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LIGNANS OF *LARIX LEPTOLEPIS*

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Key Word Index—*Larix leptolepis;* Pinaceae; larch wood; lignan; lignin; leptolepisol C.

Abstract—Five lignans have been isolated from wood of *Larix leptolepis*. They are identified as 1-(4-hydroxy-3-methoxyphenyl)-2-{4-[2-formyl-(*E*)-vinyl]-2-methoxyphenoxy}-propane-1,3-diol, 1-(4-hydroxy-3-methoxyphenyl)-2-{2-methoxy-4-[1-(*E*)-propen-3-ol]-phenoxy}-propane-1,3-diol, 1-(4-hydroxy-3-methoxyphenyl)-2-(4-formyl-2-methoxyphenoxy)-propane-1,3-diol, 1,2-bis-(4-hydroxy-3-methoxyphenyl)-propane-1,3-diol and a trilignol, leptolepisol C.

INTRODUCTION

In a previous paper, the structures of two triphenylpropane lignans, leptolepisol A and B from inner bark of *Larix leptolepis* Gord. (Pinaceae) were reported [1]. These two lignans are optically active and have propanol side chains like other lignans from the inner bark [2, 3].

The sapwood and heartwood of *L. leptolepis* also contain many lignans and *ca* 20 compounds have been isolated so far. In this paper, the structural determinations of three 1-phenyl-2-phenoxypropane-1,3-diols, 1,2-diarylpropane-1,3-diol, and leptolepisol C comprising three guaiacyl nuclei with β-1 and β-5 linkage units are described.

RESULTS AND DISCUSSION

Compound **1** was obtained from an EtOH extract of sapwood and heartwood of *L. leptolepis* as a pale yellow oil ($[\alpha]_D^{31} - 3.9°$). The MS contains peaks at *m/e* 374.1323 ($C_{20}H_{22}O_7$, M^+), 178 (coniferyl aldehyde ion) and 137 (vanillium ion). The ^{1}H NMR shows complicated signals assigned to the protons of (*E*)-coniferyl aldehyde side chain (see Experimental). The doublet at δ4.94 ($J = 6$ Hz) and the multiplet at δ4.52 are assigned to H-α and H-β of 1-phenyl-2-phenoxypropane-1,3-diol structure, respectively. The TLC and IR of the reduction product of **1** with $NaBH_4$ agree with those of the authentic sample isolated from the enzymatic dehydrogenation products of coniferyl alcohol. Consequently, compound **1** is identified as 1-(4-hydroxy-3-methoxyphenyl)-2-{4-[2-formyl-(*E*)-vinyl]-2-methoxyphenoxy}-propane-1,3-diol.

As the ^{1}H NMR data suggested that **1** may be a mixture of diastereomers, the separation of 1-phenyl-2-phenoxypropane-1,3-diol isomers was attempted using benzeneboronic acid in accordance with the procedure of Nakatsubo *et al.* [4]. The esters of the diastereomers were separated on a Si gel column, giving *erythro*- and *threo*-benzeneboronates, respectively. Elution of each ester with MeOH from a Sephadex LH-20 column gave free *erythro* and *threo* isomers. The ^{1}H NMR spectra show slight differences between them (Table 1).

Compound **2** was obtained from the EtOH extract of the sapwood as a colourless oil ($[\alpha]_D^{22} - 6.7°$). The MS contains peaks at *m/e* 376.1498 ($C_{20}H_{24}O_7$, M^+), 180 (coniferyl alcohol ion) and at 137. The ^{1}H NMR shows H-γ' at 4.22 (*d*, $J = 5$ Hz), H-β' at 6.32 (*dt*, $J = 5$ Hz,

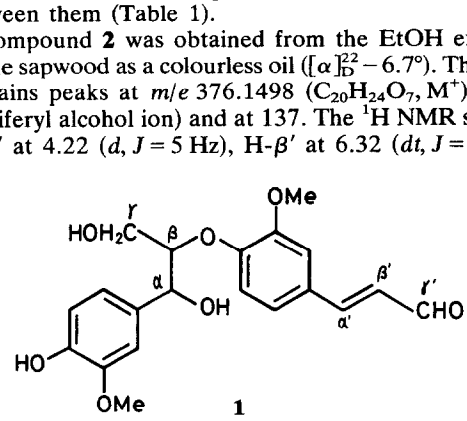

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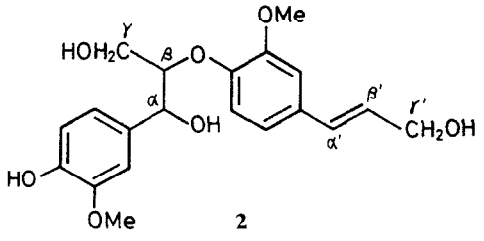
Table 1. ^{1}H NMR data for *erythro* and *threo* isomers of **1**

