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Total synthesis of syringalide B, a phenylpropanoid glycoside

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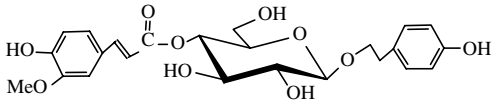
Abstract—The first total synthesis of syringalide B, 2-(4-hydroxyphenyl)ethyl 4-*O*-[(*E*)-feruloyl]-β-D-glucopyranoside, is described. The hydroxyl groups were protected with allyloxycarbonyl (Aoc) and allyl groups, which successfully prevent the migration of the feruloyl group during the deblocking procedure.

Keywords: Phenylpropanoid glycoside; Syringalide B; Allyloxycarbonyl group (Aoc); Synthesis

1. Introduction

Phenylpropanoid glycosides exist widely in various herbal plants, and most of them possess strong biological activities such as, antiviral, antimicrobial, hepatoprotective, antitumor, antifungal, plus improved immune function, and sedative effect.[1–6] More than 100 phenylpropanoid glycosides have already been isolated and identified by spectral and chemical conversions. However, the low content of phenylpropanoid glycosides in most plant species has limited further investigation of their activities, and the chemical synthesis of phenylpropanoid glycosides is thus important. In previous papers, we have reported the total synthesis of phenylpropanoid glycosides with a monosaccharide residue: grayanoside A,[7] osmanthuside B6,[8] and a disaccharide phenylpropanoid glycoside, eutigoside A.[9] Recently, the total syntheses of aceteoside,[10] isoacteoside,[11] verbascoside,[12] and conandroside[13] have been reported.

Syringalide B, a monosaccharide phenylpropanoid glycoside, was isolated from the leaves of *Syringe reticulata*.[14] After completion of the total synthesis of grayanoside A,[7] an isomer of syringalide B, we endeavored to prepare **1** similarly. Unfortunately, our attempts were frustrated by the migration of the feruloyl group from the 4-*O* to the 6-*O*-position of the sugar ring during removal of the chloroacetyl group under basic conditions.[7] Herein, we successfully completed the total synthesis of syringalide B, after protection of the hydroxyl groups with allyloxycarbonyl (Aoc) and allyl groups.



Syringalide B

2. Results and discussion

Protective-group manipulation plays an important role in the synthesis of phenylpropanoid glycosides. After consideration of all the functional groups present in the syringalide B, we choose the allyl or allyloxycarbonyl group[15] to protect both the alcoholic and the phenolic hydroxyl groups because they can be readily installed and removed under mild conditions.

The synthetic route for syringalide B is as follows (Fig. 1 and Scheme 1):

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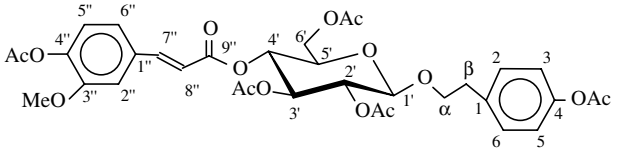


Figure 1. Pentaacetate of compound **1**.

2-(4-Allyloxyphenyl)ethyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**2**), an important intermediate for the total synthesis, was prepared following a known procedure.[7] Allylation of compound **2** with allyl bromide–NaH in DMF afforded compound **3** in high yield, and treatment with 80% acetic acid removed the benzylidene group to give the diol **4** (74.1%). The primary OH group of the diol was selectively protected with the Aoc group (yield 92%), using allyl 1-benzotriazoyl carbonate (AocOBt),[16] which was prepared and used in situ in our laboratory. The coupling of **5** and 4-*O*-allylferulic acid[7] was performed in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) in CH_2Cl_2 at 0 °C. The structure of compound **6** was confirmed by IR (1710 cm^{-1}) and by NMR spectra.

