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SEVEN AROMATIC COMPOUNDS FROM BARK OF *CINNAMOMUM CASSIA**

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Key Word Index—*Cinnamomum cassia*, Lauraceae, bark, Cinnamomi Cortex, lyoniresinol glucoside, 3,4,5-trimethoxyphenol apiosylglucoside, syringaresinol, epicatechin derivatives, cinnamic aldehyde cyclic glycerol 1,3-acetal

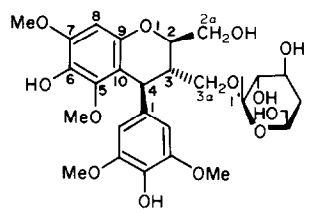
Abstract—Seven aromatic compounds have been obtained from the dried bark of *Cinnamomum cassia* lyoniresinol 3α-*O*-β-D-glucopyranoside, 3,4,5-trimethoxyphenol β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside, (±)-syringaresinol, two epicatechin derivatives and two cinnamic aldehyde cyclic glycerol 1,3-acetals

INTRODUCTION

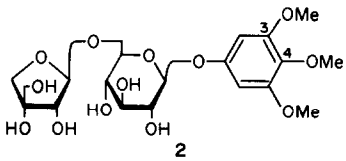
We have recently obtained a series of diterpenes [1–8] from the fraction exhibiting anti-allergic activity of the water extractive of Cinnamomi Cortex (the dried bark of *Cinnamomum cassia* Blume) In connection with our study of the above active fraction, seven aromatic compounds **1**–**7** have been further isolated This paper deals with their structural determination by chemical and spectral means

RESULTS AND DISCUSSION

Compound **1**, an amorphous powder, $[\alpha]_D + 22.4°$, showed absorptions due to the hydroxyl (3400 cm^{-1}, strong) and aromatic ring (1570 cm^{-1}) In the ^{13}C NMR spectrum (Table 1), together with the carbon signals ascribable to the glucopyranosyl residue and four aromatic methoxyl groups, those due to 18 carbons were observed, among which 12 are ascribable to two substituted benzene rings and two to the carbinol carbons The above evidence was reminiscent of a lignan monoglucopyranoside for **1** Compound **1** yielded, on enzymic hydrolysis with hesperidinase or acid hydrolysis, an aglycone (**1b**), mp 185–187°, $[\alpha]_D + 58.0°$, along with D-glucose Its aglycone was identified with the 4-aryltetralin-type lignan derivative, lyoniresinol [9–16], by analyses of the ^{13}C NMR, ^1H NMR and mass spectra of its acetate (**1c**) and direct comparison (mp, IR, TLC) with an authentic specimen Therefore, **1** is a lyoniresinol monoglucoside In order to decide the location of the glucosyl linkage to the aglycone (**1b**), a comparison of the ^{13}C NMR spectra of **1** and **1b** was undertaken In referring to the assignment (in DMSO-d_6) [17] of lyoniside (lyoniresinol 3α-*O*-β-D-xylopyranoside) [9–11, 16] by Vecchietti, we reassigned **1** and **1b** as listed in Table 1 using pyridine-d_5 as solvent The glycosidation shifts [18, 19] at C-3α were observed as +7.3 ppm suggesting that the glucopyranosyl residue combined to the hydroxyl at C-3α As regards the configuration of its glucosyl linkage, it was



1



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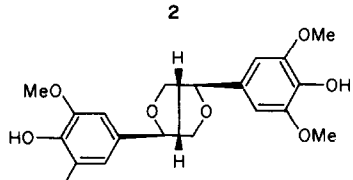

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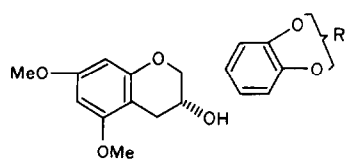
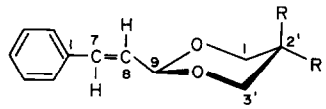


4 R=H, Me

5 R=>CH_2



6 R=H, R'=OH

7 R=OH, R'=H

*Part 8 in the series "Studies on the Constituents of Cinnamomi Cortex" For Part 7 see Nohara, T, Kashiwada, Y, Tomimatsu, T and Nishioka, I (1982) *Phytochemistry* **21**, 2130

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Table 1 ^{13}C NMR data of 1 and 1a–1c