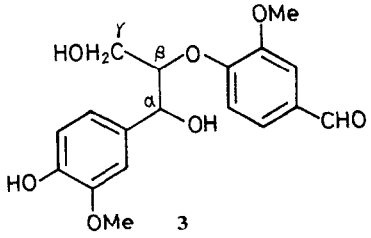
	H-α	H-β	H-γ	H-α'	H-β'	H-γ'	OMe
Erythro	4.92	4.54	3.5–4.0	7.54	6.64	9.61	3.80, 3.87
	d	*m*		*d*	*dd*	*d*	*s*
	$J = 6$			$J = 16$	$J = 8, 16$	$J = 8$	
Threo	4.90	4.34	3.5–4.0	7.48	6.61	9.57	3.80, 3.92
	d	*m*		*d*	*dd*	*d*	*s*
	$J = 6$			$J = 16$	$J = 8, 16$	$J = 8$	



2

16 Hz) and H-α' at δ6.54 (d, J = 16 Hz) for (*E*)-coniferyl alcohol side chain. The doublet at δ4.94 (J = 6 Hz, H-α) and the multiplet at δ4.34 (H-β) correspond to those of **1**. The other spectral and TLC data agree with those of an authentic sample, indicating that compound **2** is 1-(4-hydroxy-3-methoxyphenyl)-2-{2-methoxy-4-[1-(*E*)-propen-3-ol]-phenoxy}-propane-1,3-diol.

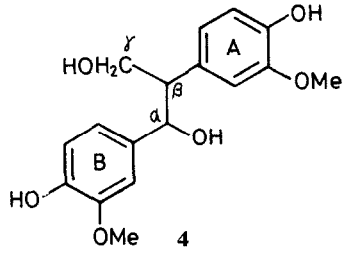
The EtOH extract of the sapwood also gave compound **3** as a colourless oil ($[\alpha]_D^{20}$ +2.1°). The UV and IR are closely related to those of vanillin. The split singlet at δ9.79 in the ^{1}H NMR is assigned to an aromatic aldehyde proton. The multiplets at δ4.96 (H-α) and δ4.68 (H-β) show that **3** may have partially the same structure as **1** and **2**. The MS fragmentation is also similar to those of **1** and **2**. Finally compound **3** is identified to be 1-(4-hydroxy-3-methoxyphenyl)-2-(4-formyl-2-methoxyphenoxy)-propane-1,3-diol.



3

The multiplicity of the ^{1}H NMR signals of **2** and **3** acetates may be due to a mixture of diastereomers, however, an attempt at further separation had to be abandoned for its small amount.

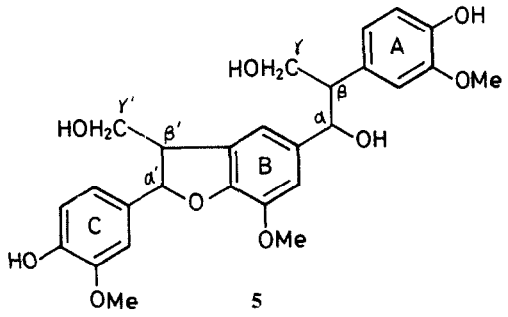
Compound **4** was isolated as amorphous powder from the EtOH extract of the heartwood. It shows no optical activity. The spectral data are closely related to those of the characteristic lignin constituent unit, 1,2-bis-(4-hydroxy-3-methoxyphenyl)-propane-1,3-diol, which was isolated in our laboratory from the hydrolysis products of protolignin [9]. The separation of



4

the diastereomers was attempted according to the same procedure as **1**, giving *erythro*(13 mg) and *threo*(4 mg) isomers, respectively. They were both optically inactive.

