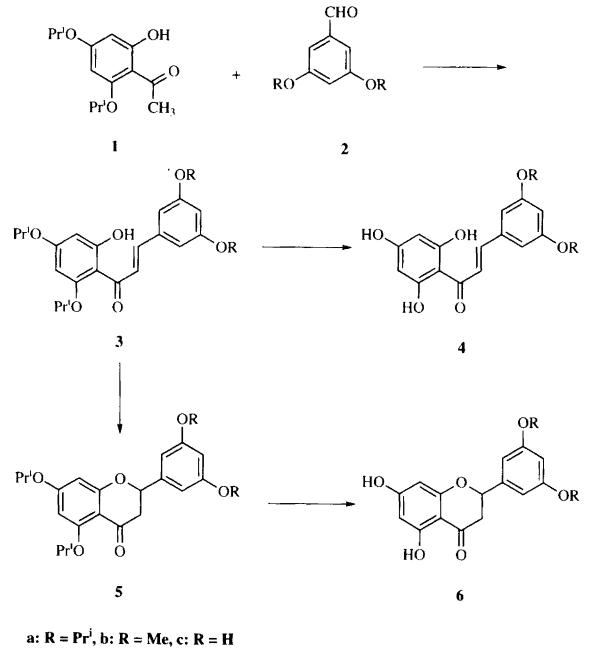
Huazhongilexone was isolated from leaves of the chinese *Ilex centrochinensis* S. Y. Hu (Celastrales, Aquifoliacea).[1] Based on spectroscopic (^{1}H NMR, IR, UV, MS) studies the structure was assigned as (*S*)-3′,5,5′,7-tetrahydroxyflavanone (*S*–**6c**). The synthesis of the racemate of this flavanone has been reported from 2,4,6-trihydroxyacetophenone and 3,5-dihydroxybenzaldehyde (**2c**) in 22% yield.[2] The m.p. of the racemic synthetic compound was reported as 186–188 °C while the natural compound had an m.p. of 286–287 °C.[2] From the ^{1}H NMR data reported for the synthetic and natural compounds it is evident that one of the structures is incorrect since these data are not mutually compatible.[1,2] Since it was not possible *a priori* to determine which of the compounds was assigned an incorrect structure attempts were made to reproduce the synthesis. In our hands these attempts only resulted in black tars chromatographically devoid of the desired compound. We therefore designed another preparation of (±)-3′,5,5′,7-tetrahydroxyflavanone (**6c**). As described below this approach unambiguously showed that the structure of the synthetic compound is correct and thus that the structure of huazhongilexone is in need of revision.

Owing to a registration error in *Chemical Abstracts* [*Chem. Abstr. 65* (1966) 8862c] 3′,5′-dimethoxy-5,7-dihydroxyflavanone (**6b**) was considered a known compound. However, closer inspection of the original reference[3] revealed that the compound was not mentioned at all. By an approach analogous to that used for the synthesis of the tetrahydroxyflavanone the new dimethylated derivative was synthezised.

Synthesis of 3′,5,5′,7-tetrahydroxyflavanone (**6c**). The starting material 2-hydroxy-4,6-diisopropoxyacetophenone (**1**) was prepared from the corresponding 2,4,6-trihydroxyacetophenone by standard methods[4] and gave, in addition to a 75% yield of the expected material, 10% of 2,6-dihydroxy-4-isopropoxyacetophenone. The chalcone, (*E*)-1-(2-hydroxy-4,6-diisopropyloxyphenyl)-3-(3,5-diisopropyloxyphenyl)propenone (**3a**), was prepared from 2-hydroxy-4,6-diisopropyloxyacetophenone (**1**) and 3,5-diisopropyloxybenzaldehyde (**2a**) by analogy with known methods.[5] The protected flavanone (**5a**) was prepared by acid-catalyzed cyclization of **3a**. Boron trichloride catalyzed deprotection of **5a** smoothly generated **6c** (Scheme 1).

