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REASSIGNMENT OF RELATIVE STEREOCHEMISTRY AT C-7 AND C-8 IN ARYLCOUMARAN NEOLIGNANS

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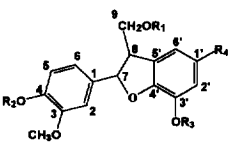
Key Word Index—arylcoumaran neolignans; 8-5′-neolignans; dilignols; relative configurations; *trans-cis* stereochemistry; ^{1}H NMR spectra; chemical shifts; coupling constants.

Abstract—^{1}H NMR spectral characteristics of synthetic *trans* and *cis* arylcoumarans and their acetates which are related to 8-5′ neolignans are given. This information is used to reassign structures to neolignans reported in nine papers, from the *cis* to the *trans* 7-aryl-8-hydroxymethyl configurations, and to neolignans in six papers in which no assignments were made. Thus far, there is no evidence for the occurrence of 8-5′ neolignans with a *cis* configuration in nature. © 1997 Elsevier Science Ltd

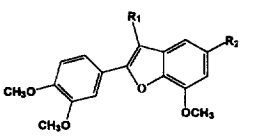
INTRODUCTION

Many arylcoumaran neolignans of type **1** which are linked through carbon atoms 8 and 5′ of the arylpropane units have been described [1]. The relative stereochemistry of the C-7 aryl and C-8 hydroxymethyl substituents has been variously proposed to be *trans* and *cis*, mainly on the basis of ^{1}H NMR spectroscopy, while in other cases, the configuration has not been specified. In particular, the magnitude of the ^{1}H NMR coupling constant $J_{7,8}$ has often been used to assign configuration at C-7 and C-8, following from the early work of Ludwig *et al.* in which a *cis* configuration for the diacetate of dehydrodiconiferyl alcohol was erroneously proposed [2]. In spite of the acknowledged uncertainty in such practice for arylcoumaran neolignans [3] and 2,3-disubstituted dihydrobenzofurans in general [4], assignments continue to be made on that basis [5]. However, some recent studies have provided more convincing evidence for the *trans* disposition of C-7 and C-8 substituents in neolignans of type **1** through nuclear Overhauser effect NMR spectroscopic observations [6, 7]. This led Fukuyama *et al.* [6] to assign the *trans* configuration to arylcoumaran neolignans for which stereochemistry was not, or only tentatively, given [8–13].

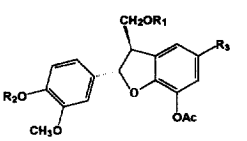
Several neolignan and dilignol analogues of type **1** have been synthesized by oxidative coupling of phenolic precursors [14, 15] or by other means [16, 17]. The configuration at C-7 and C-8 in the compounds was determined by conversion to structures of known configuration [15, 18–21] and was confirmed for compound **2d** by X-ray crystallography [22]. The ^{1}H NMR spectra of several *trans* and *cis* arylcoumarans (**2** and **3**) are given in the present report, and from these data a number of neolignans of type **1** for which *cis* structures were proposed are reassigned as *trans* neolignans [23–31], and the *trans* configuration is assigned



1 $R_1 = R_2$ = H or sugar unit
R_3 = H or CH_3
R_4 = 3-carbon sidechain



	R_1	R_2
4a	CH_3	$CH_2CH_2CH_3$
b	CHO	H



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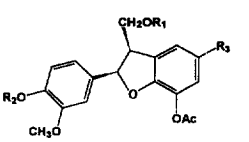
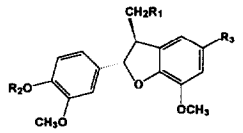


6

	R_1	R_2	R_3
a	Ac	Ac	CH_2-CH_2-CH_2OAc
b	Ac	glucosyl-(OAc)$_4$	CH_2-CH_2-CH_2OAc
c	Ac	rhamnosyl-(OAc)$_3$	CH_2-CH_2-CH_2OAc
d	*p*-OAc-cinnamoyl	Ac	CH_2-CH_2-CH_2OAc
e	Ac	Ac	*(E)*-CH=CH-CHO
f	Ac	CH_3	*(E)*-CH=CH-CHO

* Author to whom correspondence should be addressed.



