New, short synthesis of arylnaphthofuranone lignans based on reactions of *o*-aroylbenzyllithiums with furan-2(5*H*)-one

Kazuhiro Kobayashi,* Junsuke Tokimatsu, Kouji Maeda, Osamu Morikawa and Hisatoshi Konishi

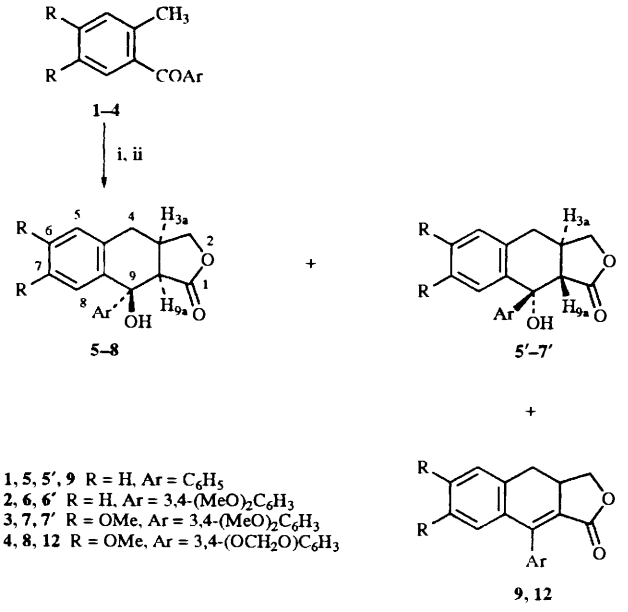
Department of Materials Science, Faculty of Engineering, Tottori University, Tottori 680, Japan

A simple and general method to prepare 9-arylnaphtho[2,3-*c*]furan-1(3*H*)-one derivatives has been developed. The reaction of *o*-aroylbenzyllithiums with furan-2(5*H*)-one gave the corresponding adducts **5–8** and **5′–7′**, which upon treatment with thionyl chloride in pyridine followed by dehydrogenation with Pd–C in refluxing *p*-cymene afforded the arylnaphthofuranone derivatives **13–16**. The process proved to be applicable to the preparation of some 1-aryl type naphthofuranone lignans (collinusin, dehydrodimethylretrodendrin and justicidin B).

We have recently reported that 3,4-dihydroisocoumarins,[1] 3-isochromanones[2] and benzocyclobutenols[3] can be obtained simply from the reactions of *o*-acylbenzyllithium compounds. Furthermore, we have examined the reaction of *o*-aroylbenzyllithiums, generated by the lithiation of *o*-methylbenzophenones **1–4** using LDA, with furan-2(5*H*)-one, and found that it provides an efficient method for the preparation of 9-arylnaphtho[2,3-*c*]furan-1(3*H*)-one derivatives **13–16** including some natural products. Compounds having this carbon skeleton are of particular interest since some display biological activity.[4] A number of methods have been developed to prepare this class of compounds.[5] In particular, a similar approach utilizing 2-(*o*-aroylphenyl)-1,3-dithiolanes has been reported by Harrowven and his co-workers.[5h,k,l] We now describe a simpler synthesis of these derivatives.

The starting material 2-methylphenyl phenyl ketone **1** was commercially available and compounds **2–4** were easily prepared in good yields as follows. 3,4-Dimethoxybenzaldehyde with 2-methylphenyllithium (which was generated *in situ* by lithium–bromide exchange between 1-bromo-2-methylbenzene and butyllithium) afforded 3,4-dimethoxyphenyl(2-methylphenyl)methanol, which was oxidized by pyridinium chlorochromate (PCC) to 3,4-dimethoxyphenyl 2-methylphenyl ketone **2**. Likewise, piperonal and 1-bromo-3,4-dimethoxy-6-methylbenzene gave 3,4-dimethoxy-6-methylphenyl 3,4-methylenedioxyphenyl ketone **4**. 3,4-Dimethoxyphenyl 3,4-dimethoxy-6-methylphenyl ketone **3** was prepared according to the reported procedure[2] from 3,4-dimethoxytoluene and 3,4-dimethoxybenzoyl chloride.

