Six New 2-(2-Phenylethyl)chromones from Agarwood

Tenji KONISHI,*[,a] Takao KONOSHIMA,[a] Yasuo SHIMADA,[b] and Shiu KIYOSAWA[a]

Kyoto Pharmaceutical University,[a] Nakauchi-cho, Misasagi, Yamashina-ku, Kyoto 607–8414, Japan and Mitsuboshi Pharmaceutical Co.,[b] Gose 639–2216, Japan. Received September 20, 2001; accepted December 6, 2001

Six new chromones, 6-methoxy-2-[2-(3-methoxy-4-hydroxyphenyl)ethyl]chromone (2), 6,8-dihydroxy-2-(2-phenylethyl)chromone (3), 6-hydroxy-2-[2-(4-hydroxyphenyl)ethyl]chromone (4), 6-hydroxy-2-[2-(2-hydroxyphenyl)ethyl]chromone (5), 7-hydroxy-2-(2-phenylethyl)chromone (6), and 6-hydroxy-7-methoxy-2-(2-phenylethyl)chromone (7) were isolated from the ether extract of agarwood in addition to a known compound, 2-(2-phenylethyl)chromone or flidersiachromone (1). Their structures were determined by spectroscopic methods including UV, IR, and NMR spectral data and comparisons with the calculated values using the hydroxyl and methoxyl substituent increments of the chromone ring.

Key words *Aquilaria malaccensis*; Aquilariaceae; agarwood; 2-(2-phenylethyl)chromone; flidersiachromone

From ancient times, agarwood ("jinkoh" in Japanese) has been used as incense in the Orient. About 40 years ago, Indian chemists isolated and characterized several sesquiterpenes from agarwood originating from *Aquilaria agallocha* ROXB. (Aquilariaceae),[1—4] and almost 20 years ago, Japanese researchers isolated many sesquiterpenes from two types of agarwood, the first probably *Aquilaria malaccensis* LAM., and the second called kanankoh in Japan.[5—7] An oxygenated chromone derivative has been reported as another constituent of agarwood[8] and Chinese researchers isolated two new chromone derivatives in 1989 and 1990.[9,10]

In the course of our studies to evaluate the quality of agarwood products, we have reported the structures of many kinds of 2-(2-phenylethyl)chromone derivatives.[11—13] In the present paper, we describe the isolation and structure elucidation of six new 2-(2-phenylethyl)chromones (**2**—**7**) from agarwood, together with those of a known 2-(2-phenylethyl)-chromone (**1**), flidersiachromone.[14,15]

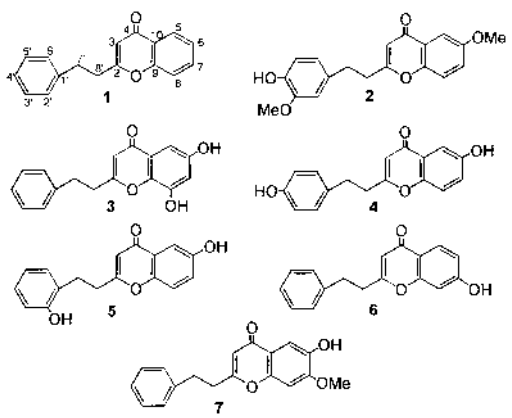
Results and Discussion

The ether extract of agarwood was purified by silica gel column chromatography to yield compounds **1**—**7**. The known compound **1** was identified as 2-(2-phenylethyl)-chromone, flidersiachromone, by comparison of the physical and spectral data with those already reported.[14,15]