Compound **5**, leptolepisol C, was also isolated as amorphous powder from the EtOH extract of the heartwood, and showed slight optical activity ($[\alpha]_D^{28}$ −1.0°) in contrast to **4**. The M^+ cannot be detected in the MS but other peaks at *m/e* 480.1789 ($C_{27}H_{28}O_8$, M-18), 420 (base peak), 150 and 137 are observed as abundant ions. The multiplet at δ2.98 and the doublet at δ5.06 in the ^{1}H NMR are assigned to be H-β and H-α of **4** (*erythro* isomer), respectively. Another characteristic doublet at δ5.54 indicates the α-proton of dihydrobenzofuran structure. The ^{13}C NMR also shows a close relation between those signals of both **5** and **4** (*erythro* isomer) (Table 2). The other data also agree with those of the compound which was isolated from the hydrolysis products of protolignin [10]. The lignan here isolated is designated as leptolepisol C (**5**).



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Earlier, lignans were designated mainly for the compounds constructed from two phenylpropanes with β–β linkage. McCredie *et al.* [5] proposed in 1968 that the definition of lignans should be extended "to cover all natural products of low MW that arise primarily from the oxidative coupling of *p*-hydroxyphenylpropane unit". Recently many new lignans have been isolated and their structures were elucidated.

Table 2. ^{13}C NMR data for **4** and leptolepisol C (**5**)

(ppm)	Assignment	(ppm)	Assignment
		55.4	β'
56.2	OMe	56.4	OMe
56.3	OMe	56.6	OMe
56.7	β	56.8	β
64.5	γ	64.4	γ
		65.1	γ'
75.5	α	75.5	α
		89.1	α'
		110.5	C-2
111.6	B-2	112.6	B-2
114.6	A-2	114.6	A-2
115.6	A-5	115.6	A-5
		116.1	C-5*
120.3	B-6	116.4	B-6*
		119.5	C-6
123.1	A-6	123.1	A-6
115.4	B-5	129.1	B-5
132.2	A-1	132.1	A-1
		134.7	C-1
136.4	B-1	138.4	B-1
146.5	B-4	144.8	B-4
146.1	A-4	146.2	A-4
		147.4	C-4*
148.3	A-3	148.3	A-3, B-3*
148.4	B-3	149.0	C-3*

*Tentatively assigned.

Among them, there are some lignans consisted of 3 or 4 pendant groups, or those with linkage units very similar to those of lignin. The same compounds described above were all so far obtained from the hydrolysis products of lignin. Compounds **1**, **2**, and **3** were isolated from lignin of *Picea excelsa* [6, 7], and compound **4** from *Fagus silvatica* [8], and *Picea jezoensis* [9]. The hydrolysis products of *P. jezoensis* lignin also gave compound **5** [10].

The compound with a β-1 linkage was proposed to be formed by coupling two radical mesomers, **Ra** and **Rb**, from *p*-hydroxycinnamyl alcohol precursors accompanying displaced side chain, as shown in Fig. 1 [11]. The displaced unit (**7**) was suggested by the formation of glyoxal in the acidolysis products of milled wood lignin [11], but direct evidence has not been obtained so far. Very recently, we isolated a glycoside which may originate from compound **7** [2]. The fact may support the biosynthesis mechanism of compound **4** as shown in Fig. 1. The displaced unit **7** might be reduced enzymatically and then glycosylated. This biogenesis of β-1 type lignans may be similar to that of lignin.

It is very interesting that compound **4** belongs to the rare lignans which have no optical activity as lignin does. Compound **5** has slight optical activity, but it may presumably be due to the dihydrobenzofuran moiety.