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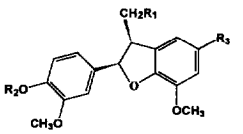

3

	R_1	R_2	R_3
a	H	CH_3	CH_2-CH_2-CH_3
b	OH	CH_3	H
c	OAc	CH_3	H
d	OH	H	H
e	OAc	Ac	H
f	OAc	Ac	CH_2-CH_2-CH_2OAc
g	OAc	glucosyl-$(OAc)_4$	CH_2-CH_2-CH_2OAc
h	OAc	$CH(CH_2OAc)_2$	CH_2-CH_2-CH_2OAc
i	OH	H	CH_2-CH_2-CH_2OH
j	OH	H	*(E)* -CH=CH-CH_2OH
k	OAc	H	*(E)* -CH=CH-CH_2OAc
l	OAc	glucosyl-$(OAc)_4$	*(E)* -CH=CH-CH_2OAc
m	OAc	Ac	*(E)* -CH=CH-$COOCH_3$
n	OH	H	*(E)* -CH=CH-CHO

to some neolignans for which no stereochemistry was originally given [32–37].

RESULTS AND DISCUSSION

The *cis* form of the arylcoumaran dihydrodehydrodiisoeugenol methyl ether (**3a**) is the only synthetic *cis* 8–5′ neolignan to have been reported, and it was prepared by catalytic hydrogenation of the corresponding arylcoumarone **4a** [38]. However, no *cis* neolignans of type **1**, with an oxygenated function on C-9, have been synthesised previously. This has now been accomplished for the *cis* arylcoumaran **3b** by catalytic hydrogenation of the arylcoumarone **4b**. The ^{1}H NMR spectra of compound **3b** and the *trans* form **2b**, their acetates (**2c** and **3c**) and the related acetates **2e** and **2f**, are given in Table 1. These spectral data are further compared with those of reported neolignans of type **1** (Table 1), and this has allowed unequivocal configurational assignment to the compounds.

Comparison of the ^{1}H NMR spectra of the *trans* and *cis* arylcoumarans **2a** and **3a** revealed that for the *trans* isomer the C-9 methyl group doublet appeared at lower field while the H-7 and H-8 signals were at higher field than those of the *cis* isomer (Table 1). This can be explained in terms of restricted rotation about the C-7-aryl bond in the *cis* isomer, which places the C-9 methyl group protons in the shielding zone of the aromatic ring, and the H-7 proton in the deshielding zone. The coupling constant $J_{7,8}$ was larger for the *trans* than for the *cis* isomer (9.1 vs 8.2 Hz, respectively). Similar trends are noted in the ^{1}H NMR spectra of the *trans* and *cis* isomers **2b** and **3b** and their acetates **2c** and **3c**, although in these cases, the *trans* isomers had smaller coupling constants $J_{7,8}$ than did the *cis* isomers (7.3 vs 8.2–8.4 Hz). Each C-9 proton occurred as a doublet of doublets and exhibited different chemical shifts, although those signals for the *cis* acetate **3c** occurred with the H-8 signal as a multiplet overlapped by methoxyl signals. Comparison of the ^{1}H NMR spectrum of the *trans* acetate **2c** with that of the *trans* triacetate **2f** reveals that the H-7, H-8, H-9 and C-9 acetate signals have similar characteristics (Table 1), which shows that the R_3 substituent in **2f** does not affect those signals. When the 3,4-dimethoxyphenyl substituent in **2c** is replaced by a 3-methoxy-4-acetoxyphenyl substituent (**2e**), the H-7 NMR signal was shifted downfield from 5.47 to 5.52 ppm, in line with previous observations [39].