Deprotection of the allyl group usually take place in the presence of acid and palladium.[17] There are four allyl groups and one allyloylcarbonyl group in **6** with different stabilities, and it was crucial to find the most rational conditions to remove all five protective groups in one step. To our delight, when compound **6** was refluxed with Pd–C and *p*-TsOH in aqueous MeOH, syringalide B was obtained in nearly 80% yield. To further confirm its structure, the pentaacetate of **1** was prepared and its NMR data were found to be identical to those in the literature.[14]

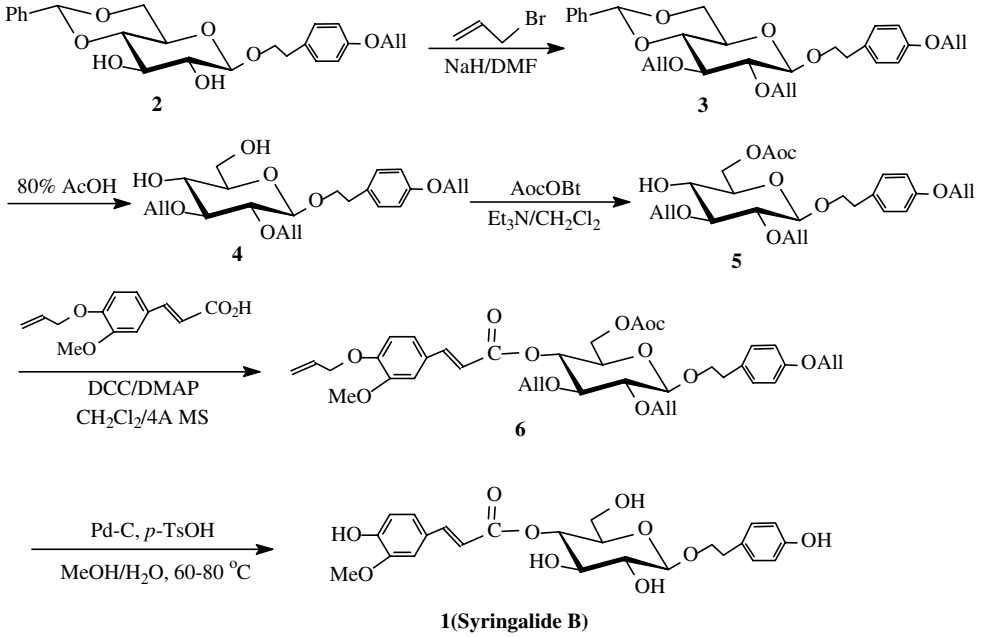
3. Experimental

3.1. General methods

Melting points are uncorrected. Spectra were recorded with the following instruments: ^1H, ^{13}C, and 2D NMR, Varian VXR 300. The ^1H NMR spectra were recorded with Me_4Si as the internal standard, and ^{13}C NMR with $CDCl_3$ and Me_2SO-d_6 as solvent and internal standard, and the mass spectra with a VG ZAB-Hs instrument, IR spectra were recorded with a Perkin–Elmer 983 instrument. Elemental analyses were performed on a Perkin–Elmer 240C instrument. Optical rotations were measured at 25 °C with an Optical Activity AA-10R polarimeter. Reactions were monitored by TLC on silica gel GF_{254} (Hai Yang Chemical Factory, Qingdao, Shandong, PR China). Detection was effected by examination under UV light and by charring with 5% phosphomolybdic acid hydrate in EtOH or 20% concd H_2SO_4 in EtOH and heating. Preparative TLC was performed on silica gel GF_{254} and by column chromatography on silica gel H (Hai Yang Chemical Factory, Qingdao, Shandong, PR China). The solvent systems indicated are volume ratios.