EXPERIMENTAL

Extraction and isolation. Plant material was collected in June 1977 at Tomakomai Expt. Forests (Tomakomai, Hokkaido, Japan). Dried sapwood meal (11.2 kg) and heartwood meal (6.8 kg) were extracted with 95% EtOH for 72 hr at room temp (×3). The former EtOH extract was concentrated and successively reextracted with *n*-hexane and Et_2O (500 ml × 5). The latter EtOH extract was further extracted in succession with *n*-hexane, $CHCl_3$, Et_2O and EtOAc (each 1 l. × 5). Et_2O extract (23 g) of sapwood was chromatographed on a Sephadex LH-20 (Me_2CO), giving 4 (A–D) fractions. Fractions B and C were then chromatographed on a Si gel column (C_6H_6–EtOAc, 2:1, satd with H_2O), yielding 8 (B_{i-viii}) and 10 (C_{i-x}) fractions, respectively. B_{vii} gave compound **1** as a pale yellow oil (74 mg) after purification on a Si gel column (*n*-hexane–Me_2CO, 2:1), and B_{vii} gave compound **3** (22 mg) as a colourless oil with the same procedure. C_x was passed through a Si gel column (*n*-hexane–EtOAc, 1:2) to give compound **2** (26 mg) as a colourless oil. EtOAc extract (18 g) of heartwood was also divided into 6 fractions (E–J) on a Sephadex LH-20 column (dioxane–H_2O, 1:1). The fourth fraction (H) was rechromatographed on Si gel columns (EtOAc) and ($CHCl_3$–MeOH, 19:1) to yield compound **1** (50 mg) and compound **4** (50 mg). Fraction G was also chromatographed on a Si gel column (EtOAc and *n*-hexane–Me_2CO, 1:3), yielding compound **5** (20 mg) as an amorphous powder.

1-(4-*Hydroxy*-3-*methoxyphenyl*)-2-{4-[2-*formyl*-(E)-*vinyl*]-2-*methoxyphenoxy*}-*propane*-1,3-*diol*(**1**). Pale yellow oil, $[\alpha]_D^{31}$ −3.9° (MeOH; *c* 1.64). ν_{max}^{KBr} cm^{-1}: 3400, 1665, 1620, 1600, 1510, 1470, 1430, 1275, 1130, 1030. λ_{max}^{EtOH} nm (log ε): 336 (4.04), 288 (3.84), 230 (4.02). MS (high resolution), found: 374.1323, calc. $C_{20}H_{22}O_7$, 374.1364. MS *m/e* (rel. int.): 374 [M^+] (0.5), 326 (42), 204 (90), 178 (100), 161 (16), 153 (32), 152 (12), 151 (26), 149 (14), 147 (14), 137 (54), 135 (12), 93 (14). ^1H NMR (100 MHz, $(CD_3)_2CO$): δ3.6–4.0 (2H, H-γ), 3.8 (3H, *s*, OMe), 3.86 and 3.91 (3H, 2×*s*, OMe), 4.52 (1H, *m*, H-β), 4.94 (1H, *d*, *J* = 6 Hz, H-α), 6.64 and 6.66 (1H, 2×*dd*, *J* = 8 Hz, 16 Hz, H-β'), 6.5–7.4 (6H, Ar-H), 7.53 and 7.55 (1H, 2×*d*, *J* = 16 Hz, H-α'), 9.57 and 9.6 (1H, 2×*d*, *J* = 8 Hz, H-γ'). Triacetate of **1**, amorphous powder, MS *m/e* (rel. int.): 500 [M^+] (1), 221 (27), 179 (39), 178 (56), 153 (20), 43 (100). ^1H NMR (100 MHz, $CDCl_3$): δ2.0, 2.03, 2.06, and 2.09 (6H, 4×*s*, alc–OAc), 2.3 (3H, *s*, Ar-OAc), 3.81 and 3.87 (6H, 2×*s*, OMe), 4.29 (2H, *m*, H-γ), 4.76 (1H, *m*, H-β), 6.08 (1H, *m*, H-α), 6.6 and 6.61 (1H, 2×*dd*, *J* = 8, 16 Hz, H-β', 6.7–7.2 (6H, Ar-H), 7.4 and 7.41 (1H, 2×*d*, *J* = 16 Hz, H-α'), 9.66 and 9.67 (1H, 2×*d*, *J* = 8 Hz, H-γ'). Compound **1** (45 mg) was converted to C_6H_6–boronic esters according to the procedure of ref. [4], and then chromatographed on a Si gel column ($CHCl_3$–Mr_2CO, 20:1), giving *erythro*(31 mg)- and *threo*(17 mg)-benzeneboronates.