A neolignan glucoside of type **1** isolated from *Pteris vittata* was assigned the *cis* configuration by the authors [31]. The acetylated aglycone has ^{1}H NMR spectral characteristics of the *trans* compound **2f** rather than the *cis* isomer **3f** (Table 1). The signals assigned to the two C-9 protons were inadequately described as a quartet centred at 4.31 ppm by Satake *et al.* [31]. In this and several following cases, the spectrometer operating at 60 MHz was not able to resolve the signals completely. A further neolignan of type **1** from the sapwood of *Larix leptolepis* for which no stereochemistry was proposed [34] had ^{1}H NMR signals for its acetate and aglycone acetate, which were similar to those of compound **2f**. These observations require the compounds to be reassigned the *trans* configuration.

A number of neolignan glycosides of type **1** have been isolated from the needles of *Picea abies* [30] and *Pinus massoniana* [11], and the inner bark of *Betula pendula* [24] and *Pinus sylvestris* [23], and the *cis* configuration **3f** was assigned to the acetylated aglycone of the compounds. However, the ^{1}H NMR spectral data given for the acetylated aglycone [30], with the exception of the coupling constants $J_{8,9}$, are identical with those of **2f** (Table 1), which requires the compounds to be reassigned the *trans* configuration. The coupling constants $J_{8,9}$ given for individual H-9 protons in the ^{1}H NMR spectrum of the acetylated aglycone [30] were transposed, probably in error, in comparison with those given in the earlier [16] and present reports for compounds **2e** and **2f**, respectively. In addition, the acetylated glucoside previously given in *cis* configuration **3g** [30] has an H-7 NMR signal identical with that of the acetylated aglycone **2f**, which allows the *trans* configuration **2g** to be given to the compound. Likewise, the hexacetate of the neolignan glucoside isolated from the inner bark of *Larix leptolepis* [35], shown above to have the *trans* configuration, had an identical H-7 NMR signal (Table 1).

Kouno *et al.* [32] described a neolignan of type **1** from the bark of *Illicium difengpi*, to which no stereochemistry was assigned. The *trans* stereochemistry (**2h**) is given to the acetylated compounds on the basis of the similarity of its ^{1}H NMR signals to those of compound **2f** (Table 1).

Table 1. ^{1}H NMR chemical shifts of arylcoumaran neolignans and their acetates (in $CDCl_3$)

