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PHENOLIC CONSTITUENTS FROM SEEDS OF *COPTIS JAPONICA* VAR. *DISSECTA*

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Key Word Index—*Coptis japonica* var. *dissecta*; Ranunculaceae, cleomiscosin A; aquillochin; 2′,4,4′-trihydroxy-6′-methoxydihydrochalcone; 7,4′-dihydroxy-5-methoxyflavanone.

Abstract—In addition to coumarinolignans (cleomiscosin A and aquillochin) and 7,4′-dihydroxy-5-methoxyflavanone, a new dihydrochalcone, 2′,4,4′-trihydroxy-6′-methoxydihydrochalcone, was isolated from the seeds of *Coptis japonica* var. *dissecta*. The structure of the dihydrochalcone was confirmed by comparison with relevant synthetic samples.

INTRODUCTION

The rhizomes of *Coptis* species are used as a Chinese crude drug for digestive problems. Previous phytochemical studies showed the occurrence of alkaloids (berberine, coptisine and magnoflorine) [1] and of flavonoids (coptiside I and II) [2]. Our preceding paper dealt with the isolation of the benzophenanthridine alkaloids, sanguinarine, norsanguinarine, oxysanguinarine and 6-acetonyl-5,6-dihydrosanguinarine [3]. In this paper, the isolation of four phenolic constituents from seeds of *C. japonica* var. *dissecta* and the confirmation by syntheses of the dihydrochalcones and the flavanones related with the natural products are discussed.

RESULTS AND DISCUSSION

Compound **1** gave a base peak in its mass spectrum of 386.0999 which agreed with a molecular formula of $C_{20}H_{18}O_8$ (386.1001). In the ^{1}H NMR spectrum, after the addition of D_2O, two peaks at 5.06 (*t*) and 9.19 (*s*) disappeared and another two at 3.39 (*ddd*) and 3.67 (*ddd*) changed to double doublets, which showed **1** contained a $-CH-CH-CH_2OH$ moiety. The ABX pattern at the region of 6.8–7.1 ppm suggested **1** also contained a trisubstituted benzene. On irradiation of the peak at 3.78 ppm of a methoxyl group, the NOE was observed at the 7.03 ppm peak (*d*, $J = 1.7$ Hz), indicating that **1** contained a coniferyl alcohol moiety. This was further supported by a fragment of *m/z* 180 in the mass spectrum. A coumarin moiety in **1** was revealed from the signals of the *cis*-olefinic protons at 6.34 and 7.96 ppm ($J = 8.2$ Hz) in the ^{1}H NMR, the absorption at 1700 cm^{-1} in the IR, and the absorption at 325 nm in the UV spectrum. The fragment of a coumarin moiety, *m/z* 208, revealed it had one methoxyl and two hydroxyl groups, and the NOE was observed at the peak (6.91 ppm *s*) on irradiation of the methoxyl at 3.78 ppm. Thus, the coumarin was identified as fraxetin. From the above spectral data, **1** was deduced to be either cleomiscosin A or B but after comparison with the authentic samples, **1** was identified as cleomiscosin A [4–8].

The ^{1}H NMR spectrum of compound **2** was similar to that of **1** except for an ABX pattern in the aromatic region. Thus, in **2**, instead of coniferyl alcohol, a sinapyl alcohol moiety was confirmed by the ^{1}H NMR data [6.75 (2H, *s* and 3.77 ppm (6H, *s*)] and supported by a fragment at *m/z* 210 in the mass spectrum. Compound **2** was therefore deduced to be aquillochin and its identity confirmed by comparison with an authentic sample [9].