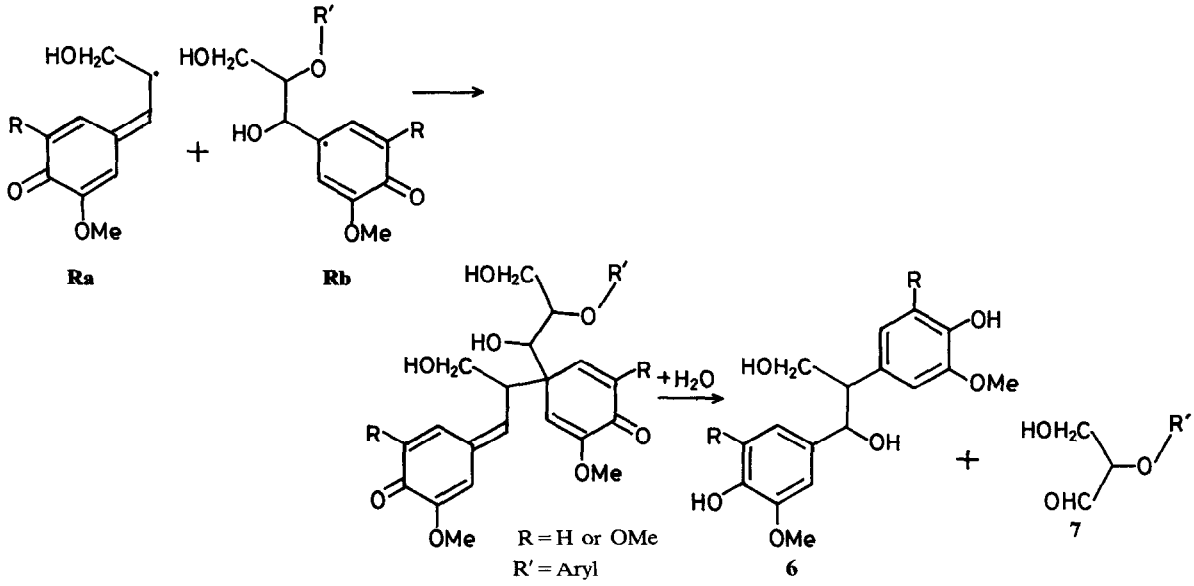

Fig. 1. Proposed mechanism for the formation of diarylpropane by Lundquist *et al.* [11].

Erythro-benzeneboronate, pale yellow oil. ^{1}H NMR (100 MHz, $CDCl_3$): δ3.84 (6H, *s*, OMe), 4.17 (2H, *m*, H-γ), 4.62 (1H, *m*, H-β), 5:4 (1H, *d*, *J* = 4 Hz, H-α), 6.62 (1H, *dd*, *J* = 8, 16 Hz, H-β′) 6.8–8.0 (12H, H-α′ and Ar-H), 9.64 (1H, *d*, *J* = 8 Hz, H-γ′). *Threo*-benzeneboronate, pale yellow oil. ^{1}H NMR (100 MHz, $CDCl_3$): δ3.69 (3H, *s*, OMe), 3.85 (3H, *s*, OMe), 4.34 (2H, *m*, H-γ), 4.78 (1H, *m*, H-β), 5.41 (1H, *d*, *J* = 2 Hz, H = α), 6.55 (1H, *dd*, *J* = 8, 16 Hz, H-β′), 6.6–8.0 (12H, H-α′ and Ar-H), 9.59 (1H, *d*, *J* = 8 Hz, H-γ′). Both benzeneboronates were hydrolysed individually on a Sephadex LH-20 column (MeOH, 55 × 1.2 cm) and obtained as the free *erythro*(21 mg) and *threo*(8 mg) isomers.

Erythro-1-(4-*hydroxy*-3-*methoxyphenyl*)-2-{4-[2-*formyl*-(E)-*vinyl*]-2-*methoxyphenoxy*}-*propane*-1,3-*diol*. Pale yellow oil, $[\alpha]_D^{20}$ −2.6° (MeOH: *c* 0.91). λ_{max}^{EtOH} nm (log ε): 336 (4.26), 288 (4.07), 230 (4.27). MS *m/e* (rel. int.): 374 [M$^+$] (2), 356 (16), 326 (30), 297 (11), 265 (13), 204 (59), 178 (100), 161 (16), 153 (19), 152 (11), 151 (15), 147 (15), 137 (34). ^{1}H NMR (100 MHz, $(CD_3)_2CO$): δ3.5–4.0 (2H, H-γ), 3.8 (3H, *s*, OMe), 3.87 (3H, *s*, OMe), 4.54 (1H, *m*, H-β), 4.92 (1H, *d*, *J* = 6 Hz, H-α), 6.64 (1H, *dd*, *J* = 8, 16 Hz, H-β′), 6.7–7.4 (6H, Ar-H), 7.54 (1H, *d*, *J* = 16 Hz, H-α′), 9.61 (1H, *d*, *J* = 8 Hz, H-γ′).