	1	1a	1b	1c
1	32 4 (*t*)	33 4	33 8	33 5
2	38 8 (*d*)	35 7	41 6	35 4
2α	65 5 (*t*)	66 3	66 4	66 2
3	45 8 (*d*)	44 8	49 4	44 3
3α	71 4 (*t*)	70 0	64 1	63 2
4	42 2 (*d*)	41 6	42 2	45 8
5	147 6 (*s*)	151 0	148 2	150 6
6	138 5 (*s*)	131 8	139 4	131 8
7	147 5 (*s*)	151 6	147 9	151 6
8	107 3 (*d*)	107 0	107 3	106 5
9	129 3 (*s*)	135 5	129 5	134 9
10	126 2 (*s*)	124 0	126 6	124 0
1′	138 9 (*s*)	144 8	138 9	144 6
2′	107 1 (*d*)	105 0	107 3	104 8
3′	148 6 (*s*)	152 0	148 9	151 6
4′	135 1 (*s*)	135 7	135 8	128 3
5′	148 6 (*s*)	152 0	148 9	151 6
6′	107 1 (*d*)	105 0	107 3	104 8
Glc-1″	104 5 (*d*)	101 3	—	—
2″	74 8 (*d*)	71 3	—	—
3″	78 1 (*d*)	72 9	—	—
4″	71 4 (*d*)	68 5	—	—
5″	78 1 (*d*)	72 0	—	—
6″	62 5 (*t*)	62 0	—	—
OMe-5	59 6 (*q*)	60 3	59 4	59 9
OMe-7	56 1 (*q*)	56 1	56 1	56 0
OMe-3′	56 5 (*q*)	56 3	56 4	56 1
OMe-5′	56 5 (*q*)	56 3	56 4	56 1

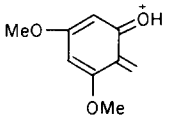
Solvents 1 and 1b, pyridine-d_5, 1a and 1c, $CDCl_3$

supposed to be β on the basis of the *J* value (*d*, *J* = 7 Hz at δ 4 47) of the anomeric proton in the ^1H NMR spectrum of the acetate of 1 (1a) Consequently, 1 is lyoniresinol 3α-*O*-β-D-glucopyranoside

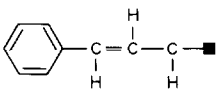
Compound 2, an amorphous powder, $[\alpha]_D$ −26 2°, was converted to the corresponding acetate (2a) showing *m/z* 730 $[M]^+$, 547 [terminal peracetylated hexosyl pentosyl cation], 259 [terminal peracetylated pentosyl cation], 184 $[C_9H_{12}O_4]^+$ aglycone] in the mass spectrum The ^1H NMR spectrum of 2a exhibited all singlet signals due to three aromatic methoxyls at δ 3 78 (× 1), 3 82 (× 2) and the aromatic protons (2H) at δ 6 27 Since no NOE effect was observed between the aromatic protons (δ 6 27) and the methoxyl at C-4 (δ 3 78), the aglycone moiety was deduced to be 3,4,5-trimethoxyphenol Compound 2 gave, on acid hydrolysis, a mixture of methyl glycosides of glucopyranose and apiofuranose Moreover, the ^{13}C NMR spectrum of 2 revealed the sugar moiety to be represented as β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranosyl due to the shifts by + 5 8 and − 1 4 ppm at C-6 and C-5, respectively, in the carbons of the glucosyl part This assignment is in good accordance with that of an alkene glycoside [20] having the same sugar part isolated from *Ligustrum japonicum* Thunb Consequently, 2 is 3,4,5-trimethoxyphenol 1-*O*-β-D-apiofuranosyl-(1 → 6)-β-D-giucopyranoside

Compound 3, colorless needles, mp 168–170°, $[\alpha]_D$ 0°, MS (*m/z*) 418 $[M]^+$, was identified as (±)-syringaresinol by the ^1H NMR spectrum of its acetate

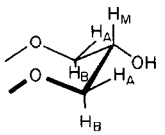
Compound 4, colorless needles, mp 117–119°, $[\alpha]_D$ − 34 0°, MS (*m/z*) 332 $[M]^+$, showed signals ascribable to 12 aromatic carbons at δ 92 2–159 7, two carbinol ones at δ 78 5 and 66 5, one methylene at δ 28 2 and three methoxyls at δ 55 4 (× 1) and 56 0 (× 2) and was thus assumed to be a catechin methyl ether The proton signals attributable to H_2-4 (δ 2 90), H-3 (δ 4 24, *m*) and H-2 (δ 4 91, *s*) in the ^1H NMR spectrum of 4 suggested 4 to be an epicatechin derivative Three methyls appeared at δ 3 70, 3 78, 3 90 in the aromatic methoxyl region Two of the three methyls were associated with the hydroxyls at C-5 and C-7 from the presence of a base peak *m/z* 167 ascribable to a fragment $[C_9H_{11}O_3]^+$ (a) Another methyl group must be located at C-3′ or C-4′, but this remains to be determined