Compound **2** had the molecular formula $C_{19}H_{18}O_5$ as determined by high-resolution electron impact-MS (HR-EI-MS). The presence of hydroxyl (3200 cm^{-1}), unsaturated carbonyl and olefin (1628, 1582 cm^{-1}), ether (1124 cm^{-1}), and phenyl groups (1476, 1458, 1236, 839, 824 cm^{-1}) in the molecule were determined from the IR spectrum. The UV spectrum showed the presence of an α,β-unsaturated carbonyl group owing to the distinct absorption maxima at 242 and 322 nm. ^{1}H-NMR spectrum (Table 1) of **2** showed the presence of two methoxyl groups at δ_H 3.82 and 3.89 (each 3H, s), one broad hydroxyl signal at δ_H 5.61, and two sets of ABX coupling systems at δ_H 6.67 (1H, d, J=2.0 Hz, H-6′), 6.70 (1H, dd, J=2.0, 8.0 Hz, H-5′), and 6.84 (1H, d, J=8.0 Hz, H-2′) and one at δ_H 7.25 (1H, dd, J=3.0, 9.0 Hz, H-7), 7.38 (1H, d, J=9.0 Hz, H-8), and 7.55 (1H, d, J=3.0 Hz, H-5). The ^{13}C-NMR spectrum (Table 2) of **2** displayed the presence of two methylene groups at δ_C 32.8 and 36.5, a trisubstituted double bond at δ_C 109.5 (d) and 168.4, two methoxyl groups at δ_C 55.8 and 55.9, and a carbonyl group at δ_C 178.2. Based on these findings, compound **2** was presumed to be a 2-(2-phenylethyl)chromone derivative with one hydroxyl and two methoxyl groups. The heteronuclear multiple-bond correlation (HMBC) spectroscopy and nuclear Overhauser and exchange spectroscopy (NOESY) correlations shown in Fig. 1 determined the positions of two methoxyl groups and the hydroxyl group in C-6, C-3′ and C-4′, respectively. These indications were confirmed by the agreement of the ^{13}C-NMR data with the calculated values shown in Table 2 using the hydroxyl and methoxyl substituent increments of the chromone ring described previously,[13] and the substituted effects in monosubstituted benzenes.[16] Consequently, compound **2** was established to be 6-methoxy-2-[2-(3-methoxy-4-hydroxyphenyl)ethyl]chromone.

Compound **3**, $C_{17}H_{14}O_4$, indicated the presence of a hydroxyl group in the IR spectrum. The ^{1}H-NMR (Table 1) spectrum of **3** was similar to that of **1** except for the signals of two *meta*-coupled doublets at δ_H 7.35 and 7.73 (each 1H, d, J=2.8 Hz) in the chromone ring moiety. Thus it was inferred that compound **3** was the same chromone derivative with additional hydroxyl groups. The locations of hydroxyl groups were assigned at C-6 (δ_C 156.5) and C-8 (δ_C 149.4) by comparison with the ^{13}C-NMR data of **1** and the calculated values shown in Table 2. Consequently, the structure of **3** was determined to be 6,8-dihydroxy-2-(2-phenylethyl)-chromone.

Compound **4** was suggested to be the same chromone derivative with hydroxyl groups as **3** by the IR, UV, and HR-EI-MS spectra. Its ^{1}H- and ^{13}C-NMR spectra (Tables 1 and 2)



* To whom correspondence should be addressed. e-mail: konishi@mb.kyoto-phu.ac.jp

showed the presence of an ABX coupling system [δ_H 8.06 (1H, dd, J=0.3, 2.5 Hz); δ_C 109.0, δ_H 7.50 (1H, dd, J=2.5, 9.0 Hz); δ_C 123.5, δ_H 7.54 (1H, dd, J=0.3, 9.0 Hz); δ_C 119.8], and an A_2B_2 coupling system at δ_H 7.15; δ_C 116.4, and δ_H 7.22; δ_C 129.9 (each, 2H, d, J=8.5 Hz). Two hydroxyl groups were located at C-6 or C-7 in the chromone ring moiety, and at C-4′ in the phenylethyl moiety. The carbon signals

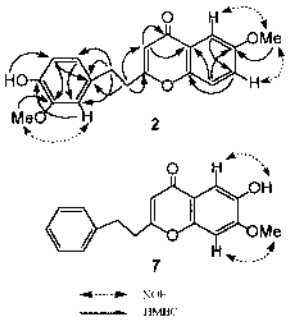


Fig. 1. The Principal NOE and HMBC Correlations of **2** and **7**

showed excellent agreement with the calculated values, as shown in Table 2. Thus compound **4** was determined to be 6-hydroxy-2-[2-(4-hydroxyphenyl)ethyl]chromone.

The MS, IR, and NMR spectra indicated that compound **5** was another dihydroxyl derivative of 2-(2-phenylethyl)-chromone. These spectral data for **5** were very similar to those of **4** except for the difference in the substitution site for the hydroxyl group in the phenylethyl moiety, with the former being a *ortho*-hydroxyphenyl group [δ_H 6.92 (1H, ddd, J=1.5, 7.5, 7.5 Hz), 7.15 (1H, dd, J=1.5, 7.5 Hz), 7.22 (1H, ddd, J=1.5, 7.5, 7.5 Hz), 7.29 (1H, dd, J=1.5, 7.5 Hz)], while the latter was a *para*-hydroxyphenyl derivative. This was supported by the agreement of the ^{13}C-NMR data with the calculated values, as shown in Table 2. Consequently, compound **5** was established to be 6-hydroxy-2-[2-(2-hydroxyphenyl)-ethyl]chromone.