Threo-1-(4-*hydroxy*-3-*methoxyphenyl*)-2-{4-[2-*formyl*-(E)-*vinyl*]-2-*methoxyphenoxy*}-*propane*-1,3-*diol*. Pale yellow oil, $[\alpha]_D^{20}$ −12.5° (MeOH; *c* 0.52). λ_{max}^{EtOH} nm (log ε): 336 (4.30), 288 (4.11), 230 (4.28). MS *m/e* (rel. int.): 374 [M$^+$] (1), 326 (16), 204 (79), 178 (100), 161 (12), 153 (17), 151 (15), 147 (11), 137 (96). ^{1}H NMR (100 MHz, $(CD_3)_2CO$): δ3.4–4.0 (2H, H-γ), 3.8 (3H, *s*, OMe), 3.92 (3H, *s*, OMe), 4.34 (1H, *m*, H-β), 4.9 (1H, *d*, *J* = 6 Hz, H-α), 6.61 (1H, *dd*, *J* = 8, 16 Hz, H-β′), 6.7–7.3 (6H, Ar-H), 7.48 (1H, *d*, *J* = 16 Hz, H-α′), 9.57 (1H, *d*, *J* = 8 Hz, H-γ′). The reduction product of **1** with $NaBH_4$ agreed with an authentic sample and **2** (TLC and IR).

1-(4-*Hydroxy*-3-*methoxyphenyl*)-2-{2-*methoxy*-4-[1-(E)-*propen*-3-*ol*]-*phenoxy*}-*propane*-1,3-*diol*(**2**). Colourless oil, $[\alpha]_D^{22}$ −6.7° (MeOH; *c* 0.53). ν_{max}^{KBr} cm^{-1}: 3400, 1650, 1600, 1510, 1460, 1420, 1270, 1225, 1155, 1130, 1025, 965, 850, 815. λ_{max}^{EtOH} nm (log ε): 266 (3.94). MS (high resolution), found: 376.1498, calc. $C_{20}H_{24}O_7$, 376.1520. MS *m/e* (rel. int.): 376 [M$^+$] (2), 358 (15), 208 (14), 206 (52), 180 (53), 153 (11), 137 (100), 124 (25), 91 (12). ^{1}H NMR (100 MHz, $(CD_3)_2CO + D_2O$): δ3.84, 3.87 and 3.92 (6H, 3 × *s*, OMe), 3.6–4.0 (2H, H-γ), 4.22 (2H, *d*, *J* = 5 Hz, H-γ′), 4.36 (1H, *m*, H-β), 4.94 (1H, *d*, *J* = 6 Hz, H-α), 6.32 (1H, *dt*, *J* = 5, 16 Hz, H-β′), 6.54 (1H, *d*, *J* = 16 Hz, H-α′), 6.7–7.1 (6H, Ar-H). Tetraacetate, amorphous powder, MS *m/e* (rel. int.): 544 [M$^+$] (1), 222 (21), 221 (12), 179 (23), 43 (100). ^{1}H NMR (100 MHz, $CDCl_3$): δ2.0, 2.02 and 2.05 (6H, 3 × *s*, alc-OAc), 2.1 (3H, *s*, alc-OAc), 2.3 (3H, *s*, Ar-OAc), 3.81 (6H, *s*, OMe), 3.9–4.5 (2H, H-γ), 4.7 (2H, *d*, *J* = 6 Hz, H-γ′), 4.5–4.8 (1H, H-β), 6.1 (1H, *m*, H-α), 5.9–6.3 (1H, H-β′), 6.56 (1H, *d*, *J* = 16 Hz, H-α′), 6.7–7.1 (6H, Ar-H).