3.2. 2-(4-Allyloxyphenyl)ethyl 2,3-di-*O*-allyl-4,6-*O*-benzylidene-β-D-glucopyranoside (3)

A mixture of 2-(4-allyloxyphenyl)ethyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**2**)[7] (6.90 g, 16.1 mmol), 70.0 mL DMF and sodium hydride (60%, 3.5 g, 87.5 mmol) was stirred for 40 min and then allyl bromide (7.0 mL, 81.0 mmol) was added dropwise. The



Scheme 1. The synthetic route for syringalide B.

mixture was stirred for 10 h and then MeOH (40 mL) was added and the mixture was poured into ice water (200 mL), and extracted by CH_2Cl_2 (50 mL × 3). The organic layer was washed with water (50 mL × 3), dried with anhydrous Na_2SO_4, and concentrated. The residue was subjected to column chromatography, eluting with 5:1 petroleum ether (60–90 °C)–EtOAc to give **3** (6.67 g, 81.4%); $[\alpha]_D$ −33.3 (*c* 3.60, $CHCl_3$); IR (cm^{-1}): 1642; ^1H NMR ($CDCl_3$): δ 7.49–7.26 (m, 5H, Ar–H), 7.13, 6.84 (dd, 4H, Ar–H), 5.95 (m, 3H, 3 × CH_2–C*H*=CH_2), 5.52 (s, 1H, benzylidene–OCHO–), 5.43–5.12 (m, 6H, 3 × CH_2–CH=C*H*$_2$), 4.52 (dd, 1H, H-2), 4.50 (t, 1H, H-3), 4.37 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.32 (dd, 1H, H-6a), 4.16 (t, 2H, OC*H*$_2$$CH_2$Ar), 4.29 and 3.60 (2m, 6H, 3 × C*H*$_2$–CH=CH_2), 4.11 (m, 1H, H-5), 3.75 (dd, 1H, H-6b), 3.72 (t, 1H, H-4), 2.89 (m, 2H, OCH_2C*H*$_2$Ar); ^{13}C NMR ($CDCl_3$): δ 157.1, 137.4, 130.7, 129.8, 128.9, 128.2, 125.9, and 114.7 (Ar), 135.4, 135.2, and 133.4 (3 × –OCH_2–*C*H=CH_2), 117.6, 116.8, and 116.7 (3 × –OCH_2–CH=*C*H_2), 103.9 (C-1), 101.1 (benzylidene–OCHO–), 80.4 (C-3), 74.0 (C-4), 73.9 (C-2), 71.3 (–O*C*$H_2$$CH_2$Ar), 69.7, 68.8, and 68.6 (3 × –O*C*H_2–CH=CH_2), 68.8 (C-6), 66.0 (C-5), 35.3 (–OCH_2*C*H_2Ar); MS(FAB), *m*/*z*: 509 $(M+1)^+$. Anal. Calcd for $C_{30}H_{36}O_7$: C, 70.84; H, 7.14. Found: C, 70.85; H, 7.13.

3.3. 2-(4-Allyloxyphenyl)ethyl 2,3-di-*O*-allyl-β-D-glucopyranoside (4)