In the ^{1}H NMR spectrum of compound **3**, two peaks at 2.76 and 3.16 ppm in the A_2B_2 pattern showed the presence of a moiety of $-C{=}O{-}CH_2{-}CH_2-$. Two peaks at 5.88 and 5.97 ppm (1H, each *d*, $J = 2.0$ Hz) and two other peaks at 6.66 and 7.28 ppm (2H, each *d*, $J = 8.5$ Hz) also showed *meta* coupled and *ortho* coupled benzene moieties. From the above spectral evidence, **3** was thought to be either 2′,4,4′-hydroxy-6′-methoxy- (**3**), 2′,4,6′-trihydroxy-4′-methoxy-(**4**) or 2′,4′,6′-trihydroxy-4-methoxydihydrochalcone (**5**). To clarify the structure of the naturally occurring compound and to compare the spectroscopic differences between **3**, **4** and **5**, the three dihydrochalcones were synthesized (see Experimental). Tables 1 and 2 show the physical and spectral data for synthetic **3**, **4** and **5**. The R_f values on thin-layer chromatography were quite similar to each other in the two solvent systems. It is also difficult to distinguish between **3** and **4**, from their UV and mass spectra, which are very similar. However, ^{1}H NMR spectra revealed sufficient differences among **3**, **4** and **5** to distinguish between them. Because of the symmetrical arrangement of substituents in both **4** and **5**, the protons at C-3′ and 5′ were observed as a singlet, but these protons in **3** were observed as a doublet. By comprehensive spectral comparisons, dihydrochalcone (**3**) was characterized as the new compound 2′,4,4′-trihydroxy-6′-methoxydihydrochalcone.

Compound **6** from its positive Mg–HCl reaction was considered to be a flavonoid. In the ^{1}H NMR, the signals at 2.72 (*dd*), 2.97 (*dd*) and 5.73 (*dd*) ppm were attributable to the protons at C-3 and C-2 of a flavanone with two hydroxyl and one methoxyl groups. An A_2B_2 pattern at 6.88 and 7.33 and a singlet at 6.08 ppm suggested **6** was trioxygenated at C-4′,5 and 7. No bathochromic shift was observed after addition of $AlCl_3$ in the UV, indicating that

Table 1. Comparison of the physical and spectroscopic properties of the prepared flavonoids (3–7)

	3	4	5	6	7
mp (°)	193	160	192	229 (dec.)	125
TLC					
I*	0.45	0.44	0.45	0.42	0.64
II	0.56	0.56	0.53	0.29	0.74
UV λ_{max}^{MeOH}	289(4.0)†	286(4.1)	286(4.2)	283(4.2), 310sh(3.8)	285(4.0), 325sh(3.8)
+ NaOMe	—	—	—	318	288, 365
+ $AlCl_3$	—	—	—	283, 310sh	312, 380
+ $AlCl_3$/HCl	—	—	—	283, 310sh	309, 370
+ NaOAc	—	—	—	285sh, 318	286, 320sh
NaOAc/H_3BO_3	—	—	—	283sh, 305sh	286, 320sh
EIMS (*m/z*) (rel. int.)	282(22), 167(100), 120(42)	288(29), 167(100), 120(45)	288(21), 153(46), 133(44), 121(100)	286(78), 167(100), 120(49)	286(81), 167(100), 120(43)

*Solvent systems; I $CHCl_3$–MeOH = 8:1, II: C_6H_6–Me_2CO = 2:1.
†Log ε.

Table 2. ^{1}H NMR spectral data of the prepared dihydrochalcones (3–5) and flavanones (6 and 7)

	3	4	5	6	7
2	7.01 *d* (8.3)	7.20 *d* (8.4)	7.14 *d* (8.6)	5.30 *dd* (1.20, 4.8)	5.34 *dd* (12.0, 4.5)
3	(6.66 *d* (8.3)	6.66 *d* (8.4)	6.83 *d* (8.6)	2.65 *dd* (18.0, 4.8)	2.68 *dd* (17.0, 4.5)
4	—	—	—	3.01 *dd* (18.0, 12.0)	3.15 *dd* (17.0, 12.0)
5	6.66 *d* (8.3)	6.66 *d* (8.4)	6.83 *d* (8.6)	—	—
6	7.01 *d* (8.3)	7.02 *d* (8.4)	7.14 *d* (8.6)	5.98 *d* (2.0)	6.06 *br s*
8	—	—	—	6.05 *d* (2.0)	6.06 *br s*
2′	—	—	—	7.30 *d* (9.0)	7.30 *d* (7.0)
3′	5.88 *d* (2.1)	5.94 *s*	5.82 s	6.78 d (9.0)	6.88 d (7.0)
5′	5.97 *d* (2.1)	5.94 *s*	5.80 *s*	6.78 *d* (9.0)	6.88 *d* (7.0)
6′	—	—	—	7.30 *d* (9.0)	7.30 *d* (7.0)
α	3.15 *t* (7.6)	3.25 *t* (7.7)	3.24 *t* (7.6)	—	—
β	2.75 *t* (7.6)	2.80 *t* (7.7)	2.82 *t* (7.6)	—	—
OMe	3.80 *s*	3.74 *s*	3.71 *s*	3.78 *s*	3.78 *s*
OH	9.50 *s*	9.14 *s*	10.33 *s*	9.40 *s*	12.05 *s*
OH	13.75 *s*	12.32 *s*	12.21 *s*	10.30 *br s*	—