The results of the reaction of *o*-aroylbenzyllithiums with furan-2(5*H*)-one are shown in Scheme 1 and Table 1. 2-Methylphenyl phenyl ketone **1** was lithiated by treatment with lithium diisopropylamide (LDA) in THF at −78 °C to give *o*-benzoylbenzyllithium, which was then treated with furan-2(5*H*)-one at the same temperature. The deep-red colour of the carbanion solution gradually changed to orange. After 5 min the reaction mixture was poured into aq. ammonium chloride. Extractive work-up followed by chromatography on silica gel afforded the hydroxy lactone adducts **5**[7] and **5′** in 24 and 27% yield, respectively (Entry 1). Quenching of the mixture after it had been stirred overnight at room temperature gave **5** in 56% yield along with the dehydrated product **9** (3%) (Entry 2) with no trace of **5′**. This result indicates that the alkoxide of **5** is thermodynamically more stable than that of **5′**. The spectral data of **5** were identical with those reported in the literature.[7] The *cis*-configuration of 3a-H and 9a-H of **5** was confirmed on the basis of a NOE experiment. Thus, irradiation of the signal at δ_H 2.78–3.21 due to 3a-H resulted in an enhancement of the



Scheme 1 *Reagents and conditions:* i, LDA, −78 °C, THF; ii, furan-2(5*H*)-one

signal at δ_H 3.67 due to 9a-H. The stereochemistry at C-9a relative to C-9 was determined on the basis of the IR spectrum which showed absorption at 1751 cm^{-1} assignable to a lactone carbonyl group. This considerable decrease in wavenumber, when compared with those reported for the corresponding 9-dehydroxylated derivatives,[8] is probably attributable to the hydrogen bonding between the carbonyl and 9-OH groups, and indicates that they are *cis*-orientated. The stereochemistry of the thermodynamically less stable adduct **5′** was also established on the basis of a NOE experiment and IR spectra. No NOE was observed between the signals at δ_H 3.1–3.25 due to 3a-H and δ_H 3.07 due to 9a-H. The IR spectra of **5′** exhibited a band at 1761 cm^{-1}, which is much lower than those reported for the corresponding 9-dehydroxylated derivatives,[8] indicating the presence of hydrogen bonding. These results imply that the carbonyl and 9-OH groups of **5′** are *cis*-orientated and that 3a-H and 9a-H are *trans*-orientated.

The lithiation products of the 2-methylbenzophenones **2–4** were also treated with furan-2(5*H*)-one. The reaction of **2** with furan-2(5*H*)-one proceeded satisfactorily to give **6** (22%) and **6′** (40%) (Entry 3). Similarly, **3** gave **7** (28%) and **7′** (31%) (Entry 4). The reaction of **4** with furan-2(5*H*)-one afforded an

Table 1 Results of the reaction of 2-aroylbenzyllithiums with furan-2(5*H*)-one

Entry	*o*-Methylbenzophenone	Conditions[a]	Products	(Yield/%)[b]
1	**1**	A	**5** (24)	**5′** (27)
2	**1**	B	**5** (56)	**9** (3)
3	**2**	A	**6** (22)	**6′** (40)
4	**3**	A	**7** (28)	**7′** (31)
5	**4**	A	**8** (25)[c]	**12** (17)[c,d]

[a] A: −78 °C, 5 min. B: −78 °C→room temp. overnight. [b] Isolated yields. [c] These products could not be separated. [d] Collinusin (ref. 6).