Fragment [a]



Partial structure A



Partial structure B

While, compound 5, colorless needles, mp 162–164°, $[\alpha]_D$ 0°, MS *m/z* 330 $[M]^+$, showed a ^1H NMR spectrum similar to that of 4 except for a decrease of one methoxyl signal and an appearance of one methylenedioxy signal (2H, *s*, δ 5 94) by comparison with that of 4 Therefore, this substance is the epicatechin derivative 5

Compound 6, a white crystalline powder, $[\alpha]_D$ 0°, MS *m/z* 206 $[M]^+$ ($C_{12}H_{14}O_3$), exhibited signals at δ 7 20–7 44 (5H, arom protons), 6 12 (1H, *dd*, *J* = 4, 16 Hz), 6 72 (1H, *d*, *J* = 16 Hz) and 5 03 (1H, *d*, *J* = 4 Hz) in the ^1H NMR spectrum, suggesting a partial structure of A A further assignment of A_2B_2M type signals, δ 3 48 (2H, *t*, *J* = 10, 10 Hz), 4 23 (2H, *dd*, *J* = 5, 10 Hz) and 3 92 (1H, *m*) led 6 to have the additional partial structure B Moreover, in consideration of the ^{13}C NMR spectrum and preferred conformational analysis, 6 must be represented as a cinnamic aldehyde cyclic glycerol 1,3-acetal possessing *trans*-substitutions at C-9 and C-2′

Compound 7, colorless crystals, mp 106–109°, $[\alpha]_D$ 0°, showed the same fragment pattern as that of 6 in its mass spectrum and its ^{13}C NMR spectrum also resembled that of 6 indicating that 7 could be a stereoisomer of 6 Although the respective signals at a lower field than around δ 5 0 were superimposable to those of 6, the signals at δ 4 08 (2H, *dd*, *J* = 2, 10 Hz), 3 94 (2H, *dd*, *J* = 2, 10 Hz), 3 54 (1H, *dd*, *J* = 2, 11 Hz) and 3 14 (1H, *d*, *J* = 11 Hz) were different from those of 6 and were assigned to the A_2B_2M portion Therefore, 7 can be represented as shown in the formula, in which substitutions at C-9 and C-2′ in the cyclic glycerol part have the *cis*-configuration

EXPERIMENTAL

General Mps are uncorr ^{1}H NMR spectra at 100 MHz and ^{13}C NMR spectra at 50 01 MHz were obtained, chemical shifts are given in δ-values with TMS as the int standard Chromatographic colums were packed with Si gel (Merck 60) or alumina (Merck active 90) and TLC plates were precoated with Si gel (Merck 60 F-254) Detection was done by spraying 10% H_2SO_4 followed by heating

Extraction and isolation The H_2O extractive of Cinnamomi Cortex (Toko Keihi, 30kg) was shaken with *n*-BuOH and the organic layer was evaporated *in vacuo* to give a residue, which was treated with Me_2CO and *n*-hexane in turn, and passed through alumina using MeOH and H_2O successively as solvent to afford the respective eluates (MeOH eluate 158 g, H_2O eluate 85 g after evaporation), both exhibiting the anti-allergic activity The residue obtained from the MeOH eluate was further partitioned between H_2O and C_6H_6, the latter of which evaporated to give a residue (31 7 g) This was Si gel column chromatographed using *n*-hexane–Me_2CO (1 1) repeatedly to give compounds **1** (68 mg), **2** (36 mg), **3** (100 mg), **4** (80 mg), **5** (80 mg), **6** (180 mg) and **7** (100 mg) The residue obtained from the aq eluate was also Si gel CC using $CHCl_3$–MeOH–H_2O (8 2 0 2) to give **1** (2 6 g)

Lyoniresinol 3α-O-β-D-glucopyranoside (**1**) An amorphous powder, $[\alpha]_D^{22}$ + 22 4° (MeOH, *c* 1 01), IR ν_{max}^{KBr} cm^{-1} 3600–3100 (OH), 1570, 1515, 1460 (arom ring) ^{1}H NMR (pyridine-d_5 δ 2 10 (*m*, H-2), 2 60 (*m*, H-3), 2 96 (*m*, H_2-1), 3 54 (OMe), 3 80 (3 × OMe), 6 68 (*s*, H-8), 6 84 (*s*, H-2′, H_2-6′) (Found C, 57 48, H, 6 61 $C_{28}H_{38}O_{13}$ requires C, 57 72, H, 6 57%)