All spectra were measured in DMSO-d_6. In parentheses *J* are shown in Hz.

the 5-position was methoxylated and thus suggesting that **6** was 7,4′-dihydroxy-5-methoxyflavanone. To confirm the structure, 7,4′-dihydroxy-5-methoxyflavone (**6**) and its isomer, 5,4′-dihydroxy-7-methoxyflavanone (**7**) were prepared. The syntheses are described in Experimental and the physical and spectral data are shown in Tables 1 and 2. By comparison of the synthetic flavanones, the naturally occurring flavanone was confirmed to have the structure **6**, which was previously isolated from *Achyrocline flaccida* [10].

EXPERIMENTAL

Mps are uncorr. MS were obtained on a JEOL JMS-D300 operating at 70 eV. ^{1}H NMR and ^{13}C NMR spectra were taken on a Hitachi Perkin-Elmer R-20B 60 MHz instrument, a JEOL JNM-GX 270 instrument at 270 MHz, and a Varian XL-300 spectrometer at 300 MHz, chemical shifts were given in δ (ppm) with tetramethylsilane as an int. standard. TLC was carried out with Kiesel-gel 60F-254 (Merck). Fujigel BW820-MH and Sephadex LH-60 were used for CC.

Extraction and isolation Fresh seeds (7 kg) were percolated successively with *n*-hexane and MeOH. The MeOH solution was concd. and chromatographed on silica gel using C_6H_6–EtOAc (30:1) as solvent system. The eluate was rechromatographed on silica gel and Sephadex LH-60 (MeOH) for further purification. As the result of recryst., **1** (5 mg), **2** (10 mg), **3** (5 mg) and **6** (20 mg) were obtained.

Cleomiscosin A **1**. Colourless needles, mp 224° (MeOH), $C_{20}H_{18}O_8$ (M_r 386). EIMS *m/z* (rel. int.): 386 (71.6), 368 (35.9), 208 (8.9), 180 (97.4), 131 (100). UV λ_{max}^{MeOH} nm (log ε): 233 (4.45), 288 (3.84), 325 (4.09). IR ν_{max}^{KBr} cm^{-1}: 3300, 1700, 1610, 1570, 1420, 1290, 1140. ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.39 (1*H*, *ddd*, *J* = 3.5, 4.3, 11.3 Hz, H-9′a), 3.67 (1H, *ddd*, *J* = 2.2, 4.3, 11.3 Hz, H-9′b), 3.78 (3H, *s*, C3′-OCH_3), 3.79 (3H, *s*, C6-OCH_3), 4.32 (1H, *ddd*, *J* = 2.2, 3.5, 7.0 Hz, H-8′), 4.99 (1H, *d*, *J* = 7.0 Hz, H-7′), 5.06 (1H, *t*, *J* = 4.3 Hz, C9′-OH), 6.34 (1H, *d*, *J* = 8.1 Hz, H-3), 6.82 (1H, *d*, *J* = 7.2 Hz, H-5′), 6.88 (1H, *dd*, *J* = 1.7, 7.2 Hz, H-6′), 6.91

(1H, *s*, H-5), 7.03 (1H, *d*, J = 1.7 Hz, H-2'), 7.96 (1H, *d*, J = 8.1 Hz, H-4), 9.19 (1H, *s*, C4'-OH). ^{13}C NMR (pyridine-d_5): δ55.9, 56.3 (each q, 2 × OCH_3), 60.8 (*t*, C9'), 77.6 (*d*, C8'), 80.0 (*d*, C7'), 101.2 (*d*, C5), 112.0 (*s*, C10), 112.4 (*d*, C2'), 113.9 (*d*, C3), 116.7 (*d*, C5'), 121.8 (*d*, C6'), 127.7 (*s*, C1'), 134.9 (*s*, C8), 136.3 (*s*, C7), 138.5 (*s*, C9), 144.6 (*d*, C4), 146.5 (*s*, C6), 149.0 (*s*, C4'), 160.9 (*s*, C3), 171.5 (*s*, C2).