Table 2 Dehydration of the hydroxy lactones **5–8**, **5′–7′**

Entry	Hydroxy lactone	Conditions[a]	Product	Yield (%)[b]
1	**5**	A	**9**	75
2	**5′**	A	**9**	83
3	**6**	A	**10**	94
4	**6′**	B	**10**	~100
5	**7**	A	**11**	90
6	**7′**	B	**11**	~100
7	**8** + **12**	A	**12**[c]	86

[a] A: $SOCl_2$, pyridine, room temp., overnight. B: $CHCl_3$, room temp., overnight. [b] Isolated yields. [c] Collinusin (ref. 6).

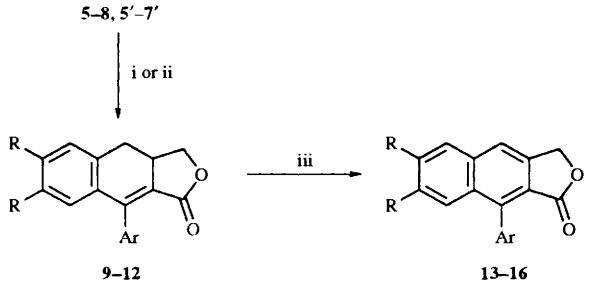
Table 3 Dehydrogenation of the dihydronaphthofuranones **9–12**

Entry	Dihydronaphthofuranone	Product	Yield (%)[a]
1	**9**	**13**	80
2	**10**	**14**	85
3	**11**	**15**[b]	86
4	**12**	**16**[c]	67

[a] Isolated yields. [b] Dehydrodimethylretrodendrin (ref. 9). This compound has been successfully converted into taiwanin C (ref. 5*j*). [c] Justicidin B (ref. 10).

inseparable mixture of **8** and the dehydrated product **12** (collinusin)[6] in 25 and 17% yield, respectively, as determined by ^{1}H NMR (Entry 5). The stereochemical assignments of these adducts were derived by comparison of their spectral data with those of **5** and **5′**.

Conversion of **5–8** and **5′–7′** into the 9-arylnaphtho[2,3-*c*]-furan-1(3*H*)-one derivatives **13–16** was successfully achieved through dehydration followed by dehydrogenation as outlined in Scheme 2. The results are summarized in Tables 2 and 3. The separated adducts **5** and **5′** were easily dehydrated on treatment with thionyl chloride in pyridine resulting in the formation of **9**[11] in 75 and 83% yields, respectively (Table 2, Entries 1 and 2). Subsequent dehydrogenation of **9** with 10% Pd–C in refluxing *p*-cymene gave **13**[11] in 80% yield (Table 3, Entry 1). The adducts **6** and **7** were likewise dehydrated to give **10**[11] and **11**[12] in 94 and 90% yields, respectively (Table 2, Entries 3 and 5). The adducts **6′** and **7′** proved to be extremely sensitive to dehydration in chloroform to give **10** and **11** quantitatively (Table 2, Entries 4 and 6). The reactivity of **6′** and **7′** may be attributed to their distorted structures and the stabilisation of the carbocationic intermediate by the two methoxy substituents of the 9-aryl group. Dehydrogenation of **10** and **11** was performed using the same conditions employed for the formation of **13**, and so **14**[12] and **15**[9,12] (dehydrodimethylretrodendrin) were obtained in 85 and 86% yields, respectively (Table 3, Entries 2 and 3). Compound **15** has been converted into taiwanin C by us.[5j] The mixture of **8** and **12** was converted into pure collinusin **12** in 86% yield as illustrated for **5–7** (Table 2, Entry 7). Sequential dehydrogenation of **12** as described above afforded justicidin B **16**[10] in 67% yield (Table 3, Entry 4). IR and ^{1}H NMR data as well as melting points for **12**[6] and **16**[10] are consistent with those previously reported.