A mixture of **3** (4.60 g, 9.05 mmol) and 80% HOAc (100 mL) was stirred at 80 °C for 4 h and then toluene (50 mL) was added, and the solvent was evaporated in vacuo. he residue was dissolved in $CHCl_3$ (50 mL) and the organic layer was washed with ice water, aqueous $NaHCO_3$ (5%), and water, and then dried and evaporated. The resulting residue was purified by column chromatography (2:1 petroleum ether (60–90 °C) –EtOAc) to give **4** (3.41 g) as a syrup; yield 74.1%; $[\alpha]_D$ −22.5 (*c* 8.9, $CHCl_3$); IR (cm^{-1}): 3410, 1642; ^1H NMR ($CDCl_3$): δ 7.12, 6.83 (dd, 4H, Ar–H), 5.94 (m, 3H, 3 × –OCH_2–C*H*=CH_2), 5.42–5.10 (m, 6H, 3 × –OCH_2–CH=C*H*$_2$), 4.50 (dd, 1H, H-2), 4.47 (t, 1H, H-3), 4.35 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.30 (dd, 1H, H-6a), 4.17 (t, 1H, H-4), 4.12 (m, 2H, H-5), 4.09 and 3.67 (2m, 6H, 3 × –O*C*H_2–CH=CH_2), 3.74 (dd, 1H, H-6b), 3.70 (t, 2H, –O*C*$H_2$$CH_2$Ar), 2.87 (m, 2H, –$OCH_2$C*H*$_2$Ar), 2.35 (br s, 2H, 2 × –OH); ^{13}C NMR ($CDCl_3$): δ 157.2 (Ar), 134.9, 133.4 and 131.4 (3 × –OCH_2–*C*H=CH_2), 130.7, 129.8 and 114.7 (Ar), 117.5, 117.2, and 116.8 (3 × –OCH_2CH=*C*H_2), 103.6 (C-1), 81.5 (C-3), 74.1 (C-4), 73.4 (C-2), 73.4, 70.2 and 68.8 (3 × –O*C*H_2–CH=CH_2), 71.1 (–*C*$H_2$$CH_2$Ar), 70.2 (C-6), 62.6 (C-5), 35.3 (–CH_2*C*H_2Ar); MS(FAB), *m*/*z*: 459 $(M+1)^+$. Anal. Calcd for $C_{23}H_{32}O_7$: C, 65.55; H, 7.77. Found: C, 65.70; H, 7.67.

3.4. 2-(4-Allyloxyphenyl)ethyl 2,3-di-*O*-allyl-6-*O*-allyloxycarbonyl-β-D-glucopyranoside (5)

To a solution of **4** (7.67 g, 4.29 mmol) and AocOBt[16] (1.13 g, 5.14 mmol) in anhydrous CH_2Cl_2 (20 mL) was added 3.0 mL triethylamine, and then the mixture was stirred for 3 h. The mixture was evaporated and the residue purified by column chromatography (4:1 petroleum ether (60–90 °C)–EtOAc) to give **5** (1.16 g, syrup, 92.2%); $[\alpha]_D$ −35.3 (*c* 3.4, $CHCl_3$); IR (cm^{-1}): 3488, 1742, 1642; ^1H NMR ($CDCl_3$): δ 7.11 and 6.82 (dd, 4H, Ar–H), 6.06–5.85 (m, 4H, 4 × –OCH_2–C*H*=CH_2), 5.43–5.10 (m, 8H, 4 × –OCH_2–CH=C*H*$_2$), 4.63 (dd, 1H, H-2), 4.61 (t, 1H, H-3), 4.50 (m, 1H, H-5), 4.33 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.32 (dd, 1H, H-6a), 4.16 (t, 1H, H-4), 4.07 and 3.69 (2m, 8H, 4 × –O*C*H_2 –CH=CH_2), 3.84 (dd, 1H, H-6b), 3.69 (t, 2H, –O*C*H_2-CH_2Ar), 2.87 (t, 2H, –OCH_2C*H*$_2$Ar); ^{13}C NMR ($CDCl_3$): δ 157.1(Ar), 155.1 (allyloylcarbonyl, C=O), 130.8, 129.8 and 114.6 (Ar), 135.1, 134.9, 133.4, and 131.4 (4 × –OCH_2–*C*H=CH_2), 119.0, 117.5, 117.2, and 116.8 (4 × –OCH_2–CH=*C*H_2), 103.5 (C-1), 81.3 (C-3), 74.1 (C-4), 73.4 (C-2), 73.2 (C-6), 73.2, 69.7, 68.8, and 68.6 (4 × –O*C*H_2–CH=CH_2), 70.9 (–O*C*$H_2$$CH_2$Ar), 66.8 (C-5), 35.2 (–$OCH_2$*C*$H_2$Ar); MS(FAB), *m*/*z*: 543 $(M+K)^+$. Anal. Calcd for $C_{27}H_{36}O_9$: C, 64.27; H, 7.19. Found: C, 64.35; H, 7.34.