Compound	Previous designation	C-9 $OCOCH_3$	H-9a	H-9b	H-8	H-7	Reference
2a	—	—	1.37 (*d*, *J* = 6.6)		3.48 (*dq*)	5.12 (*d*, *J* = 9.1)	this work
3a	—	—	0.82 (*d*, 6.9)		3.58 (*dq*)	5.78 (*d*, *J* = 8.2)	this work
2b	—	—	3.92 (*dd*, *J* = 4.6, 10.9)	4.00 (*dd*, *J* = 6.0, 10.9)	3.66 (*m*)	5.60 (*d*, *J* = 7.3)	this work
3b	—	—	3.45 (*dd*, *J* = 5.7, 11.5)	3.55 (*dd*, *J* = 7.3, 11.5)	3.71 (*m*)	5.88 (*d*, *J* = 8.4)	this work
2c	—	2.03 (*s*)	4.33 (*dd*, *J* = 7.4, 11.0)	4.44 (*dd*, *J* = 5.7, 11.0)	3.82 (*m*)	5.47 (*d*, *J* = 7.3)	this work
3c	—	1.89 (*s*)	3.78–3.96 (*m*)	3.78–3.96 (*m*)	3.84 (*m*)	5.87 (*d*, *J* = 8.2)	this work
2e	**2e**	2.04 (*s*)	4.32 (*dd*, *J* = 7.6, 11.1)	4.45 (*dd*, *J* = 5.5, 11.1)	3.79 (*m*)	5.52 (*d*, *J* = 6.8)	16
2f	—	2.05 or 2.06 (*s*)	4.29 (*dd*, *J* = 7.8, 11.2)	4.45 (*dd*, *J* = 5.3, 11.2)	3.77 (*m*)	5.51 (*d*, *J* = 6.7)	this work
2f	**3f**	2.04 (*s*)	4.31 (*q*, *J* = 7)		3.7–3.9 (*m*)	5.46 (*d*, *J* = 7)	31
2f	unassigned	2.05 or 2.07 (*s*)	4.41 (*m*)		3.76 (*m*)	5.54 (*d*, *J* = 6.0)	34
2f	**3f**	2.05 or 2.07 (*s*)	4.31 (*dd*, *J* = 5.6, 10.9)	4.47 (*dd*, *J* = 7.1, 10.9)	not reported	5.51 (*d*, *J* = 7.2)	30
2g	**3g**	not reported	not reported	not reported	not reported	5.47 (*d*, *J* = 7.2)	30
2g	unassigned	not reported	4.0–4.3 (*m*)		3.6–3.9 (*m*)	5.46 (*d*, *J* = 6.0)	35
2h	unassigned	2.02	4.27–4.56 (*m*)		not reported	5.48 (*d*, *J* = 6.6)	32
2i	**3i**	—	3.85–4.0 (*m*)		3.60 (*br ddd*)	5.42 (*d*, *J* = 6.5)	26
2j	**3j**	—	3.85–4.0 (*m*)		3.62 (*br ddd*)	5.58 (*d*, *J* = 6.5)	26
2k	**3k**	2.04 (*s*)	4.32 (*dd*, *J* = 8, 11)	4.45 (*dd*, *J* = 6.11)	3.79 (*ddd*, *J* = 8, 7.5, 6)	5.49 (*d*, *J* = 7.5)	28
2l	**3l**	not reported	4.14–4.4 (*m*)		3.74 (*m*)	5.48 (*d*, *J* = 7)	29
2m	**3m**	2.00 (*s*)	4.25 (*dd*, *J* = 6)		4.30 (*td*, *J* = 6, 6)	5.54 (*d*, *J* = 6)	25
2n	**2n**	—	3.50–4.00 (*m*)		3.50–4.00 (*m*)	5.64 (*d*, *J* = 7)	14
5a	unassigned	2.05 or 2.07 (*s*)	4.36 (*m*)		3.72 (*m*)	5.54 (*d*, *J* = 6.0)	34
5a	unassigned	2.00 or 2.08 (*s*)	4.38 (*m*)		3.76 (*m*)	5.56 (*d*, *J* = 6.0)	35
5a	unassigned	2.05 or 2.08 (*s*)	4.13 (*q*, *J* = 8, 10)	4.48 (*q*, *J* = 6, 10)	3.70 *m*)	not reported	36
5b	unassigned	not reported	4.0–4.6 (*m*)		4.0–4.6 (*m*)	5.54 (*d*, *J* = 6.0)	35
5c	unassigned	not reported	3.6–4.2 (*m*)		3.6–4.2 (*m*)	5.64 (*d*, *J* = 6.0)	35
5d	**6d**	—	4.43 (*dd*, *J* = 7.7, 11.0)	4.58 (*dd*, *J* = 5.1, 11.0)	3.72–3.86 (*m*)	5.63 *d*, *J* = 5.9)	27
5e	**6e**	2.10 (*s*)	4.33–4.48 (*m*)		3.74–3.83 (*m*)	5.64 (*d*, *J* = 5.9)	27
5e	unassigned	2.10 (*s*)	4.4 (*m*)		3.6–4.0 (*m*)	5.63 (*d*, *J* = 6.0)	37
5f	unassigned	2.06 (*s*)	4.40 (*m*)		3.72 (*m*)	5.59 (*d*, *J* = 7.0)	33 and 34

The *cis* configuration was given to two neolignans **3i** and **3j** isolated from the roots of *Vladimiria souliei* [26]. However, as the ^{1}H NMR spectra of the neolignans had signals corresponding to the *trans* compound **2b**, rather than the *cis* compound **3b** (Table 1), they are reassigned to the former configuration **2i** and **2j**.