1-(4-*Hydroxy*-3-*methoxyphenyl*)-2-(4-*formyl*-2-*methoxy*-*phenoxy*)-*propane*-1,3-*diol* (**3**). Colourless oil, $[\alpha]_D^{20}$ +2.1° (MeOH; *c* 1.10). ν_{max}^{KBr} cm^{-1}: 3400, 1680, 1600, 1590, 1510, 1470, 1430, 1280, 1240, 1160, 1130, 1030, 865, 820, 780, 730. λ_{max}^{EtOH} nm (log ε): 310 (3.92), 280 (4.03), 230 (4.24). MS (high resolution), found: 348.1257, calc. $C_{18}H_{20}O_7$, 348.1209. MS *m/e* (rel. int.): 348 [M$^+$] (0.4), 178 (100), 153 (37), 152 (29), 151 (26), 137 (33), 93 (16). ^{1}H NMR (100 MHz, $(CD_3)_2CO + D_2O$): δ3.5–3.9 (2H, H-γ), 3.8, 3.88 and 3.94 (6H, 3 × *s*, OMe), 4.68 (1H, *m*, H-β), 4.96 (1H, *m*, H-α), 6.74 (1H, *d*, *J* = 8 Hz, H-6′), 6.92 (2H, *dd*, *J* = 2, 8 Hz, H-3′ and H-5′), 7.0–7.5 (3H, Ar-H), 9.79 (1H, split *s*, CHO). Triacetate, amorphous powder. MS *m/e* (rel. int.): 474 [M$^+$] (2), 237 (32), 221 (18), 195 (78), 179 (42), 178 (49), 153 (97), 152 (21), 151 (11), 43 (100). ^{1}H NMR (100 MHz, $CDCl_3$): δ1.99, 2.04 and 2.07 (6H, 3 × *s*, alc-OAc), 2.29 (3H, *s*, Ar-OAc), 3.81, 3.87 and 3.9 (6H, 3 × *s*, OMe), 4.0–4.6 (2H, H-γ), 4.86 (1H, *m*, H-β), 6.07 (1H, *m*, H-α), 6.9–7.4 (6H, Ar-H), 9.8 (1H, split *s*, CHO).

1,2-*Bis*-(4-*hydroxy*-3-*methoxyphenyl*)-*propane*-1,3-*diol* (**4**). Amorphous white powder. ν_{max}^{KBr} cm^{-1}: 3400, 1605, 1515, 1465, 1445, 1425, 1270, 1225, 1150, 1120, 1065, 1030, 845, 790. λ_{max}^{EtOH} nm (log ε): 282 (3.53). MS *m/e* (rel. int.): 302 [M$^+$-18] (1), 284 (6), 273 (6), 272 (100), 150 (25). ^{1}H NMR (100 MHz, $(CD_3)_2CO + D_2O$): δ3.02 (1H, *m*, H-β), 3.5–4.0 (2H, H-γ), 3.7 (3H, *s*, OMe), 3.74 (3H, *s*, OMe), 4.92 (1/4H, *d*, *J* = 8 Hz, H-α_{threo}), 5.06 (3/4H, *d*, *J* = 6 Hz, H-$\alpha_{erythro}$), 6.5–6.8 (6H, Ar-H). ^{13}C NMR (25.0 M Hz, CD_3OD): see Table 2. Tetraacetate, amorphous powder. MS (high resolution), found: 488.1708, calc. $C_{25}H_{28}O_{10}$, 488.1683. MS *m/e* (rel. int.): 488 [M$^+$] (0.5), 446 (2), 237 (8), 209 (10), 195 (53), 192 (14), 153 (71), 150 (100). ^{1}H NMR (100 MHz, $CDCl_3$): δ2.04 and 2.12 (6H, 2 × *s*, alc-OAc), 2.26 (6H, *s*, Ar-OAc), 3.44 (1H, *m*, H-β), 3.64 (3H, *s*, OMe), 3.66 (3H, *s*, OMe), 4.1–4.6 (2H, H-γ), 5.96 (1H, *d*, *J* = 8 Hz, H-α), 6.4–7.0 (6H, Ar-H). Compound **4** (23 mg) was converted to C_6H_6-boronates as described in the case of **1**, giving *erythro*(18 mg)- and *threo*(7 mg)-benzeneboronates. *Erythro*-benzeneboronate, amorphous powder. ^{1}H NMR (100 MHz, $CDCl_3$): δ3.57 (3H, *s*, OMe), 3.68 (3H, *s*, OMe), 3.4–3.8 (1H, H-β), 4.32 (1H, *d*, *J* = 6 Hz, H-γ), 4.33 (1H, *d*, *J* = 7 Hz, H-γ), 5.4 (1H, *d*, *J* = 4.5 Hz, H-α), 6.1–8.0 (11H, Ar-H). *Threo*-benzeneboronate, amorphous powder. ^{1}H NMR (100 MHz, $CDCl_3$): δ2.98 (1H, *td*, *J* = 10, 5.5 Hz, H-β), 3.7 (3H, *s*, OMe), 3.73 (3H, *s*, OMe), 4.3 (1H, *d*, *J* = 5.5 Hz, H-γ), 4.34 (1H, *d*, *J* = 10 Hz, H-γ), 5.14 (1H, *d*, *J* = 10 Hz, H-α), 6.3–8.0 (11H, Ar-H). Both benzeneboronates were passed through a Sephadex LH-20 column (MeOH, 55 × 1.2 cm), giving free *erythro* (13 mg) and *threo* (4 mg) isomers.