9, **13** R = H, Ar = C_6H_5
10, **14** R = H, Ar = 3,4-$(MeO)_2C_6H_3$
11, **15** R = OMe, Ar = 3,4-$(MeO)_2C_6H_3$
12, **16** R = OMe, Ar = 3,4-$(OCH_2O)C_6H_3$

Scheme 2 *Reagents and conditions:* i, $SOCl_2$, pyridine, room temp.; ii, $CHCl_3$, room temp.; iii, 10%, Pd–C, *p*-cymene, reflux

Experimental

Mps were recorded with a Laboratory Devices MEL-TEMP II melting point apparatus and are uncorrected. The IR spectra were determined for KBr discs unless stated otherwise with a Perkin-Elmer 1600 Series FT IR spectrometer. The ^{1}H NMR spectra were determined using $SiMe_4$ as an internal reference with either a JEOL JNX-PMX 60 spectrometer operating at 60 MHz (in CCl_4 unless stated otherwise) or a JEOL JNM-GX270 FT NMR spectrometer operating at 270 MHz (in $CDCl_3$ unless stated otherwise). *J* Values are given in Hz. High- and low-resolution mass spectra were recorded with a JEOL JMS-DX 303 spectrometer. Column chromatography was carried out on Merck Kieselgel 60 F_{254}. TLC was carried out on Merck Kieselgel 60 PF_{254}. All solvents used were dried over appropriate drying agents and distilled under argon prior to use. All of the reactions were carried out under argon.

Starting materials

2-Methylphenyl phenyl ketone **1** was commercially available. 3,4-Dimethoxy-6-methylphenyl 3,4-dimethoxy-phenyl ketone **3** was prepared by the procedure reported by us.[2]

3,4-Dimethoxyphenyl(2-methylphenyl)methanol

2-Methylphenyllithium was generated from 1-bromo-2-methylbenzene (1.7 g, 10 mmol) and butyllithium (1.6 mol dm^{-3} in hexane; 20 mmol) in Et_2O (40 cm^3) and to the resulting stirred solution was added dropwise a solution of 3,4-dimethoxybenzaldehyde (1.7 g, 10 mmol) in Et_2O (10 cm^3). The mixture was stirred for 1.5 h, after which the reaction was quenched by addition of aq. NH_4Cl. The mixture was extracted with Et_2O (70 cm^3) and the extract was washed with brine, dried ($MgSO_4$) and evaporated. The resulting crude product was recrystallized from hexane–$CHCl_3$ to give the alcohol (1.5 g, 58%), mp 78–79 °C; ν_{max}/cm^{-1} 3504 (OH); δ_H(60 MHz) 2.0 (1 H, br, OH), 2.13 (3 H, s, 2′-Me), 3.69 and 3.72 (combined 6 H, 2s, OMe), 5.71 (1 H, s, C*H*OH), 6.6–6.75 (3 H, m, ArH) and 7.05–7.45 (4 H, m,

ArH); *m/z* 258 (M^+, 85%) and 139 (100) (Found: C, 74.1; H, 7.1. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%).

3,4-Dimethoxyphenyl 2-methylphenyl ketone 2

A mixture of the above alcohol (1.5 g, 5.8 mmol), PCC (3.7 g, 17 mmol) and Celite (5 g) in CH_2Cl_2 (140 cm^3) was stirred overnight at room temperature. The mixture was filtered and the filtrate was washed successively with aq. HCl (5%) and brine, dried ($MgSO_4$), filtered through a thin layer of silica gel and evaporated. The resulting crude product was recrystallized from hexane–$CHCl_3$ to give **2** (1.3 g, 87%), mp 73–74 °C (lit.,[13] 72–73 °C): ν_{max}/cm^{-1} 1651 (C=O); δ_H(60 MHz) 2.23 (3 H, s, 2'-Me), 3.83 (6 H, s, OMe), 6.64 (1 H, d, *J* 8.0, 5-H) and 6.95–7.5 (6 H, m).