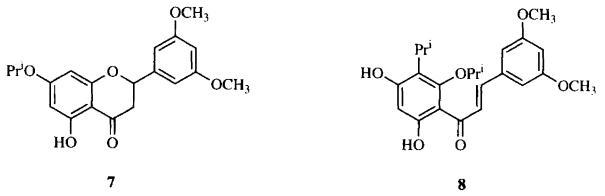
Synthesis of 3′,5′-dimethoxy-5,7-dihydroxyflavanone (**6b**). By analogy with the preparation described above 2′-hydroxy-4′,6′-diisopropoxyacetophenone (**1**) reacted with 3,5-dimethoxybenzaldehyde (**2b**) to form the chalcone (*E*)-1-(2-hydroxy-4,6-diisopropyloxyphenyl)-3-(3,5-dimethoxyphenyl)propenone (**3b**). On treatment with boron trichloride in methylene chloride this chalcone gave only the deprotected compound, (*E*)-1-(2,4,6-trihydroxyphenyl) - 3 - (3,5 - dimethoxyphenyl)propenone (**4b**). The chalcone **3b** could, however, be cyclized to the corresponding flavanone (**5b**) on treatment with phosphoric acid. In addition the phosphoric acid catalyzed reaction gave rise to the formation of a rearranged product, (*E*)-1-(2,4-dihydroxy-5-isopropyl-6-isopropoxyphenyl)-3-(3,5-dimethoxyphenyl)propenone (**8**). Also, hydrogen chloride in EtOH gave rise to some cyclization,

* To whom correspondence should be addressed.



Scheme 1.

but turned out to catalyze the retro aldol reaction regenerating the diisopropoxyacetophenone (**1**) from the chalcone (**3b**). Removal of the protecting isopropyl groups from the flavanone (**5b**) was only partly effected by aluminium chloride in refluxing acetonitrile giving rise to 5-hydroxy-7-isopropoxy-3′,5′-dimethoxyflavanone (**7**). Eventually the desired reaction **5b** to **6b** was effected by treatment with boron trichloride in methylene chloride at −78 °C.



Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian UNITY 400 spectrometer, operating at 400 MHz for protons and at 100.6 MHz for carbons, respectively. Spectra were recorded for samples in DMSO-d_6, acetone-d_6 or $CDCl_3$, which were also used as internal standards in the ^{13}C NMR spectroscopy; in ^{1}H NMR spectroscopy Me_4Si was used as an internal standard. The ^{1}H NMR data are given as δ (number of protons, multiplicity, *J* in Hz, assignment). Mass spectra were obtained on a JEOL JMS-HX/HX110A spectrometer using the direct inlet system.

2-Hydroxy-4,6-diisopropoxyacetophenone (**1**). The partial alkylation of 2,4,6-trihydroxyacetophenone was performed with 2-bromopropane and potassium carbonate in *N,N*-dimethylformamide.[5,6] Purification of the reaction mixture by column chromatography (Silica gel) with 10% EtOAc in heptane gave a yield of 75% of pure **1**. ^{13}C NMR ($CDCl_3$): δ 21.7, 21.8, 33.0, 70.1, 70.6, 92.8, 94.0, 106.1, 161.0, 164.3, 167.4, 202.9.

From one of the chromatographic fractions 2,4-dihydroxy-6-isopropoxyacetophenone was isolated in 10% yield, m.p. 147–148 °C. MS [E_i 70 eV; *m/z* (% rel. int.)] 210 (M^+, 25), 168 (20), 153 (100). ^{1}H NMR ($CDCl_3$): δ 13.97 (1 H, s, HO–), 7.3 (1 H, br s, HO–), 5.97 (1 H, d, *J* 2), 5.89 (1 H, d, *J* 2), 4.59 (1 H, septet, *J* 6), 2.60 (3 H, s), 1.38 (6 H, d, *J* 6). ^{13}C NMR ($CDCl_3$): δ 21.7, 70.9, 92.0, 95.8, 106.3, 161.8, 163.4, 166.9, 203.3.