Hepta-acetate (**1a**) of **1** 1 was acetylated with Ac_2O–pyridine in the usual manner to give the hepta-acetate (**1a**) of **1**, colorless needles, mp 87–90°, $[\alpha]_D^{23}$ 0° ($CHCl_3$, *c* 1 00) MS (*m/z*) 876 $[M]^+$, 834, 792, 774, 732, 588, 546, 505, 486, 460, 443, 425, 413, 384, 331 $[C_{14}H_{19}O_9$, glc4Ac$]^+$, 169, 109 ^{1}H NMR ($CDCl_3$) δ 2 01–2 30 (7 × OAc), 2 62–2 80 (*m*, H_2-1), 3 18, 3 29 (each *s*, OMe-5), 3 71, 3 74, 3 82 (each *s*, 3 × arom OMe), 4 34 (*d*, *J* = 6 Hz, H-4, 4 47 (*d*, *J* = 7 Hz, glc anomeric proton), 6 32 (*d*, *J* = 2 Hz, H_2-2′, H_2-6′), 6 54 (*br s*, H-8)

Aglycone (**1b**) (*lyoniresinol*) *of* **1** A soln of **1** (300 mg) in 0 5 N H_2SO_4 (10 ml) was refluxed for 22 hr, diluted with H_2O and extracted with EtOAc The organic layer was evaporated *in vacuo* to give a residue, which was crystallized from H_2O to give an aglycone (**1b**), colorless needles, mp 185–187°, $[\alpha]_D^{20}$ + 58 0° (MeOH, *c* 0 50), ΔM_D (**1–1b**) = − 113 2° IR ν_{max}^{KBr} cm^{-1} 3600–3100 (OH), 1610, 1520, 1502, 1460 (arom ring) MS (*m/z*) 420 $[M]^+$, 402, 371, 248, 217, 205, 183, 157 (Found C, 62 71, H, 6 67 Calc for $C_{22}H_{28}O_8$ C, 62 84, H, 6 71%) The aq layer was passed through Amberlite IRA 400 to give D-glucose, $[\alpha]_D^{21}$ + 50 2° (H_2O, *c* 0 62) **1b** was identified with an authentic specimen by TLC, IR and MS

Tetra-acetate (**1c**) *of* **1b** **1b** was acetylated in the usual manner to give the tetra-acetate (**1c**) of **1b** MS (*m/z*) 588, 546, 505, 486, 460, 444, 413, 384, 230, 217, 167 ^{1}H NMR ($CDCl_3$) δ 2 03, 2 08, 2 28, 2 30 (each *s*, 4 × OAc), 3 18 (*s*, OMe-5), 3 72 (*s*, 2 × OMe), 3 81 (OMe), 6 33 (*s*, H_2-2′, H_2-6′), 6 53 (*s*, H-8)

3,4,5-Trimethoxyphenol β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside (**2**) A white amorphous powder, $[\alpha]_D^{26}$ − 26 2° (MeOH, *c* 0 54) ^{1}H NMR (pyridine-d_5) δ 3 79 (*s*, OMe), 6 74 (*s*, arom H_2) ^{13}C NMR (pyridine-d_5) δ 155 1 (C-1), 96 0 (C-2, C-6), 154 0 (C-3, C-5), 56 2 (2 × OMe, OMe-3, OMe-5), 60 6 (OMe, OMe-4), 103 1, 74 6, 78 1, 71 4, 77 0, 68 8 (glucosyl C-1′–C-6′), 110 6, 77 5, 80 1, 74 6, 65 0 (apiosyl C-1′–C-5″) (Found C, 50 12, H, 6 26 $C_{20}H_{30}O_{13}$ requires C, 50 20; H, 6 32%) A trace of **2** was acid hydrolysed with 2 N HCl–MeOH for 2 hr to detect methyl glucopyranoside and methyl apiofuranoside on TLC