Aquillochin **2**. Colourless needles, mp 195° (decomp.) (MeOH), $C_{21}H_{20}O_9$ (M_r 416). EIMS *m/z* (rel. int.): 416 (31.7), 398 (19.5), 249 (41.5), 210 (68.3), 208 (100). UV λ_{max}^{MeOH} nm (log ε): 225 sh (3.49), 315 (3.25), 383 (2.39). IR ν_{max}^{KBr} cm^{-1}: 1690, 1440. ^{1}H NMR (300 MHz, DMSO-d_6): δ3.39 (1H, *ddd*, J = 2.2, 4.3, 11.3 Hz, H-9'a) 3.66 (1H, *ddd*, J = 3.5, 4.3, 11.3 Hz, H-9'b), 3.77 (6H, *s*, C3', 5'-OCH_3), 3.78 (3H, *s*, C6-OCH_3), 4.36 (1H, *ddd*, J = 2.2, 3.5, 7.0 Hz, H-8'), 4.99 (1H, *d*, J = 7.0 Hz, H-7'), 5.06 (1H, *t*, J = 4.3 Hz, C9'-OH), 6.34 (1H, *d*, J = 8.1 Hz, H-3), 6.75 (2H, *s*, H-2', 6'), 6.91 (1H, *s*, H-5), 7.92 (1H, *d*, J = 8.1 Hz, H-4), 8.53 (1H, *s*, C4'-OH).

2',4,4'-Trihydroxy-6'-methoxydihydrochalcone **3**. Colourless needles, mp 195° (EtOH), $C_{16}H_{16}O_5$ (M_r288). For MS (see Table 1). ^{1}H NMR (300 MHz, DMSO-d_6): δ2.76 (2H, *t*, J = 7.5 Hz, H_2-β), 3.16 (2H, *t*, J = 7.5 Hz, H_2-α), 3.81 (3H, *s*, OCH_3), 5.88, 5.97 (1H, each *d*, J = 2.0 Hz, H-3' and 5'), 6.66 (2H, *d*, J = 8.5 Hz, H-3, 5), 7.28 (2H, *d*, J = 8.5 Hz, H-2, 6), 9.12, 10.62, 13.75 (1H, each *s*, 3 × OH).

Synthesis of 2',4,4'-trihydroxy-6'-methoxydihydrochalcone **3**. 4-Benzyloxy-2-hydroxy-6-methoxyacetophenone (2.2 g, 8.1 mmol) and *p*-benzyloxybenzaldehyde (**8**) (1.7 g, 8.0 mmol) were added to methylcellosolve soln. (200 ml) containing KOH (30 g), and the mixture was stirred at room temp. overnight. The reaction mixture was acidified with 20 % HCl and extracted with H_2O and EtOAc. The EtOAc extract was purified by CC on silica gel to give 4,4'-dibenzyloxy-2'-hydroxy-6'-methoxychalcone (**9**) (3.0 g, 6.4 mmol) as yellow needles, mp 133° (EtOH). EIMS *m/z* (rel. int.): 466 (10.0), 375 (5.0), 191 (4.5), 91 (100). ^{1}H NMR (60 MHz, $CDCl_3$): δ3.88 (3H, *s*, OCH_3), 5.04, 5.08 (2H, each *s*, CH_2Ph), 6.01, 6.16 (1H, each *d*, J = 2.4 Hz, H-3', 5'), 6.94, 7.53 (2H, each *d*, J = 9.0 Hz, H-2, 3, 5, 6), 7.37 (10 H, br *s*, 2 × Ph), 7.45 (2H, *s*, H-α and β), 14.31 (1H, *s*, OH). The chalcone **9** (1.5 g 3.2 mmol) was debenzylated and reduced with Pd–C/H_2 (atmospheric pressure) in EtOAc (100 ml) for 6 hr and purified by silica gel chromatography to give 2',4,4'-trihydroxy-6'-methoxydihydrochalcone (**3**) (0.7 g, 2.4 mmol) as colourless needles from EtOH. Physical and spectral data are shown in Tables 1 and 2.