(E)-1-(2-Hydroxy-4,6-diisopropoxyphenyl)-3-(3,5-dimethoxyphenyl)propenone (**3b**). In accordance with the directions given,[4] **1** (6.2 g, 252 mmol) and 3,5-dimethoxybenzaldehyde (**2b**) (4.1g, 166 mmol) were treated with KOH (10 g) in 80% EtOH (200 ml) overnight at room temperature. The oily product was isolated by EtOAc extraction of the reaction mixture poured onto ice. Column chromatography (Silica gel) with EtOAc heptane 10:90 gave rise to a yield of 85% of **3b**, m.p. 81–82 °C (EtOH/H_2O). Anal. $C_{23}H_{28}O_6$: C, H. ^{1}H NMR ($CDCl_3$): δ 14.23 (1 H, s, HO–), 7.96 (1 H, d, *J* 16, =CH), 7.63 (1 H, d, *J* 16, =CH), 6.72 (2 H, d, *J* 2), 6.47 (1 H, t, *J* 2), 6.04 (1 H, d, *J* 2), 5.90 (1 H, d, *J* 2), 4.68–4.51 (2 H, m), 3.78 (6 H, s), 1.44 (6 H, d, *J* 6), 1.34 (6 H, d, *J* 6). ^{13}C NMR ($CDCl_3$): δ 192.4 (CO), 168.2 (C-4′), 164.5 (C-6′), 160.8 (C-3′, C-5′), 160.6 (C-2′), 141.5 (Cβ), 137.3 (C-1), 128.1 (Cα), 106.6 (C-1′), 105.8 (C-6, C-2), 102.3 (C-4), 94.5 (C-3′ or C-5′), 93.7 (C-3′ or C-5′), 71.0 (Pr^i–CH), 70.1 (Pr^i–CH), 55.1 (2 × MeO), 22.0 (Pr^i–Me), 21.7 (Pr^i–Me). MS [E_i 70 eV; *m/z* (% rel. int.)] 400 (M^+, 100), 399 (23), 357 (23), 315 (17), 263 (33), 221 (17), 179 (16).

(E)-1-(2,4,6-Trihydroxyphenyl)-3-(3,5-dimethoxyphenyl)-propenone (**4b**). To a solution of **3b** (85 mg, 0.2 mmol) in dichloromethane (15 ml) was added at −80 °C a solution of boron trichloride (6 ml, 1 M) in dichloromethane with stirring. The reaction mixture was protected from air and moisture with nitrogen. After the addition the red reaction mixture was allowed to come to room temperature and was poured onto water after 2 h. Repeated extraction with dichloromethane gave, after evaporation, 40 mg crude product, which was subjected to column chromatography (Si gel) with EtOAc–heptane 45:55 as the eluent. Compound **4b** (18 mg) was isolated in 75% yield, m.p. 110–120 °C (subl., closed tube). ^{1}H NMR (DMSO-d_6): δ 12.46 (2 H, s, 2 × OH), 10.47 (1 H, s, HO), 8.08 (1 H, d, *J* 16, =CH), 7.60 (1 H, d, *J* 16, =CH), 6.83 (2 H, d, *J* 2), 6.57 (1 H, t, *J* 2), 5.85 (2 H, s), 3.78 (6 H, s, 2 × OMe), 3.33 (H_2O). ^{13}C NMR (DMSO-d_6): δ 191.7, 165.2, 164.5, 160.8, 141.3, 137.1, 128.2, 106.1, 104.4, 102.3, 95.0, 55.4. UV [EtOH λ_{max} nm (log ε)] 207 (3.39), 295sh (2.89), 347 (3.10). MS [E_i

70 eV; *m/z* (% rel. int.)] 316 (100, M^+), 315 (30), 289 (9), 285 (6), 191 (6), 179 (36), 164 (32), 137 (8), 135 (6).