The roots of *Lasiolaena morii* were found to contain a neolignan of type **1** to which the *cis* configuration **3k** was given [28]. However, the ^{1}H NMR spectrum of the compound had signals corresponding to the *trans* compound **2f** (Table 1), which shows that the *trans* configuration should be assigned to the compound. A related compound, isolated from *Euphrasia rostkoviana*, was also reported to have a *cis* configuration [29]. However, comparison of the ^{1}H NMR signals of its acetate **3l** with those of compound **2f** (Table 1) showed that once more, the compound has the *trans* configuration **2l**.

The stem bark of *Xylopia buxifolia* yielded a type **1** neolignan, for which a *cis* structure was proposed [25]. The ^{1}H NMR spectrum of its acetate **3m** had signals more consistent with those of the *trans* compound **2f** than those of the *cis* structure **3c** (Table 1). The chemical shift given for the C-8 proton, 4.30 ppm, is about 0.5 δ downfield from that of analogous structures, possibly due to an error in assigning different chemical shifts to the C-9 protons. The structure should be reassigned as the *trans* compound **2m**.

A neolignan of type **1** was isolated by Takehara and Sasaya from the sapwood of *Larix leptolepis*, although no configurational assignment was made [34]. From comparison of the ^{1}H NMR signals of the acetylated compound with those of compound **2f** (Table 1), the *trans* configuration **5a** is given to the compound. On the same basis, compound **5a** is assigned to the acetylated aglycone of two neolignans from the inner bark of *Larix leptolepis* [35]. The two glycosides thus have the *trans* configuration and are represented by structures **5b** and **5c**, respectively. Their ^{1}H NMR spectra have similar characteristics to those of the aglycone (Table 1). The aglycone (cedrusin) has also been described as a component of the wood of *Cedrus deodara* [36], and although ^{1}H NMR data for the H-7 signal of the tetracetate was not recorded, the similarity of the signals to those of **5a** require the compound to have the *trans* configuration (Table 1).

Ozawa *et al.* isolated two neolignans of type **1** from the wood of *Abies sachalinensis*, to which they assigned the *cis* configuration [27]. The acetylated neolignans **6d** and **6e** had ^{1}H NMR signals similar to those of the *trans* compound **2f** and different from those of the *cis* compound **3c** (Table 1). Furthermore, the H-7 proton of **6e** had a chemical shift (5.64 ppm) identical with that of the synthetic analogous compound **2n** with a *trans* configuration. Based on these observations, the *trans* configuration **5d** and **5e** should be reassigned to the acetylated compounds. Following similar reasoning, the acetylated neolignan isolated from *Larix leptolepis* heartwood, for which no configuration was assigned [37], should be given the *trans* configuration **5e**, and the acetylated neolignan from the sapwood of *Larix leptolepis* [33, 34] should also be given the *trans* configuration (**5f**) (Table 1).

The biogenesis of neolignans is considered to proceed by oxidative coupling of *p*-hydroxyphenylpropane monomers through the intermediacy of free radical intermediates [40]. For 8-5′ neolignans, radical coupling gives an intermediate quinonemethide, to which an adjacent phenol adds intramolecularly to form the arylcoumaran structure. The oxidative coupling of both (*E*)- and (*Z*)-isoeugenol has given rise, in both cases, to an arylcoumaran with a *trans* arrangement of aryl and methyl substituents about the coumaran ring. This suggests that the ring closure will always proceed to give *trans* arylcoumarans, because rotation about the C-7—C-8 bond to give the more stable *trans* configuration is faster than the cyclisation reaction [38, 41]. There is thus no evidence for the occurrence of neolignans of type **1** with the *cis* configuration in nature.