Erythro-1,2-*bis*-(4-*hydroxy*-3-*methoxyphenyl*)-*propane*-1,3-*diol*. Mp 143–144° (from EtOAc). ^{1}H NMR (100 MHz, $(CD_3)_2CO + D_2O$): δ2.96 (1H, *m*, H-β), 3.5–4.1 (2H, H-γ), 3.66 (3H, *s*, OMe), 3.7 (3H, *s*, OMe), 5.02 (1H, *d*, *J* = 6 Hz, H-α), 6.6–6.8 (6H, Ar-H).

Threo-1,2-*bis*-(4-*hydroxy*-3-*methoxyphenyl*)-*propane*-1,3-*diol*. Colourless oil. ^{1}H NMR (100 MHz, $(CD_3)_2CO + D_2O$): δ3.08 (1H, *m*, H-β), 3.7 (6H, *s*, OMe), 3.7–4.2 (2H, H-γ), 4.9 (1H, *d*, *J* = 8 Hz, H-α), 6.5–6.8 (6H, Ar-H).

Leptolepisol C (**5**). Amorphous white powder, $[\alpha]_D^{28}$ −1.0° (MeOH; *c* 1.28). ν_{max}^{KBr} cm^{-1}: 3400, 1605, 1520, 1465, 1450, 1215, 1130, 1030, 850, 810. λ_{max}^{EtOH} nm (log ε): 280 (3.78). MS (high resolution), found: 480.1789, calc. $C_{27}H_{28}O_8$, 480.1784 [M-18]. MS *m/e* (rel. int.): 480 [M$^+$-18] (1), 450 (14), 432 (81), 420 (100), 312 (13), 300 (11), 210 (12), 151 (18), 150 (29), 149 (10), 137 (38). ^{1}H NMR (100 MHz, $(CD_3)_2CO + D_2O$): δ2.98 (1H, *m*, H-β), 3.74 (6H, *s*, OMe), 3.80 (3H, *s*, OMe), 3.3–4.1 (5H, H-β′, H-γ, H-γ′), 5.06 (1H, *d*, *J* = 5 Hz, H-α), 5.54 (1H, *d*, *J* = 5 Hz, H-α′), 6.5–7.1 (8H, Ar-H). ^{13}C NMR (25.0 MHz, CD_3OD): see Table 2. Penta-acetate, amorphous powder. MS *m/e* (rel. int.): 708 [M$^+$] (2), 457 (12), 415 (68), 313 (82), 137 (62), 43 (100). ^{1}H NMR (100 MHz, $CDCl_3$): δ1.96, 1.98 and 2.03 (9H, 3 × *s*, alc-OAc), 2.3 (6H, *s*, Ar-OAc), 3.38 (1H, *m*, H-β), 3.77 (3H, *s*, OMe), 3.8 (6H, *s*, OMe), 4.0–4.6 (4H, H-γ and H-γ′), 5.52 (1H, *d*, *J* = 6.5 Hz, H-α′), 6.04 (1H, *d*, *J* = 6.5 Hz, H-α), 6.5–7.1 (8H, Ar-H). Penta-Me ether (Hakomori method), colourless oil. MS (high resolution), found: 568.2627, calc. $C_{32}H_{40}O_9$, 568.2670. MS *m/e* (rel. int.): 568 [M$^+$] (0.1), 374 (12), 373 (100), 341 (94).

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