Hexa-acetate (**2a**) *of* **2** Compound **2** (37 mg) was acetylated with Ac_2O–pyridine in the usual manner to give the hexa-acetate (**2a**) (10 8 mg) of **2**, colorless needles from C_6H_6–Me_2CO, mp 132–134°, $[\alpha]_D^{23}$ − 38 9° ($CHCl_3$, *c* 0 54) MS (*m/z*) 730 $[M]^+$, 547 [terminal peracetylated glucosyl apiosyl cation], 504, 487, 445, 402, 384, 361, 359, 331, 317, 259 [terminal peracetylated apiosyl cation], 184 $[C_9H_{12}O_4]^+$, 139 ^{1}H NMR ($CDCl_3$) δ 2 01–2 11 (*m*, 6 × OAc), 3 78 (*s*, arom OMe), 3 82 (*s*, arom OMe × 2), 4 46, 4 78 (each 1H, *d*, *J* = 12 Hz, api-H_2-4), 6 27 (*s*, arom H-2) ^{13}C NMR ($CDCl_3$) δ 153 7 (× 2, *s*), 153 2 (*s*), 105 7 (*d*), 99 7 (*d*), 95 6 (× 2, *d*), 83 9 (*s*), 73 5 (*d*), 72 9 (*d*), 72 8 (*d*), 72 5 (*d*), 71 5 (*d*), 68 8 (*d*), 66 1 (*t*), 63 0 (*t*), 60 9 (*q*), 56 3 (*q*)

(±)-*Syringaresinol* (**3**) Colorless needles, mp 168–170°, $[\alpha]_D^{26}$ 0° (MeOH, *c* 0 50) IR ν_{max}^{KBr} cm^{-1} 3600–3200 (OH), 1606, 1510, 1460 (arom ring) MS (*m/z*) 418 $[M]^+$, 235, 210, 193, 182, 181, 167 ^{1}H NMR ($CDCl_3$) δ 3 10 (*m*, H_2-β), 3 89 (*s*, 4 × OMe), 3 80–4 38 (*m*, H_4-γ), 4 70 (*br d*, *J* = 3 Hz H_2-α), 6 56 (*s*, arom H_4) (Found C, 63 31, H, 6 25 Calc for $C_{22}H_{26}O_8$ C, 63 15, H, 6 26%)

Diacetate of **3** Colorless needles from MeOH, mp 116–118°, ^{1}H NMR ($CDCl_3$) δ 2 35 (2 × arom OAc), 3 12 (*m*, H_2-β), 3 84 (4 × OMe), 3 95–4 40 (*m*, H_4-γ), 4 76 (*m*, H_2-α), 6 58 (arom H_4)

5,7,3′ (*or* 4′)-*Trimethyl-(−)-epicatechin* (**4**) Colorless needles from *n*-hexane–Me_2CO, mp 117–119°, $[\alpha]_D^{26}$ − 34 0° ($CHCl_3$, *c* 0 50), IR ν_{max}^{KBr} cm^{-1} 3400 (OH), 1610, 1590, 1510 (arom ring) MS (*m/z*) 332 $[M]^+$, 314, 178, 167 $[C_9H_{11}O_3]^+$, 151, 137 ^{1}H NMR ($CDCl_3$) δ 2 82–2 98 (*m*, H_2-4), 3 76, 3 78, 3 90 (each *s*, arom OMe × 3), 4 24 (*m*, H-3), 4 91 (*br s*, H-2), 6 12 (*d*, *J* = 2 Hz, H-6), 6 17 (*d*, *J* = 2 Hz, H-8), 6 93–7 06 (*m*, H-2′, H-5′, H-6′) ^{13}C NMR ($CDCl_3$) δ 78 5, 66 5, 28 2, 155 2, 92 2, 159 7, 92 2, 159 7, 100 3 (C-2–C-10), 130 2, 109 1 (C-1′, C-2′), 145 5, 146 7, (C-3′, C-4′ or alternation), 114 4, 119 4 (C-5′, C-6′) (Found C, 64 98, H, 6 02 $C_{18}H_{20}O_6$ requires C, 65 05, H, 6 07%)

Tetra-acetate of **4** Compound **4** (40 mg) was acetylated with Ac_2O (2 ml) and pyridine (2 ml) in the usual manner to afford the tetra-acetate of **4**, ^{1}H NMR ($CDCl_3$) δ 1 88, 2 28 (each *s*, OAc × 2), 2 90 (*d*, *J* = 4 Hz, H_2-4), 3 75 (*s*, arom OMe × 2), 3 81 (*s*, arom OMe), 5 00 (*br s*, H-2), 5 42 (*m*, H-3), 6 08 (*d*, *J* = 2 Hz, H-6), 6 17 (*d*, *J* = 2 Hz, H-8), 7 01–7 10 (*m*, H-2′, H-5′, H-6′)