The IR spectrum of **6**, $C_{17}H_{14}O_3$, showed a hydroxyl absorption band (3326 cm^{-1}). The ^{1}H-NMR spectrum showed the signals of the ABX coupling system at δ_H 6.89 (1H, d, J=2.2 Hz), 6.95 (1H, dd, J=2.2, 8.6 Hz), and 8.06 (1H, d,

Table 1. ^{1}H-NMR (300 MHz) Data for Compounds **2**—**7** (TMS=0)[a)]

Proton	**2** ($CDCl_3$)	**3** (C_5D_5N)	**4** (C_5D_5N)	**5** (C_5D_5N)	**6** ($CDCl_3$)	**7** (C_5D_5N)
3	6.16 s	6.35 s	6.35 s	6.42 s	6.12 s	6.32 s
5	7.55 d (3.0)	7.73 d (2.8)	8.06 dd (0.3, 2.5)	8.06 dd (0.3, 2.5)	8.06 d (8.6)	8.12 s
6					6.95 dd (2.2, 8.6)	
7	7.25 dd (3.0, 9.0)	7.35 d (2.8)	7.50 dd (2.5, 9.0)	7.46 dd (2.5, 9.0)		
8	7.38 d (9.0)		7.54 dd (0.3, 9.0)	7.49 dd (0.3, 9.0)	6.89 d (2.2)	7.14 s
7′	2.97 (2H) m	2.94 (2H) m	2.97 (2H) m	3.29 (2H) m	3.03 (2H) m	3.01 (2H) m
8′	2.90 (2H) m	2.81 (2H) m	2.88 (2H) m	3.08 (2H) m	2.91 (2H) m	2.88 (2H) m
2′—6′	6.67 d (2.0)	7.1—7.3 (5H) m	7.15 (2H) d (8.5)	6.92 ddd (1.5, 7.5, 7.5)	7.17—7.32 (5H) m	7.22—7.36 (5H) m
	6.70 dd (2.0, 8.0)		7.22 (2H) d (8.5)	7.15 dd (1.5, 7.5)		
	6.84 d (8.0)			7.22 ddd (1.5, 7.5, 7.5)		
				7.29 dd (1.5, 7.5)		
OH	5.61 br s	12.3 br s				11.9 br s
		12.7 br s				
OMe	3.82 s					3.98 s
	3.89 s					

a) Expressed as δ values in ppm, with J values in Hz in parentheses.

Table 2. ^{13}C-NMR (75 MHz) Data for Compounds **1**—**7** (TMS=0)[a)]

Carbon	**1** ($CDCl_3$)	**2** ($CDCl_3$)	**3** (C_5D_5N)	**4** (C_5D_5N)	**5** (C_5D_5N)	**6** ($CDCl_3$)	**7** (C_5D_5N)
2	168.4	168.4	167.8	168.6	169.2	168.6	167.5
3	109.5	109.5	109.4	109.4	109.3	109.6	109.7
4	178.2	178.2	178.0	177.8	177.8	178.2	177.2
5	104.8	104.8 (102.1)	99.1 (103.1)	109.0 (106.5)	108.9 (106.5)	127.4 (126.9)	109.1 (108.4)
6	156.8	156.8 (158.8)	156.5 (157.7)	156.2 (155.5)	156.1 (155.5)	114.9 (115.6)	146.7 (144.8)
7	133.5	123.6 (124.3)	109.5 (116.0)	123.5 (123.4)	123.3 (123.4)	161.8 (162.5)	154.2 (153.4)
8	117.8	119.2 (118.4)	149.4 (149.0)	119.8 (119.0)	119.6 (119.0)	102.9 (102.3)	100.5 (100.8)
9	156.4	151.3 (151.8)	140.6 (143.3)	150.6 (150.2)	150.7 (150.2)	158.4 (158.4)	151.8 (152.0)
10	123.7	124.2 (124.0)	126.4 (123.5)	125.4 (125.1)	127.5 (125.1)	115.0 (117.7)	118.3 (119.2)
1′	139.7	131.6 (135.4)	141.6 (141.7)	130.9 (134.3)	128.8 (128.9)	139.7 (141.7)	140.8 (141.7)
2′	128.6	114.5 (116.7)	128.8 (128.5)	129.9 (129.9)	156.8 (155.4)	128.6 (128.5)	129.0 (128.5)
3′	128.2	144.2 (140.8)	128.6 (128.3)	116.4 (115.5)	115.7 (115.5)	128.3 (128.3)	128.8 (128.3)
4′	126.5	146.5 (144.5)	126.7 (125.9)	157.5 (152.8)	128.1 (127.3)	126.6 (125.9)	126.8 (125.9)
5′	128.2	110.8 (115.3)	128.6 (128.3)	116.4 (115.5)	119.8 (120.9)	128.3 (128.3)	128.8 (128.3)
6′	128.6	120.9 (122.1)	128.8 (128.5)	129.9 (129.9)	130.6 (129.9)	128.6 (128.5)	129.0 (128.5)
7′	33.0	32.8	33.1	32.4	32.4	33.0	33.1
8′	36.1	36.5	35.9	36.5	36.5	36.0	35.9
OMe		55.8					55.3
		55.9					