3,4-Dimethoxy-6-methylphenyl(3,4-methylenedioxyphenyl)-methanol

This compound was prepared from 1-bromo-3,4-dimethoxy-6-methylbenzene[14] and 3,4-methylenedioxybenzaldehyde by the same procedure described above in 55% yield, mp 110–111 °C (hexane–$CHCl_3$); ν_{max}/cm^{-1} 3494 (OH); δ_H(270 MHz) 2.09 (1 H, OH), 2.17 (3 H, s, 6'-Me), 3.86 (6 H, s, OMe), 5.86 (1 H, s, C*H*OH), 5.92 (1 H, d, *J* 1.4, OC*H*HO), 5.93 (1 H, d, *J* 1.4, OCH*H*O), 6.65 (1 H, s, 5'-H), 6.7–6.8 (3 H, m) and 7.09 (1 H, s, 2-H); *m/z* 302 (M^+ 100%) (Found: C, 67.3; H, 5.95. $C_{17}H_{18}O_5$ requires C, 67.55; H, 6.0%).

3,4-Dimethoxy-6-methylphenyl 3,4-methylenedioxyphenyl ketone 4

The above alcohol was oxidized by a similar procedure described above to give **4** (86%), mp 56–58 °C (hexane–$CHCl_3$); ν_{max}/cm^{-1} 1650 (C=O); δ_H(270 MHz) 2.26 (3 H, s, 6'-Me), 3.82 (3 H, s, OMe), 3.93 (3 H, s, OMe), 6.06 (2 H, s, OCH_2O), 6.74 (1 H, s, 5'-H), 6.82 (1 H, d, *J* 8.0, 5-H), 6.86 (1 H, s, 2'-H), 7.31 (1 H, dd, *J* 8.0 and 1.5, 6-H) and 7.35 (1 H, d, *J* 1.5, 2-H); *m/z* 300 (M^+, 100%) (Found: C, 67.95; H, 5.5. $C_{17}H_{16}O_5$ requires C, 68.0; H, 5.35%).

Synthesis of compounds 5 and 5'

The carbanion of the ketone **1** was generated by the procedure reported by us.[2] To a stirred solution of the carbanion (2 mmol) in THF at −78 °C was added dropwise furan-2(5*H*)-one (0.34 g, 4.0 mmol). The colour of the mixture turned gradually from red to orange and after 5 min, the reaction was quenched by addition of aq. NH_4Cl. The precipitates were filtered off and the filtrate was worked up in a similar manner as described for 3,4-dimethoxyphenyl(2-methylphenyl)methanol above. The precipitates were recrystallized from hexane–Et_2O to give (3a*R**,9*R**,9a*S**)-9-hydroxy-9-phenyl-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1(3*H*)-one **5'** (0.11 g, 20%). The filtrate was separated by preparative TLC on silica gel to give (3a*R**,9*S**,9a*R**)-9-hydroxy-9-phenyl-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1(3*H*)-one **5**[7] (0.13 g, 24%) and **5'** (39 mg, 7%). For compound **5**: R_F 0.34 (1:3 EtOAc–hexane); mp 144–145 °C (hexane–Et_2O) (lit.,[8] 144–145 °C). For compound **5'**: R_F 0.24 (1:3 EtOAc–hexane); mp 122–124 °C (hexane–Et_2O); ν_{max}/cm^{-1} (KBr disk) 3437 (OH) and 1761 (C=O); δ_H[270 MHz, $(CD_3)_2SO$] 2.56 (1 H, dd, *J* 15.6 and 8.4, 4-H), 3.00 (1 H, dd, *J* 15.6 and 8.7, 4-H), 3.07 (1 H, d, *J* 10.9, 9a-H), 3.1–3.25 (1 H, m, 3a-H), 3.32 (1 H, dd, *J* 9.4 and 8.3, 3-H), 4.42 (1 H, br t, *J* 8.0, 3-H), 6.09 (1 H, s, OH), 7.2–7.45 (8 H, m, ArH) and 7.78 (1 H, dd, *J* 7.4 and 1.5, Ar-H); *m/z* 280 (M^+, 4%), 262 [$(M - H_2O)^+$, 5] and 196 (100) (Found: C, 77.05; H, 5.7. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.75%).