3.5. 2-(4-Allyloxyphenyl)ethyl 2,3-di-*O*-allyl-4-*O*-[(*E*)-(4-*O*-allyl)feruloyl]-6-*O*-allyloylcarbonyl-β-D-glucopyranoside (6)

A mixture of **5** (0.66 g, 1.31 mmol), 4-*O*-allylferulic acid[7] (0.46 g, 1.96 mmol), DCC (270 mg, 1.31 mmol), DMAP (10 mg), powdered 4 Å molecular sieves (200 mg), and anhydrous CH_2Cl_2 (20 mL) was stirred for 16 h, during which time the mixture was allowed to warm to room temperature. The reaction mixture was filtered and the filtrate evaporated to dryness. The residue was purified by preparative TLC (40:1 benzene–EtOAc) to give **6** (0.87 g, 92.3%); $[\alpha]_D$ −8.7 (*c* 4.6, $CHCl_3$); IR (cm^{-1}): 1742, 1710; ^1H NMR ($CDCl_3$): δ 7.65 (d, 1H, *J* 15.2 Hz, *trans*-CH=C*H*–C=O), 7.26 (s, 1H), 7.14 and 6.85 (dd, 4H), 7.06 and 6.88 (AB, 2H) [Ar–H], 6.29 (d, 1H, *J* 15.2 Hz, *trans*-C*H*=CH–C=O), 6.03, and 5.83 (2m, 5H, 5 × –OCH_2–C*H*=CH_2), 5.43–5.00 (m, 10H, 5 × –OCH_2–CH=C*H*$_2$), 4.65 (dd, 1H, H-2), 4.58 (dd, 1H, H-3), 4.50 (m, 1H, H-6a), 4.37 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.25 (dd, 1H, H-4), 4.23, and 4.09 (2m, 10H, 5 × –O*C*H_2–CH=CH_2), 3.92 (s, 3H, OCH_3), 3.90 (t, 1H, H-6b), 3.70 (t, 1H, H-5), 3.68 (m, 2H, –O*C*H_2-CH_2Ar), 2.89 (m, 2H, –OCH_2C*H*$_2$Ar); ^{13}C NMR ($CDCl_3$): δ 165.8 (CH=CH–*C*=O), 157.1 (Ar), 154.7 (allyloylcarbonyl C=O), 150.3 and 149.5 (Ar), 146.0 (CH=*C*H–C=O), 134.9, 133.4, 132.6, 131.4, and 131.3 (5 × –OCH_2–*C*H=CH_2), 130.8, 129.8, 127.3, and 120.7

(Ar), 116.9 (*C*H=CH–C=O), 114.7, 112.8, and 110.0 (Ar), 119.7, 118.9, 118.5, 117.5, and 116.9 (5× –OCH_2–CH=*C*H_2), 103.3 (C-1), 81.3 (C-3), 81.2 (C-4), 74.0 (C-6), 73.6 (C-2), 71.1 (–O*C*H_2*C*H_2Ar), 69.7, 68.8, 68.6, 68.6, and 68.3 (5× –O*C*H_2–CH=CH_2), 66.7 (C-5), 55.9 (–OCH_3), 35.3 (–OCH_2*C*H_2Ar); MS(FAB), *m*/*z*: 759 $(M+K)^+$. Anal. Calcd for $C_{40}H_{48}O_{12}$: C, 66.65; H, 6.71. Found: C, 66.92; H, 6.68.