(±)-3',5'-Dimethoxy-5,7-diisopropoxyflavanone (**5b**). A solution of **3b** (2.0 g, 5 mmol) in methylcellosolve (35 ml) and 85% phosphoric acid (3.5 g) was refluxed for 5 h. The reaction mixture, after addition of EtOAc, was washed with aqueous KOH (1 M) and, on evaporation of the EtOAc phase, left 1.5 g material. Column chromatography (Si60) with EtOAc–heptane 45:55 as the mobile phase gave 43 mg **1**, which must have been formed in a retro-reaction, recovery of 36% (716 mg) starting material (**3b**) and 26% (370 mg) **5a** m.p. 79–80 °C. ^{1}H NMR ($CDCl_3$): δ 6.60 (2 H, d, *J* 2, H-6', H-2'), 6.44 (1 H, t, *J* 2, H-4'), 6.13 (1 H, d, *J* 2, H-8 or H-6), 6.07 (1 H, d, *J* 2, H-8 or H-7), 5.31 (1 H, dd, *J* 13, 3, H-2), 4.57–4.53 (2 H, m, Pr^i–CH), 3.80 (6 H, s, 2 × MeO–), 2.96 (1 H, dd, *J* 16, 13, H-2), 2.73 (1 H, dd, *J* 16, 3, H-2), 1.44–1.34 (12 H, m, Pr^i–Me). ^{13}C NMR ($CDCl_3$): δ 188.4 (C-4), 164.8 (C-7), 164.1 (C-5 or C-9), 161.1 (C-5', C-3'), 160.8 (C-5 or C-9), 141.3 (C-1'), 106.6 (C-10), 104.1 (C-6', C-2'), 100.2 (C-4'), 96.9 (C-8 or C-6), 94.6 (C-8 or C-6), 79.0 (C-2), 71.6 (Pr^i–CH), 70.3 (Pr^i–CH), 55.4 (2 × MeO–), 45.9 (C-3), 22.0 (Pr^i–Me), 21.9 (Pr^i–Me). MS [E_i 70 eV; *m/z* (% rel. int.)] 400 (M^+, 100), 399 (26), 385 (14), 357 (29), 315 (23), 263 (30), 221 (19), 179 (19), 164 (13). In addition a small amount (5%) of **8** (see below) was secured from the chromatography.

(±)-3',5'-Dimethoxy-5-hydroxy-7-isopropoxyflavanone (**7**). To a solution of **5b** (90 mg, 0.25 mmol) in acetonitrile (35 ml) aluminium chloride (150 mg) was added at room temperature and the solution was refluxed for 1.5 h under nitrogen. After evaporation of most of the solvent, the reaction mixture was poured onto ice and the yellow precipitate was removed by filtration and subjected to ^{1}H NMR spectroscopy. Yield 80%. ^{1}H NMR ($CDCl_3$): δ 11.97 (1 H, s, 5-OH), 6.59 (2 H, d, *J* 2, H-6', H-2'), 6.46 (1 H, t, *J* 2, H-4'), 6.04 (2 H, 2 × d, *J* 2, H-6, H-8), 5.34 (1 H, dd, *J* 3, 13, H-2) 4.56 (1 H, septet, *J* 6, Pr^i–CH), 3.82 (6 H, s, 2 × OMe), 3.05 (1 H, dd, *J* 13, 17, H-3), 2.80 (1 H, dd, *J* 3, 17, H-2), 1.35 (6 H, d, *J* 6, Pr^i–Me). MS [E_i 70 eV; *m/z* (% rel. int.)] 358 (100, M^+), 357 (22), 316 (23), 315 (24), 298 (15), 221 (30), 179 (26), 164 (27).