Synthesis of compound 9

To a stirred solution of the carbanion of **1** (2 mmol) was added furan-2(5*H*)-one (0.34 g, 4.0 mmol) at −78 °C and the reaction mixture was stirred overnight at room temperature. Work-up as described above gave **5** (0.31 g, 56%) and 9-phenyl-3a,4-dihydronaphtho[2,3-*c*]furan-1(3*H*)-one **9** (15 mg, 3%), R_F 0.33 (1:1 AcOEt–hexane); mp 185–186 °C (hexane–$CHCl_3$) (lit.,[7] 185–187 °C).

Synthesis of compounds 6–8, 6', 7' and 12

The lithiation of *o*-methylbenzophenones **2–4** and the subsequent treatment of the resulting carbanions with furan-2(5*H*)-one were carried out using the method described for **5** above.

(3a*R,9*S**,9a*R**)-9-(3,4-Dimethoxyphenyl)-9-hydroxy-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1(3*H*)-one 6.** R_F 0.51 (Et_2O); mp 124–125.5 °C (hexane–CH_2Cl_2); ν_{max}/cm^{-1} 3435 (OH) and 1743(C=O); δ_H(270 MHz) 2.50 (1 H, dd, *J* 15.8 and 2.0, 4-H), 2.70 (1 H, dd, *J* 15.8 and 8.6, 4-H), 2.95–3.05 (1 H, m, 3a-H), 3.68 (1 H, d, *J* 9.6, 9a-H), 3.79 (3 H, s, OMe), 3.84 (3 H, s, OMe), 4.07 (1 H, dd, *J* 9.2 and 2.0, 3-H), 4.52 (1 H, dd, *J* 9.2 and 7.3, 3-H), 5.46 (1 H, s, OH), 6.61 (1 H, dd, *J* 8.6 and 2.0, 6'-H), 6.74 (1 H, d, *J* 8.6, 5'-H), 6.86 (1 H, d, *J* 2.0, 2'-H), 7.14 (1 H, d, *J* 7.3), 7.30 (1 H, t, *J* 7.3), 7.38 (1 H, td, *J* 7.3 and 1.7) and 7.83 (1 H, dd, *J* 7.3 and 1.7); *m/z* 340 (M^+, 52%) and 225 (100) (Found: C, 70.5; H, 6.0. $C_{20}H_{20}O_5$ requires C, 70.6; H, 5.9%).

(3a*R,9*R**,9a*S**)-9-(3,4-Dimethoxyphenyl)-9-hydroxy-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1(3*H*)-one 6'.** R_F 0.49 (Et_2O); mp 190–191 °C (hexane–CH_2Cl_2); ν_{max}/cm^{-1} 3505 (OH) and 1757 (C=O); δ_H(270 MHz) 2.55 (1 H, dd, *J* 15.2 and 8.3, 4-H), 2.97 (1 H, dd, *J* 15.2 and 8.3, 4-H), 3.03 (1 H, d, *J* 10.9, 9a-H), 3.1–3.25 (1 H, m, 3a-H), 3.32 (1 H, t, *J* 8.5, 3-H), 3.51 (1 H, s, OH), 3.79 (3 H, s, OMe), 3.85 (3 H, s, OMe), 4.41 (1 H, br t, *J* 8.5, 3-H), 6.48 (1 H, dd, *J* 8.3 and 2.2, 6'-H), 6.67 (1 H, d, *J* 8.3, 5'-H), 7.00 (1 H, d, *J* 2.2, 2'-H), 7.21 (1 H, d, *J* 7.3), 7.3–7.45 (2 H, m) and 7.78 (1 H, dd, *J* 7.6 and 1.5); *m/z* 340 (M^+, 3%) and 262 [$(M - H_2O)^+$, 100] (Found: C, 70.3; H, 5.8. $C_{20}H_{20}O_5$ requires C, 70.6; H, 5.9%).