a) Expressed as δ values in ppm, calculated values shown in parentheses.

J=8.6 Hz) in the chromone ring. The only significant difference between the ^{13}C-NMR spectra of **6** and **1** was in the resonance for C-7: a singlet at δ_C 161.8 for **6** *vs.* a doublet at δ_C 133.5 for **1**. This is consistent with the presence of a hydroxyl group at C-7 in **6**. Thus compound **6** was confirmed to be the 7-hydroxy-2-(2-phenylethyl)chromone.

Comparison of ^{1}H- and ^{13}C-NMR spectra with those of **6** showed that compound **7**, $C_{18}H_{16}O_4$, differed from **6** only in an additional methoxyl group (δ_H 3.98) on the chromone ring. The ^{1}H-NMR spectrum exhibited two singlet protons at δ_H 8.12 and 7.14, which are assumed to be located at C-5 and C-8. The position of the methoxyl group was confirmed by the observation of NOE correlations between H-8 and the methoxyl group in the difference NOE experiment. The agreement of the ^{13}C-NMR data with the calculated values supports the conclusion that **7** is 6-hydroxy-7-methoxy-2-(2-phenylethyl)chromone.

The 2-(2-phenylethyl)chromones identified in this paper (**2**—**7**) and previous studies[11—13] were all isolated from the resinous tissues of the agarwood *A. malaccensis* ("jinkoh"). Such chromones have not been isolated from the nonresinous tissues of the genus of *Aquilaria*, except for the two 2-(2-phenylethyl)chromones that have been isolated from the roots of *Aquilaria sinensis*.[9,10] The application of the calculated values described previously is very useful for the structure elucidation of new chromone derivatives using the only one-dimensional (1D) NMR measurements without 2D NMR experiments.

Experimental

IR spectra were obtained using a Shimadzu FT-IR-8100A spectrometer with samples prepared as a KBr disk. UV spectra were recorded on a Shimadzu UV-1600 spectrophotometer. EI-MS (ionization voltage, 70 eV) were measured using a JEOL MS-BU 20 spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian XL-300 spectrometer. Chemical shifts were expressed in δ (ppm) downfield from tetramethylsilane (TMS) as an internal standard, and coupling constants (J) were reported in Hertz (Hz). The NMR spectra data of compounds **3**—**5** and **7** were recorded in C_5D_5N, because these compounds did not dissolve in $CDCl_3$. HMBC and NOESY data were recorded on a Varian UNITY *INOVA* 400NB spectrometer. Column chromatography was performed on silica gel 60 (70—230 mesh, Merck). TLC was carried out on precoated silica gel 60 F_{254} plates (0.25 mm thick, Merck), and spots were detected by illumination with an ultraviolet lamp or spraying 2% H_2SO_4–MeOH, followed by heating.

Plant Material Agarwood was purchased from a drug market in Hong Kong. This agarwood was imported *via* Singapore from Kalimantan Island, Indonesia. The source plant belongs to the genus *Aquilaria* and has been identified by Mr. K. Gotoh (Medicinal Plant Garden, Kyoto Pharmaceutical University, Kyoto, Japan) as *A. malaccensis* Lam. A voucher specimen (KP-1979123) is deposited in the herbarium of Kyoto Pharmaceutical University.