(±)-3',5'-Dimethoxy-5,7-dihydroxyflavanone (**6b**). To a solution of **5b** (95 mg, 0.30 mmol) in dichloromethane (15 ml) at −80 °C under nitrogen was added a solution of boron trichloride (6 ml, 1 M) in dichloromethane. The reaction mixture was allowed to reach room temperature and after 2 h poured into water and stirred for 30 min. The dichloromethane, combined with an EtOAc phase obtained by extraction of the aqueous solution yielded 34 mg crude product, which after column chromatography (Silica gel) with EtOAc–heptane 45:55 as the eluent, gave **6b** (20 mg), 65% yield. After recrystallization from EtOAc–heptane 20:60 the product had m.p. 159.5–160 °C. ^{1}H NMR (DMSO-d_6): δ 12.10 (1 H, s, 5-OH), 10.82 (1 H, s, 7-OH), 6.67 (2 H, d, *J* 2, H-2', H-6'), 6.49 (1 H, t, *J* 2, H-4'), 5.94 (1 H, d, *J* 2, H-6 or H-8), 5.90 (1 H, d, *J* 2, H-6 or H-8), 5.49 (1 H, dd, *J* 13, 3, H-2), 3.76 (6 H, s, 3'–OMe and 5'–OMe), 3.34 (H_2O), 3.24 (1 H, dd, *J* 13, 17, H-3), 2.77 (1 H, dd, *J* 17, 3, H-2). ^{13}C NMR (DMSO-d_6): δ 195.9 (C-4), 166.7, 163.5, 162.6, 160.6, 141.0, 104.7 (C-2', C-6'), 101.8, 100.0 (C-4'), 96.0 (C-6 or C-8), 95.1 (C-6 or C-8), 78.3 (C-2), 55.3 (2 × OMe), 42.2 (C-3). MS [E_i 70 eV; *m/z* (% rel. int.)] 316 (M^+, 100), 315 (40), 179 (50), 164 (50), 84 (55), 66 (58). UV [EtOH λ_{max} nm (log ε)] 210 (4.64), 229sh (4.31), 288 (4.22), 326 (3.80).

1-(4,6-dihydroxy-2-isopropoxy-3-isopropylphenyl)-3-(3,5-dimethoxyphenyl)propenone (**8**). Isolated as described under **5b**. M.p. 179–180 °C. ^{1}H NMR ($CDCl_3$): δ 14.00 (1 H, s, HO–), 7.88 (1 H, d, *J* 16, =CH), 7.57 (1 H, d, *J* 16, =CH), 6.68 (2 H, d, *J* 2), 6.42 (1 H, t, *J* 2), 5.85 (1 H, s), 4.51 (1 H, septet, *J* 6, Pr^i–CH), 4.40 (1 H, septet, *J* 6, Pr^i–CH), 3.75 (6 H, s, 2 × OMe), 3.42 (1 H, s, HO–), 1.33 (6 H, d, *J* 6, Pr^i–Me), 1.05 (6 H, d, *J* 6, Pr^i–Me). ^{13}C NMR ($CDCl_3$): δ 192.8, 164.7, 162.3, 160.9, 158.8, 140.8, 137.6, 128.9, 111.2, 107.2, 105.9, 102.3, 90.8, 71.4, 69.7, 55.3, 22.2, 21.6. MS [E_i 70 eV; *m/z* (% rel. int.)] 400 (M^+, 100), 358 (31), 315 (22), 263 (72), 221 (72).

3,5-Diisopropoxybenzaldehyde (**2a**). The aldehyde was prepared by Swern oxidation of the corresponding 3,5-diisopropoxybenzylic alcohol prepared by treatment of 3,5-dihydroxybenzylic alcohol with isopropyl bromide. The oily product was obtained in 80% yield after distillation. ^{1}H NMR ($CDCl_3$): δ 9.87 (1 H, s, CHO), 6.96 (2 H, d, *J* 2, H-2, H-6), 6.67 (1 H, t, *J* 2, H-4), 4.59 (2 H, septet, *J* 6, Pr^i–CH), 1.35 (12 H, d, *J* 6, Pr^i–Me). ^{13}C NMR ($CDCl_3$): δ 192.1 (CO), 159.6 (C-3, C-5), 110.4 (C-4), 108.7 (C-2, C-6), 106.4 (C-1), 70.4 (2 × Pr^i–CH), 22.0 (Pr^i–Me).