(3a*R,9*S**,9a*R**)-9-(3,4-Dimethoxyphenyl)-9-hydroxy-6,7-dimethoxy-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1(3*H*)-one 7.** R_F 0.32 (1:1 AcOEt–hexane); mp 157–159 °C (hexane–$CHCl_3$); ν_{max}/cm^{-1} 3430 (OH) and 1740 (C=O); δ_H(270 MHz) 2.46 (1 H, dd, *J* 15.8 and 2.0, 4-H), 2.71 (1 H, dd, *J* 15.8 and 8.2, 4-H), 2.85–3.0 (1 H, m, 3a-H), 3.59 (1 H, d, *J* 9.2, 9a-H), 3.81 (3 H, s, OMe), 3.84 (3 H, s, OMe), 3.89 (6 H, s, OMe), 4.09 (1 H, dd, *J* 9.2 and 2.0, 3-H), 4.49 (1 H, dd, *J* 9.2 and 6.9, 3-H), 5.57 (1 H, s, OH), 6.57 (1 H, dd, *J* 8.6 and 2.0, 6'-H), 6.66 (1 H, s, 5- or 8-H), 6.74 (1 H, d, *J* 8.6, 5'-H), 6.88 (1 H, d, *J* 2.0, 2'-H) and 7.35 (1 H, s, 5- or 8-H); *m/z* 400 (M^+, 46%), 382 [$(M - H_2O)^+$, 39] and 285 (100) (Found: C, 66.0; H, 5.75. $C_{22}H_{24}O_7$ requires C, 66.0; H, 6.05%).

(3a*R,9*R**,9a*S**)-9-(3,4-Dimethoxyphenyl)-9-hydroxy-6,7-dimethoxy-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1(3*H*)-one 7'.** R_F 0.21 (1:1 AcOEt–hexane); mp 188–190 °C (hexane–CH_2Cl_2); ν_{max}/cm^{-1} 3495 (OH) and 1762 (C=O); δ_H[270 MHz, $(CD_3)_2SO$] 2.50 (1 H, dd, *J* 14.8 and 7.3, 4-H), 3.04 (1 H, d, *J* 10.2, 9a-H), 3.12 (1 H, dd, *J* 14.8 and 9.2, 4-H), 3.2–3.35 (1 H, m, 3a-H), 3.46 (1 H, t, *J* 8.3, 3-H), 3.80 (3 H, s, OMe), 3.85 (3 H, s, OMe), 3.94 (6 H, s, OMe), 4.39 (1 H, t, *J* 8.3, 3-H), 6.12 (1 H, s, OH), 6.47 (1 H, dd, *J* 8.6 and 2.0, 6'-H), 6.92 (1 H, d, *J* 8.6, 5'-H), 7.01 (1 H, s, 5- or 8-H), 7.18 (1 H, d, *J* 2.0, 2'-H) and 7.33 (1 H, s, 5- or 8-H); *m/z* 382 [$(M - H_2O)^+$, 100%] (Found: C, 65.8; H, 6.0. $C_{22}H_{24}O_7$ requires C, 66.0; H, 6.05%).

(3a*R,9*S**,9a*R**)-9-Hydroxy-6,7-dimethoxy-9-(3,4-methylenedioxyphenyl)-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1(3*H*)-one 8.** R_F 0.43 (1:1 AcOEt–hexane); mp 220–222 °C (hexane–CH_2Cl_2); ν_{max}/cm^{-1} 3436 (OH) and 1742 (C=O); δ_H(270 MHz) 2.45 (1 H, dd, *J* 16.0 and 1.8, 4-H), 2.70 (1 H, dd, *J* 16.0 and 8.7, 4-H), 2.85–2.95 (1 H, m, 3a-H), 3.53 (1 H,