3.6. 2-(4-Hydroxyphenyl)ethyl 4-*O*-[(*E*)-feruloyl]-β-D-glucopyranoside (1, syringalide B)

A mixture of **6** (0.36 g, 0.5 mmol), Pd–C (0.3 g, 10%), *p*-TsOH (10 mg), CH_3OH (20 mL), and H_2O (2 mL) was stirred at 60–80 °C for 24 h. The mixture was filtered and then toluene (50 mL) was added. The solvent was evaporated to dryness. The residue was purified by PTLC (10:1 $CHCl_3$–MeOH) to give **1** as a yellow solid (0.19 g, yield 79.8%); $[\alpha]_D$ −33.3 (*c* 2.4, CH_3OH); IR (cm^{-1}): 3387; ^1H NMR (Me_2SO-d_6): δ 9.25 (br, 2H, 2× Ar–OH), 7.53 (d, 1H, *J* 15.9 Hz, *trans*-CH=C*H*–C=O), 7.32 (s, 1H), 7.09 (d, 1H), 7.03 (d, 2H), 6.68 (d, 2H) and 6.69 (d, 1H) [Ar–H], 6.46 (d, 1H, *J* 15.9 Hz, *trans*-C*H*=CH–C=O), 4.64 (dd, 1H, H-2), 4.56 (m, 1H, H-3), 4.28 (d, 1H, $J_{1,2}$ 8.1 Hz, H-1), 3.83 (m, 1H, H-5), 3.81 (s, 3H, OCH_3), 3.80 (m, 1H, H-6a), 3.62 (t, 2H, –O*C*H_2*C*H_2Ar), 3.38 (m, 1H, H-6b), 2.74 (t, 2H, –OCH_2CH_2Ar); ^{13}C NMR (Me_2SO-d_6): δ 166.0 (CH=CH–*C*=O), 155.7, 149.5 (Ar), 147.9 (CH=*C*H–C=O), 145.4, 129.8, 128.5, 125.5, 123.29, 115.53, and 115.1 (Ar), 114.4 (*C*H=CH–C=O), 111.1 (Ar), 102.8 (C-1), 74.7 (C-3), 74.1 (C-2), 73.7 (C-4), 71.2 (–O*C*H_2-CH_2Ar), 70.2 (C-5), 60.9 (C-6), 55.7 (–OCH_3), 34.8 (–OCH_2*C*H_2Ar); MS(FAB), *m*/*z*: 515 $(M+K)^+$. Anal. Calcd for $C_{24}H_{28}O_{10}\cdot H_2O$: C, 58.29; H, 6.11. Found: C, 58.39; H, 5.74.

This yellow solid just obtained above was acetylated by using Ac_2O and pyridine to give the pentaacetate as an amorphous white solid, mp 56–57 °C (lit.[14] 55–57 °C); The NMR data of pentaacetate of **1** were the same as those in the literature.[14] ^1H NMR ($CDCl_3$) (lit.[14]): δ 7.64 (7.67) [d, 1H, *J* 15.9 Hz (16.0 Hz), $C_{7''}$–H], 7.09 (7.08) [q, 4H, $A'_2B'_2$, *J* 8.4 Hz (8.7 Hz), Ar–H], 6.98–7.27 (6.82–7.15) (3H, m, aromatic proton), 6.30 (6.40) [d, 1H, *J* 15.9 Hz (16.0 Hz), $C_{8''}$–H], 3.87 (3.88) (s, 3H, OCH_3), 3.69 (3.73) [t, 2H, *J* 6.9 Hz (6.6 Hz), α-H_2], 2.89 (2.87) [t, 2H, *J* 6.9 Hz (6.6 Hz), β-H_2], 2.33 (2.32) (s, 3H, CH_3CO_2–), 2.29 (2.27) (s, 3H, CH_3CO_2–), 2.05 (2.03), 1.97 (1.99) and 1.91 (1.91) (3s, 9H, 3× CH_3CO_2–); ^{13}C NMR ($CDCl_3$) (lit.[14]): δ 170.7, 170.2, 169.6, 169.3, and 168.7 (170.6, 169.7, 169.0) (5× CH_3*C*=O), 165.1 (166.7) (C-9″), 151.4 (151.8) (C-3″), 149.1 (149.5) (C-4), 145.9 (145.9) (C-7″), 141.8 (142.0) (C-4″), 136.1 (136.3) (aglycone C-1), 133.4 (133.5) (C-1″), 129.9 (130.2) (C-6), 129.9 (130.2) (C-2), 123.3 (123.6) (C-5″), 121.7 (121.7) (C-5), 121.6 (121.7) (C-3), 121.4 (121.7) (C-6″), 116.4 (117.8) (C-8″), 111.2 (111.6) (C-2″), 100.7 (101.0) (C-1′), 72.5 (73.0) (C-3′), 71.1 (71.4) (C-2′), 70.4 (70.5) (C-α), 68.6 (68.9) (C-5′), 62.2 (62.4) (C-6′), 55.9 (56.1) (–OCH_3), 35.4 (35.4) (C-β), 21.1, 21.0, 20.8 and 20.6 (21.1, 20.6) (*C*H_3C=O).