Synthesis of 2',4,6'-trihydroxy-4'-methoxydihydrochalcone **4**. 2,6-Diisopropyloxy-4-methoxyacetophenone (0.6 g, 2.1 mmol) and *p*-isopropyloxybenzaldehyde (0.3 g, 2.1 mmol) were condensed to give 2',4,6'-triisopropyloxy-4'-methoxychalcone (0.7 g, 1.7 mmol) as an orange oil. EIMS *m/z* (rel. int.): 412 (78.9), 392 (20.0), 167 (100), 120 (48.9). ^{1}H NMR (60 MHz, $CDCl_3$): δ1.20 (12H, *d*, J = 6.0 Hz, 2 × Me_2), 1.32 (6H, *d*, J = 6.0 Hz, Me_2), 3.78 (3H, *s*, OCH_3), 4.43 [3H, *m*, J = 6.0 Hz, 3 × $CH(Me)_2$], 6.11 (2H, *s*, H-3', 5'), 6.71, 7.22 (1H, each *d*, J = 15.0 Hz, H-α and β), 6.85, 7.45 (2H, each *d*, J = 7.5 Hz, H-2, 3, 5, 6). The resulting chalcone (0.7 g, 1.7 mmol) was reduced with Pd-C/H_2 in EtOAc for 3 hr to give 2',4,6'-triisopropyloxy-4'-methoxydihydrochalcone (0.5 g, 1.2 mmol) as an orange oil. EIMS *m/z* (rel. int.): 414 (12.9), 355 (4.9), 167 (100), 120 (48.8). ^{1}H NMR (60 MHz, $CDCl_3$): δ1.26 (18H, *d*, J = 6.0 Hz, 3 × Me_2), 2.96 (4H, *br s*, H_2-α and β), 3.70 (3H, *s*, OCH_3), 4.48 [3H, *m*, J = 6.0 Hz, 3 × $CH(Me)_2$], 6.14 (2H, s, H-3', 5'), 6.80, 7.15 (2H, each *d*, J = 8.2 Hz, H-2, 3, 5, 6). The reduced chalcone (0.7 g, 1.2 mmol) in CH_2Cl_2 (30 ml) was cooled and treated with BCl_3 (2 ml) in CH_2Cl_2 (10 ml) at −70°C. The soln was allowed to warm room temp. poured into H_2O (100 ml) and the mixture extracted with EtOAc. The conc. EtOAc extract was recryst. from EtOH to give 2',4,6'-trihydroxy-4'-methoxydihydrochalcone (**4**) (0.3 g, 1.0 mmol) as colourless needles.

Synthesis of 2',4',6'-trihydroxy-4-methoxydihydrochalcone **5**. 4,6-Dibenzyloxy-2-hydroxyacetophenone (0.8 g, 2.4 mmol) and *p*-methoxybenzaldehyde (0.3 g, 2.2 mmol) were condensed to give 4',6'-dibenzyloxy-2'-hydroxy-4-methoxychalcone (0.8 g, 1.7 mmol) as yellow needles, mp 138° from EtOH. EIMS *m/z* (rel. int.): 466 (86.6), 375 (100), 161 (97.7), 121 (72.2). ^{1}H NMR (270 MHz, $CDCl_3$): δ3.83 (3H, *s*, OCH_3), 5.06, 5.10 (2H, each *s*, CH_2Ph), 6.17, 6.22 (1H, each *d*, J = 2.3 Hz, H-3', 5'), 6.71, 7.02 (2H, each *d*, J = 8.8 Hz, H-2, 3, 5, 6), 7.35–7.67 (10H, m, 2 × Ph), 7.70, 7.80 (1H, each *d*, J = 15.4 Hz, H-α and β), 14.70 (1H, *s*, OH). The resulting dihydrochalcone (0.8 g, 1.4 mmol) was debenzylated and recduced with Pd-C/H_2 in EtOAc for 6 hr to give 2',4',6'-trihydroxy-4-methoxydihydrochalcone (**5**) (0.4 g, 1.4 mmol) as colourless needles from EtOH.