(E)-1-(2-Hydroxy-4,6-diisopropoxyphenyl)-3-(3,5-diisopropoxyphenyl)propenone (**3a**). 3,5-Diisopropoxybenzaldehyde (5 mmol, 1.1 g) was added to a solution of 2-hydroxy-4,6-diisopropoxyacetophenone (5 mmol, 1.2 g) in 80% EtOH (25 ml) with KOH (2 g). The reaction mixture was left overnight at room temperature and then poured onto acidified (HCl) ice and extracted with EtOAc. Separation using VLC on RP18 with 33–10% H_2O in EtOH gave the pure compound, m.p. 74–75 °C. ^{1}H NMR ($CDCl_3$): δ 14.23 (1 H, s, HO–), 7.93 (1 H, d, *J* 16, =CH), 7.63 (1 H, d, *J* 16, =CH), 6.70 (2 H, d, *J* 2), 6.46 (1 H, t, *J* 2), 6.04 (1 H, d, *J* 2), 5.90 (1 H, d, *J* 2), 4.65–4.49 (4 H, m, Pr^i–CH), 1.44–1.32 (24 H, m, Pr^i–Me). ^{13}C NMR ($CDCl_3$): δ 192.5, 168.1, 164.5, 160.7, 159.1, 141.9, 137.2, 107.8, 106.7, 106.1, 94.5, 93.8, 71.1, 70.2, 70.0, 22.0, 21.9, 21.8, 21.8. MS [E_i 70 eV; *m/z* (% rel. int.)] 456 (M^+, 100), 455 (35), 413 (31), 371 (17),

329 (14), 287 (17), 263 (63), 221 (31), 179 (28), 153 (24). Anal. $C_{27}H_{36}O_6$: C, H.

(E)-1-(2,4,6-Trihydroxyphenyl)-3-(3,5-dihydroxyphenyl)-propenone (**4c**). Prepared exactly as described for the conversion of **3b** into **4b**. ^{1}H NMR (DMSO-d_6): δ 12.59 (2 H, s, 2 × OH), 10.6 (1 H, s, OH), 9.6 (2 H, s, 2 × OH), 7.99 (1 H, d, *J* 16, =CH), 7.48 (1 H, d, *J* 16, =CH), 6.51 (2 H, d, *J* 2), 6.31 (1 H, dd, *J* 2), 5.87 (2 H, s), 3.82 (H_2O). ^{13}C NMR (DMSO-d_6): δ 192.0, 165.6, 164.9, 159.1, 142.5, 137.0, 127.3, 106.6, 105.2, 104.6, 95.3. UV [EtOH λ_{max} nm (log ε)] 290sh (3.43), 349 (3.77).

(±)-3',5,5',7-Tetraisopropoxyflavanone (**5a**). The propenone **3a** (5 g) was boiled with phosphoric acid for 5 h. VLC separation using RP18 and H_2O–EtOH 60:40 to 0:100 gave around 25% of the product as an oil. Anal. $C_{27}H_{36}O_6$, C, H. ^{1}H NMR ($CDCl_3$): δ 6.57 (2 H, d, *J* 2, H-6', H-2'), 6.41 (1 H, t, *J* 2, H-4'), 6.13 (1 H, d, *J* 2, H-8 or H-6), 6.07 (1 H, d, *J* 2, H-8 or H-6), 5.30 (1 H, dd, *J* 13, 3, H-2), 4.54 (4 H, m, Pr^i–CH), 2.95 (1 H, dd, *J* 16, 13, H-2), 2.73 (1 H, dd, *J* 16, 3, H-2), 1.43–1.29 (24 H, m, Pr^i–Me). ^{13}C NMR ($CDCl_3$): δ 188.3, 164.8, 164.1, 160.8, 159.3, 141.3, 106.6, 105.8, 103.3, 96.9, 94.7, 79.1, 71.6, 70.2, 70.0, 69.8, 46.0, 22.1, 22.0, 22.0, 21.9.