5 7-*Dimethyl* 3′,4′-*di-O-methylene-(±)-epicatechin* (**5**) Colorless needles from *n*-hexane–Me_2CO, mp 162–164°, $[\alpha]_D^{26}$ 0° ($CHCl_3$, *c* 0 50), IR ν_{max}^{KBr} cm^{-1} 3400 (OH), 1610, 1590, 1510 (arom ring) MS (*m/z*) 330 $[M]^+$, 167 $[C_9H_{11}O_3]^+$ ^{1}H NMR ($CDCl_3$) δ 2 84–2 96 (*m*, H_2-4), 3 75, 3 77 (each *s*, arom OMe × 2), 4 22 (*m*, H-3), 4 90 (*br s*, H-2), 5 94 (*s*, dioxymethylene), 6 07 (*d*, *J* = 2 Hz, H-6) 6 13 (*d*, *J* = 2 Hz, H-8), 6 74–7 06 (*m*, H-2′, H-5′, H-6′) (Found C, 65 26, H, 5 47 $C_{18}H_{18}O_6$ requires C, 65 44, H, 5 49%)

Cinnamic aldehyde cyclic glycerol 1,3-*acetal* (9,2′-trans) (**6**) An amorphous powder, $[\alpha]_D^{26}$ 0° ($CHCl_3$, *c* 0 50) IR ν_{max}^{KBr} cm^{-1} 3500 (OH), 2000–1600 (monosubstituted C_6C_6), 1758, 1650, 1590, 1570 (arom ring) MS (*m/z*) 206 $[M]^+$, 175, 149, 131, 115, 104, 77 ^{1}H NMR ($CDCl_3$) δ 3 48 (*dd*, *J* = 8, 10 Hz, H_A-1′, H_A-3′), 4 23 (*dd*, *J* = 5, 10 Hz, H_B-1′, H_B-3′) 3 92 (*m*, H-2′), 5 03 (*d*, *J* = 4 Hz, H-9), 6 15 (*dd*, *J* = 4, 16 Hz, H-8), 6 79 (*d*, *J* = 16 Hz, H-7), 7 10–7 46 (*m*, arom H-5) ^{13}C NMR ($CDCl_3$) δ 135 8 (C-1), 126 8 (C-2, C-6), 128 5 (C-3, C-5), 128 2 (C-4), 124 6 (C-7), 133 9 (C-8), 100 1 (C-9), 71 3 (C-1′, C-3′), 61 3 (C-2′) (Found C, 69 72, H, 6 79 $C_{12}H_{14}O_3$ requires C, 69 88, H, 6 84%)

Cinnamic aldehyde cyclic glycerol 1,3-*acetal* (9,2′-cis) (**7**) Colorless leaflets, mp 106–109°, $[\alpha]_D^{26}$ 0° ($CHCl_3$, *c* 0 50), IR ν_{max}^{KBr} cm^{-1} 3500 (OH), 2000–1600 (monosubstituted C_6H_6), 1758, 1650, 1590, 1570 (arom ring) MS (*m/z*) 206 $[M]^+$, 175, 149, 131, 115, 104, 77 ^{1}H NMR ($CDCl_3$) δ 3 14 (*d*, *J* = 11 Hz, OH-2′), 3 54 (*br d*, *J* = 11 Hz, H-2′), 3 94 (*dd*, *J* = 2, 10 Hz, H_A-1′, H_A-3′), 4 08 (*dd*, *J* = 2, 10 Hz, H_B-1′, H_B-3′), 5 14 (*d*, *J* = 4 Hz, H-9), 6 15 (*dd*, *J* = 4, 16 Hz, H-8), 6 79 (*d*, *J* = 16 Hz, H-7), 7 10–7 46 (*m*, arom H-5) ^{13}C NMR ($CDCl_3$) δ 135 9 (C-1), 126 8 (C-2, C-6), 128 5 (C-3, C-5), 128 4 (C-4), 125 1 (C-7), 133 7 (C-8), 101 1 (C-9),

71 9 (C-1′, C-3′), 63 9 (C-2′) (Found C, 69 68, H, 6 86 $C_{12}H_{14}O_3$ requires C, 69 88, H, 6 84%)

Acknowledgements—We are very grateful to Professor Dr J Sakakibara, Nagoya City University, for providing the lyoniresinol and Associate Professor Dr M Shibuya, Tokushima University and Dr G Nonaka, Kyushu University, for discussion and suggestions for the assignment of ^{1}H NMR spectra

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