d, *J* 9.1, 9a-H), 3.887 and 3.894 (6 H, 2s, OMe), 4.09 (1 H, dd, *J* 9.4 and 1.8, 3-H), 4.49 (1 H, dd, *J*9.4 and 7.3, 3-H), 5.56 (1 H, s, OH), 5.93 (1 H, d, *J* 1.5, OC*H*HO), 5.94 (1 H, d, *J* 1.5, OCH*H*O), 6.55–6.75 (4 H, m, Ar-H) and 7.33 (1 H, s, 5- or 8-H); *m/z* 384 (M^+, 2%) and 382 [$(M - H_2O)^+$, 100] (Found: C, 65.85; H, 5.2. $C_{21}H_{20}O_7$ requires C, 65.6; H, 5.25%).

6,7-Dimethoxy-9-(3,4-methylenedioxyphenyl)-3a,4-dihydronaphtho[2,3-*c*]furan-1(3*H*)-one [(±)-collinusin] 12. R_F 0.43 (1:1 AcOEt–hexane); mp 198–200 °C (hexane–$CHCl_3$) (lit.,[6a] 196–198 °C; lit.,[6b] 197–198 °C).

General procedure for the dehydration of the hydroxy lactones 5–8 and 5′–7′ into the dihydronaphthofuranones 9–12 (Method A)

To a stirred solution of **5** or **5′** (0.12 g, 0.41 mmol) in pyridine (2 cm^3) at 0 °C was added thionyl chloride (59 mg, 0.49 mmol) and the mixture was stirred overnight at room temperature. The excess of pyridine and thionyl chloride was removed under reduced pressure to give a solid residue, which was triturated with water and then filtered. The precipitate was recrystallized from hexane–$CHCl_3$ to give **9** (81 mg, 75% from **5**; 95 mg, 83% from **5′**).

Compounds **10–12** were obtained by the same procedure described above from **6**, **7** and a mixture of **8** and **12**, respectively.

Method B. A solution of **6′** or **7′** in $CHCl_3$ was allowed to stand overnight at room temperature which gave compounds **10** or **11** quantitatively.

9-(3,4-Dimethoxyphenyl)-3a,4-dihydronaphtho[2,3-*c*]furan-1(3*H*)-one 10. Mp 190–192 °C (lit.,[12] 188–189 °C).

9-(3,4-Dimethoxyphenyl)-6,7-dimethoxy-3a,4-dihydronaphtho[2,3-*c*]furan-1(3*H*)-one 11. Mp 216–218 °C (hexane–$CHCl_3$) (lit.,[9] 216–217 °C; lit.,[12] 221–222 °C).

9-Phenylnaphtho[2,3-*c*]furan-1(3*H*)-one 13

A solution of compound **9** (52 mg, 0.20 mmol) in *p*-cymene (2 cm^3) containing palladium-on-carbon (10%, 50 mg) was refluxed for 4 h. The catalyst was filtered off and the filtrate was concentrated under reduced pressure. Recrystallization of the solid residue from hexane–$CHCl_3$ gave **13** (41 mg, 80%), mp 183–184 °C (lit.,[11] 183–184.5 °C).

Compounds **14–16** were obtained by a similar method.

9-(3,4-Dimethoxyphenyl)naphtho[2,3-*c*]furan-1(3*H*)-one 14

Mp 214–216 °C (hexane–$CHCl_3$) (lit.,[12] 208.5–209.5 °C).

9-(3,4-Dimethoxyphenyl)-6,7-dimethoxynaphtho[2,3-*c*]furan-1(3*H*)-one 15 (dehydrodimethylretrodendrin)

Mp 254–256 °C (hexane–$CHCl_3$) (lit.,[9] 254–255 °C; lit.,[12] 251.5–253 °C).

6,7-Dimethoxy-9-(3,4-methylenedioxyphenyl)naphtho[2,3-*c*]-furan-1(3*H*)-one 16 (justicidin B)

Mp 238–240 °C (hexane–$CHCl_3$) (lit.,[10] 235–238 °C).

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