EXPERIMENTAL

General. ^{1}H NMR spectra were measured at 60 MHz (compounds **2a** and **3a**), 270 MHz (compound **2f**) and 400 MHz (compounds **2b**, **3b**, **2c** and **3c**). The spectra were obtained with deuteriochloroform solns of the compounds, and chemical shifts are given in ppm from tetramethylsilane (δ 0.00), added as an int. standard. *trans*-Dihydrodehydrodiisoeugenol methyl ether was prepd from isoeugenol, and the arylcoumarone **4a** was prepd according to ref. [38, 41]. The *trans* arylcoumaran **2d** was prepd by the methods reported in ref. [16]. *trans*-Dihydrodehydrodiconiferyl alcohol triacetate (**2f**) was prepd from (*E*)-coniferyl alcohol according to ref. [15].

cis-*Dihydrodehydrodiisoeugenol methyl ether* (**3a**). A soln of the phenylcoumarone **4a** (100 mg) in EtOH (25 mL) containing 5% Pd-C (25 mg) was hydrogenated at 20° for 7 days. The catalyst was removed by filtration, and the solvent was removed *in vacuo* to give an oil, which was adsorbed on a column of silica gel. Elution with petrol–dichloromethane 4:1 gave successively starting material (10 mg) and compound **3a** as an oil (70 mg). ^{1}H NMR δ 0.82 (3H, *d*, J = 6.9 Hz, H-9), 0.95 (3H, *t*, J = 6.5 Hz, H-9′), 1.65 (2H, *m*, H-8′), 2.57 (2H, *t*, J = 6.5 Hz, H-7′), 3.58 (1H, *dq*, J = 8.2, 6.9 Hz, H-8), 3.85 (3H, *s*, OCH_3), 3.87 (3H, *s*, OCH_3), 3.90 (3H, *s*, OCH_3), 5.78 (1H, *d*, J = 8.2, H-7), 6.64 (2H, *s*, H-2′,6′) and 6.89 (3H, *s*, H-2,5,6).

2-(3,4-*Dimethoxyphenyl*)-3-*formyl*-7-*methoxybenzofuran* (**4b**). 1-(3,4-Dimethoxyphenyl)-3-[2-(tetrahydropyran-2-yl)-3-methoxyphenyl]-2,3-epoxy-1-propanone (mixt. of two diasteromeric forms) was prepd from 3′,4′-dimethoxyacetophenone and *o*-vanillin using procedures applied to the synthesis of related compounds [16, 42]. Freshly distilled boron trifluoride diethyl etherate (22.6 g) was added to a soln of the epoxide (8.28 g) in anhydrous Et_2O (500

mL) at 20°. After stirring for 25 min, the soln was washed ×3 with H_2O (200, 2×50 mL), and most of the Et_2O was removed by distillation. The residual oil was dissolved in a mixt. of 0.5 M HCl (30 mL) and THF (60 mL), and the mixt. was stirred for 22 hr at 20°. The resulting crystals were filtered and washed with Me_2CO (4×5 mL) to give product (2.6 g). Recrystallisation from Me_2CO gave 2-(3,4-dimethoxyphenyl)-3-formyl-7-methoxybenzofuran (**4b**), m.p. 185–6°. ^{1}H NMR. δ 3.98 (3H, *s*, OCH_3), 4.00 (3H, *s*, OCH_3), 4.04 (3H, *s* OCH_3), 6.91 (1H, *dd*, J = 0.8, 8.0 Hz, Ar-H), 7.02 (1H, *d*, J = 8.4, Ar-H), 7.30 (1H, *t*, J = 8.0, Ar-H), 7.40 (1H, *d*, J = 2.0, Ar-H), 7.46 (1H, *dd*, J = 2.0, 8.4, Ar-H), 7.83 (1H, *dd*, J = 0.8, 8.0, Ar-H), 10.32 (1H, *s*, CHO).