Extraction and Isolation Powdered agarwood (245.0 g) was extracted 3 times with ether (1 l) under reflux for 3 h. The combined filtrate was concentrated under reduced pressure to give a brown viscous ether extract (36.8 g). The residual plant material was refluxed for 3 h in acetone, yielding the acetone extract (45.0 g). The ether extract (36.8 g) was adsorbed onto silica gel. The preliminary silica gel column chromatography of the ether extract of the powdered agarwood has been reported previously.[13] Rechromatography of fraction 6 (1.5 g) collected from the preliminary column chromatography with hexane–AcOEt (1 : 1) on silica gel (100 g) with hexane–AcOEt (1 : 2) afforded four fractions 6-1—6-4. Fraction 6-1 (457.6 mg) was subjected to silica gel column chromatography with hexane–AcOEt (2 : 3) to give compounds **3** (42 mg), **4** (18.9 mg), and **5** (71.9 mg) as well as flidersiachromone (**1**, 10.7 mg). The physical and spectral data of **1** were in good agreement with those reported in the literature. Fraction 6-2 (570.0 mg) was separated as described above for fraction 6-1 to afford compound **2** (10 mg). Fraction 6-3 (430.5 mg) was further separated by silica gel column chromatography with hexane–acetone (4 : 1) to yield pure compounds **6** (17.6 mg) and **7** (3.1 mg).

6-Methoxy-2-[2-(3-methoxy-4-hydroxyphenyl)ethyl]chromone (**2**): Colorless needles, mp 152—153 °C (MeOH). UV (MeOH) λ_{max} nm (ε): 228 (30241), 242.0 (26636), 274 (8035), 322 (6136). IR (KBr) ν_{max}: 3200 (OH), 1628, 1582 (γ-pyrone), 1476, 1458, 1236, 1124, 972, 839, 824 cm^{-1}. EI-MS *m/z* (rel. int.): 326 $[M]^+$ (16.6), 310 (7.5), 190 (100), 137 (29.8), 91 (32.1), 77 (5.8); HR-EI-MS *m/z*: 326.1149 $[M]^+$ (Calcd for $C_{19}H_{18}O_5$: 326.1154). The ^{1}H- and ^{13}C-NMR spectral data are given in Tables 1 and 2, respectively.

6,8-Dihydroxy-2-(2-phenylethyl)chromone (**3**): Colorless needles, mp 218—220 °C (MeOH). UV (MeOH) λ_{max} nm (ε): 204 (25568), 244.5 (26062), 263.0 (11750), 338.0 (4254). IR (KBr) ν_{max}: 3310 (OH), 1634, 1592 (γ-pyrone), 1554, 1490, 1399, 1300, 1142, 852, 839 cm^{-1}. EI-MS *m/z* (rel. int.): 282 $[M]^+$ (18.2), 176 (2.4), 91 (100); HR-EI-MS *m/z*: 282.0898 $[M]^+$ (Calcd for $C_{17}H_{14}O_4$: 282.0892). The ^{1}H- and ^{13}C-NMR spectral data are given in Tables 1 and 2, respectively.

6-Hydroxy-2-[2-(4-hydroxyphenyl)ethyl]chromone (**4**): Colorless needles, mp 215—218 °C (MeOH). UV (MeOH) λ_{max} nm (ε): 227.5 (36052), 240.0 (27427), 273 (8930), 328.5 (7003). IR (KBr) ν_{max}: 3326 (OH), 1635, 1626 (γ-pyrone), 1589, 1516, 1472, 1226, 978, 843, 822 cm^{-1}. EI-MS *m/z* (rel. int.): 282 $[M]^+$ (30.3), 176 (100), 147 (73), 137 (15.09), 107 (69.7), 91 (33.4), 77 (14.3); HR-EI-MS *m/z*: 282.0895 $[M]^+$ (Calcd for $C_{17}H_{14}O_4$: 282.0892). The ^{1}H- and ^{13}C-NMR spectral data are given in Tables 1 and 2, respectively.

6-Hydroxy-2-[2-(2-hydroxyphenyl)ethyl]chromone (**5**): Colorless needles, mp 185—186 °C (MeOH). UV (MeOH) λ_{max} nm (ε): 226.5 (29174), 243.4 (23253), 274 (8434), 329 (6255). IR (KBr) ν_{max}: 3279 (OH), 1635, 1595 (γ-pyrone), 1483, 1370, 1285, 1246, 1208, 1034, 966, 849, 839 cm^{-1}. EI-MS *m/z* (rel. int.): 282 $[M]^+$ (37.7), 176 (100), 137 (29.6), 107 (22.2), 91 (20.4), 77 (12.3); HR-EI-MS *m/z*: 282.0888 $[M]^+$ (Calcd for $C_{17}H_{14}O_4$: 282.0892). The ^{1}H- and ^{13}C-NMR spectral data are given in Tables 1 and 2, respectively.