(±)-3',5',5,7-Tetrahydroxyflavanone (**6c**). A solution of **5a** (475 mg, 1.04 mmol) in dichloromethane (60 ml) was cooled to −80 °C under nitrogen and boron trichloride (20 ml, 1 M in dichloromethane) added. The reaction mixture was brought to room temperature, poured into water and extracted with AcOEt. After evaporation of the AcOEt extract the residue was re-extracted with AcOEt–heptane (150 ml) leaving 276 mg on evaporation. Purification on a silica gel column with 60% AcOEt in heptane gave pure almost colorless **6c** (121 mg, 40%), m.p. 208–209 °C (AcOEt–heptane). Anal. $C_{15}H_{12}O_6$, C, H. MS [E_i 70 eV; *m/z* (% rel. int.)] 288 (M^+, 100), 287 ($M^+ - 1$, 29), 271 (9), 270 (11), 217 (9), 179 (44), 153 (47), 152 (14), 136 (14), 124 (9). FAB-MS (*m*-NBA) *m/z* 289 (MH^+, 10%). UV [EtOH λ_{max} nm (log ε)] 331sh (3.20), 289 (3.84). ^{1}H NMR (DMSO-d_6): δ 5.39 (1 H, dd, *J* 12, 3, H-2), 3.09 (1 H, dd, *J* 12, 17, H-3a), 2.74 (1 H, dd, *J* 17, 3, H-3b), 5.92 (1 H, d, *J* 2, H-6 or H-8), 5.89 (1 H, d, *J* 2, H-6 or H-8), 6.33 (1 H, d, *J* 2, H-2'), 6.21 (1 H, t, *J* 2, H-4'), 6.33 (1 H, d, *J* 2, H-6'), 12.10 (1 H, s, 5-OH), 10.78 (1 H,s) and 9.34 (2 H, s) 7,3',5'-OH, 3.43 (2 H, s, H_2O). ^{1}H NMR [$(CD_3)CO$] (assignments as above): δ 5.37 (12, 3), 3.04 (12, 17), 2.75 (17, 3), 5.94 (2), 5.98 (2), 6.50 (2), 6.35 (2), 6.50 (2), 12.15, 4.5 (5 H, br, s). ^{13}C NMR (DMSO-d_6): δ 78.4 (C-2), 42.3 (C-3), 196.0 (C-4), 163.6 (C-5 or C-7), 95.1 (C-6 or C-8), 166.8 (C-5 or C-7), 96.0 (C-6 or C-8), 162.8 (C-8a), 102.0 (C-1'), 104.6 (C-2'), 158.6 (C-3'), 102.6 (C-4'), 158.6 (C-5'), 104.6 (C-6'). The ^{13}C NMR assignments were confirmed by HMQC experiments optimized for $J_{C,H}$ 120 Hz.

Acknowledgements. The present work was supported by the Danish Research Council.

References

1. Li-dong, L., Guo-wei, Q. and Ren-sheng, X. *Acta Botanica Sinica 36* (1994) 393.
2. Chan, W. L., Lin, Y. C., Zhang, W. H., Tang, P. L. and Szeto, Y. S. *Heterocycles 43* (1996) 551.
3. Su, F-T. *Hua Hsueh* 1966, No. 1, 9.
4. Iinuma, M., Tanaka, T., Mizuno, M. and Wollenweber, E. *Z. Naturforsch., Teil C 45* (1990) 135.
5. Ichino, K., Tanaka, H. and Ito, K. *J. Nat. Prod. 51* (1988) 906.
6. Iinuma, M., Iwashima, K. and Matsuura, S. *Chem. Pharm. Bull. 32* (1984) 1472.

Received March 9, 1998.