trans-2-(3,4-*Dimethoxyphenyl*-3-*hydroxymethyl*-7-*methoxy*-2,3-*dihydrobenzofuran* (**2b**). The *trans* arylcoumaran **2d** after methylation with CH_2N_2 in Et_2O gave the *trans* arylcoumaran **2b** as an oil (*cf* [16, 43]). ^{1}H NMR δ 3.66 (1H, *m*, H-3), 3.86 (3H, *s*, OCH_3), 3.87 (3H, *s*, OCH_3), 3.90 (3H, *s*, OCH_3), 3.92 (1H, *dd*, J = 4.6, 10.9 Hz, $C\underline{H}_{2a}OH$), 4.00 (1H, *dd*, J = 6.0, 10.9 Hz, $C\underline{H}_{2b}OH$), 5.60 (1H, *d*, J = 7.3 Hz, H-2), 6.8–7.0 (6H, *m*, Ar-H).

cis-2-(3,4-*Dimethoxyphenyl*-3-*hydroxymethyl*-7-*methoxy*-2,3-*dihydrobenzofuran* (**3b**). A soln of the benzofuran **4b** (1.20 g) in dioxane (80 mL) containing 10% Pd-C (600 mg) was hydrogenated for 48 hr at 20° and 275 kPa H_2 pressure. After filtration of the catalyst and evapn of the solvent *in vacuo*, the resulting solid was recrystallised from EtOAc to give 2-(3,4-diimethoxyphenyl)-7-methoxy-3-methylbenzofuran (410 mg) m.p. 136–7° (lit. [44] m.p. 85–6°). ^{1}H NMR δ 2.43 (3H, *s*, CH_3), 3.93 (3H, *s*, OCH_3), 3.97 (3H, *s*, OCH_3), 4.03 (3H, *s*, OCH_3), 6.7–7.4 (6H, *m*, Ar-H). The mother liquor was adsorbed on a column of silica gel, and successive elution of the column with EtOAc–dichloromethane 1:20, 1:15 and 1:10 gve further amounts of the above benzofuran contaminated with *cis*-2-(3,4-dimethoxyphenyl)-7-methoxy-3-methyl-2,3-dihydrobenzofuran. ^{1}H NMR δ 0.84 (3H, *d*, J = 7.3 Hz, H-9), 3.63 (1H, *m*, H-8), 3.87 (3H, *s*, OCH_3), 3.89 (3H, *s*, OCH_3), 3.92 (3H, *s*, OCH_3), 5.80 (1H, *d*, J = 8.6 Hz, H-7), 6.78–6.91 (6H, *m*, Ar-H), 2-(3,4-dimethoxyphenyl-3-hydroxymethyl-7-methoxybenzofuran (70 mg) and *cis*-2-(3,4-dimethoxyphenyl-3-hydroxymethyl-7-methoxy-2,3-dihydrobenzofuran (**3b**) (210 mg) as an oil ^{1}H NMR δ 3.44 (1H, *dd*, J = 5.7, 11.5 Hz, $C\underline{H}_{2a}OH$), 3.53 (1H, *dd*, J = 7.1, 11.5 Hz, $C\underline{H}_{2b}OH$), 3.71 (1H, *m*, H-3), 3.886 (3H, *s*, OCH_3), 3.894 (3H, *s*, OCH_3), 3.92 (3H, *s*, OCH_3), 5.88 (1H, *d*, J = 8.4 Hz, H-2), 6.8–7.1 (6H, *m*, Ar-H) ^{13}C NMR δ 49.5 (C-3), 55.9 (OCH_3), 56.0 (OCH_3), 56.1 (OCH_3), 63.0 (CH_2OH), 86.9 (C-2), 109–150 (109.6, 111.2, 112.3, 117.3, 118.7, 121.6, 129.1, 129.3, 144.6, 148.0, 148.9, 149.1) (aromatic C).

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