7,4'-Dihydroxy-5-methoxyflavanone **6**. Colourless needles, mp 232° (decomp.) (MeOH), $C_{16}H_{14}O_5$ (M_r 286). For MS and UV data see Table 1. IR ν_{max}^{KBr} cm^{-1}: 1600, 1590, 1450, 1210, 1100. ^{1}H NMR (60 MHz, DMSO-d_6): δ2.72 (1H, *dd*, J = 4.5, 18.0 Hz, H-3a), 2.97 (1H, *dd*, J = 12.0, 18.0 Hz, H-3b), 3.84 (3H, *s*, OCH_3), 5.73 (1H, *dd*, J = 4.5, 12.0 Hz, H-2), 6.08 (2H, br *s*, H-6, 8), 6.88 (2H, *d*, J = 8.3 Hz, H-3', 5'), 7.33 (2H, *d*, J = 8.3 Hz, H-2', 6'), 9.30, 10.24 (1H, each br *s*, OH).

Synthesis of 5,4'-dihydroxy-7-methoxyflavanone **7**. Compound **7** was prepared in a similar way to **6**, by condensation of 2-hydroxy-4,6-dimethoxyacetophenone (2.0 g, 9.4 mmol) and **6** (2.0 g, 9.4 mmol) to give 4-benzyloxy-2'-hydroxy-4',6'-dimethoxychalcone (3.0 g, 7.7 mmol) as yellow needles mp 130° from EtOH. EIMS *m/z* (rel. int.): 390 (20.0), 197 (10.0), 91 (100). ^{1}H NMR (60 MHz, $CDCl_3$): δ3.82, 3.90, (3H, each *s*, OCH_3), 5.15 (2H, *s*, CH_2Ph), 5.97, 6.13 (1H, each *d*, J = 2.4 Hz, H-3', 5'), 7.02, 7.58 (2H, each *d*, J = 9.0 Hz, H-2, 3, 5, 6), 7.43 (5H, *s*, Ph), 7.82 (2H, *br s*, H-α and β), 14.43 (1H, *s*, OH). On treatment with phosphoric acid, the chalcone (3.0 g, 7.7 mmol) was converted to 4'-benzyloxy-5,7-dimethoxyflavanone (1.2 g, 3.1 mmol), mp 159° (EtOH), pale yellow plates. EIMS *m/z* (rel. int.) 390 (15.0), 180 (8.5), 91 (100). ^{1}H NMR (60 MHz, $CDCl_3$): δ2.65 (1H, *dd*, J = 4.8, 16.5 Hz, H-3a), 3.02 (1H, *dd*, J = 12.0, 16.5 Hz, H-3b), 3.78, 3.86 (3H, each *s*, OCH_3), 5.07 (1H, *s*, CH_2Ph), 5.33 (1H, *dd*, J = 4.8, 12.0 Hz, H-2), 6.07, 6.13 (1H, each *d*, J = 1.8 Hz, H-6, 8), 6.98, 7.37 (2H, each *d*, J = 9.0 Hz, H-2', 3', 5', 6'), 7.39 (5H, *s*, Ph). The above flavanone (1.2 g, 3.1 mmol) was debenzylated with Pd–C/H_2 (atmospheric pressure) to give 5,7-dimethoxyflavanone (0.6 g, 2.0 mmol) as colourless mp 158°, from EtOH. EIMS *m/z* (rel. int.): 300 (70.0), 181 (100), 120 (35.8). ^{1}H NMR (60 MHz, DMSO-d_6): δ2.57 (1H, *dd*, J = 4.8, 16.5 Hz, H-3a), 3.01 (1H, *dd*, J = 12.0, 16.5 Hz, H-3b), 3.80, 3.83 (3H, each *s*, OCH_3), 5.35 (1H, *dd*, J = 4.8, 12.0 Hz, H-2), 6.12 (2H, *br s*, H-6, 8), 6.83, 7.30 (2H, each *d*, J = 9.0 Hz, H-2', 3', 5', 6'), 9.22 (1H, *s*, OH). The debenzylated flavanone (0.6 g, 2.0 mmol) in CH_2Cl_2 (30 ml) was cooled, treated with BCl_3 (0.5 ml) at −70° and worked up in the same manner as far **4** plus silica gel CC to give 5,4'-dihydroxy-7-methoxy-flavanone (0.3 g, 1.0 mmol) as colourless needles from EtOH.

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