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References

1. (a) Cometa, F.; Tomassini, L.; Nicoletti, M.; Pieretti, S. *Fitoterapia* **1993**, *64*, 195; (b) Kurkin, V. A. *Chem. Nat. Compd.* **2003**, *39*, 123; (c) Pan, J.; Yuan, C. S.; Lin, C. J.; Jia, Z. J.; Zheng, R. L. *Pharmazie* **2003**, *58*, 767.
2. Molgaard, P.; Ravn, H. *Phytochemistry* **1988**, *27*, 2411.
3. Ravn, H.; Nishibe, S.; Sasahara, M.; Lu, X. B. *Phytochemistry* **1990**, *29*, 3627.
4. Shoyama, Y.; Matsumoto, M.; Nishioka, I. *Phytochemistry* **1987**, *26*, 983.
5. Xiong, Q.; Hase, K.; Tezuka, Y.; Tani, T.; Namba, T.; Kadota, S. *Planta Med.* **1998**, *64*, 120.
6. Nakamura, T.; Okuyama, E.; Tsukada, A.; Yamazaki, M.; Satake, M.; Nishibe, S.; Deyama, T.; Moriya, A.; Maruno, M.; Nishimura, H. *Chem. Pharm. Bull.* **1997**, *45*, 499.
7. Zhang, S. Q.; Li, Z. J.; Wang, A. B.; Cai, M. S.; Feng, R. *Carbohydr. Res.* **1997**, *299*, 281.
8. Zhang, S. Q.; Li, Z. J.; Wang, A. B.; Cai, M. S.; Feng, R. *Carbohydr. Res.* **1998**, *308*, 281.
9. Li, Z. J.; Zhang, S. Q.; Wang, A. B.; Cai, M. S. *Acta Chim. Sinica (Chinese)* **1998**, *56*, 1128.
10. Toshinari, K.; Ryuji, A.; Shiho, H.; Tomoyasu, S. *J. Org. Chem.* **1999**, *64*, 9268.
11. Kawada, T.; Asano, R.; Makino, K.; Sakuno, T. *J. Wood Sci.* **2002**, *48*, 512.
12. Duynstee, H. I.; de Koning, M. C.; Ovaa, H. *Eur. J. Org. Chem.* **1999**, 2623.
13. Kawada, T.; Asano, R.; Makino, K.; Sakuno, T. *Eur. J. Org. Chem.* **2000**, 2723.
14. Kibuchi, M.; Yamauchi, Y.; Tanabe, F. *Yakugaku Zasshi (J. Pharm. Soc. Jpn.)* **1987**, *107*, 350.
15. Harada, T.; Yamada, H.; Tsukamoto, H.; Takahashi, T. *J. Carbohydr. Chem.* **1995**, *14*, 165.
16. Kim, S.; Chang, H.; Kim, W. J. *J. Org. Chem.* **1985**, *50*, 1751.
17. Boss, R.; Scheffold, R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 558.