7-Hydroxy-2-(2-phenylethyl)chromone (**6**): Colorless needles, mp 163—164 °C (MeOH). UV (MeOH) λ_{max} nm (ε): 207 (20287), 242 (13336), 249 (13424), 280 (6898), 296 (6703). IR (KBr) ν_{max}: 3326 (OH), 1636, 1576 (γ-pyrone), 1456, 1395, 1250, 1175, 1093, 993, 849 cm^{-1}. EI-MS *m/z* (rel. int.): 266 $[M]^+$ (48.9), 249 (3.3), 137 (8.5), 121 (2.2), 91 (100), 65 (4.9); HR-EI-MS *m/z*: 266.0940 $[M]^+$ (Calcd for $C_{17}H_{14}O_3$: 266.0943). The ^{1}H- and ^{13}C-NMR spectral data are given in Tables 1 and 2, respectively.

7-Hydroxy-8-methoxy-2-(2-phenylethyl)chromone (**7**): Colorless needles, mp 187—188 °C (MeOH). UV (MeOH) λ_{max} nm (ε): 207 (34932), 234 (27118), 279 (9976), 322 (10687). IR (KBr) ν_{max}: 3320 (OH), 1630, 1586 (γ-pyrone), 1472, 1458, 1390, 1270, 1264, 1218, 1200, 1197, 1082, 847 cm^{-1}. EI-MS *m/z* (rel. int.): 296 $[M]^+$ (60.5), 190 (4.1), 167 (3.1), 121 (3.8), 91 (100), 65 (4.5); HR-EI-MS *m/z*: 296.1041 $[M]^+$ (Calcd for $C_{18}H_{16}O_4$: 296.1048). The ^{1}H- and ^{13}C-NMR spectral data are given in Tables 1 and 2, respectively.

Acknowledgment The authors are grateful to Dr. M. Tsushima (Kyoto Pharmaceutical University) for MS measurements.

References

1) Jain T. C., Bhattacharyya S. B., *Tetrahedron Lett*., **1959**, 13—17.
2) Maheshwari M. L., Jain T. C., Vates R. B., Bhattacharyya S. C., *Tetrahedron*, **19**, 1079—1090 (1963).
3) Maheshwari M. L., Varma K. R., Bhattacharyya S. C., *Tetrahedron*, **19**, 1519—1525 (1963).
4) Varma K. R., Maheshwari M. L., Bhattacharyya S. C., *Tetrahedron*, **21**, 115—138 (1965).
5) Nakanishi T., Yamagata E., Yoneda K., Miura I., *Phytochemistry*, **20**, 1597—1599 (1981).
6) Nakanishi T., Yamagata E., Yoneda K., Miura I., Mori H., *J. Chem. Soc., Perkin Trans. 1*, **1983**, 601—604.
7) Nakanishi T., Yamagata E., Yoneda K., Nagashima T., Kawasaki I., Yoshida T., Mori H., Miura I., *Phytochemistry*, **23**, 2066—2067 (1984).
8) Yoshii E., Koizumi T., Oribe T., Takeuchi F., Kubo K., *Tetrahedron Lett*., **1978**, 3921—3924.
9) Yang J.-S., Wang Y. L., Su Y. L., *Yaoxue Xuebao*, **24**, 678—683 (1989).
10) Yang J.-S., Wang Y. L., Su Y. L., *Yaoxue Xuebao*, **25**, 186—190 (1990).
11) Konishi T., Sugimoto A., Kiyosawa S., Fujiwara Y., *Chem. Pharm. Bull*., **40**, 778—779 (1992).
12) Konishi T., Iwagoe K., Kiyosawa S., Fujiwara Y., *Phytochemistry*, **28**, 3548—3550 (1989).
13) Shimada Y., Tominaga T., Konishi T., Kiyosawa S., *Chem. Pharm.*

Bull., **30**, 3791—3795 (1982).
14) Hashimoto K., Nakahara S., Inoue T., Sumida Y., Takahashi M., Masada Y., *Chem. Pharm. Bull*., **33**, 5088—5091 (1985).
15) Picker K., Ritchie E., Taylor W. C., *Aust. J. Chem*., **29**, 2023—2036 (1976).
16) Kalinowski H.-O., Berger S., Braun S., "Carbon-13 NMR Spectroscopy," John Wiley & Sons, New York, 1988, pp. 313—317.