A simple method for the synthesis of 4-aryl-9-oxynaphthofuranone lignans

Kazuhiro Kobayashi,* Kouji Maeda, Tomokazu Uneda, Osamu Morikawa and Hisatoshi Konishi

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

The 9-aryl-4-oxynaphthofuran-1(3H)-one system is generally synthesized in two steps from α-aryl-o-toluic acid derivatives. The method involves a tandem conjugate addition–Dieckmann type condensation between α-lithiated α-aryl-o-toluic acid derivatives and 2-furan-2(5H)-one as a key step followed by simple dehydrogenation or dehydration, and can be applied to the synthesis of two natural lignans (neojusticidin A and neojusticidin B).

We have recently reported the synthesis of 9-arylnaphtho[2,3-c]furan-1(3H)-one derivatives including natural lignans, such as collinusin, dehydrodimethylretrodendrin and justicidin B.[1f] The key step in our procedure was the reaction of o-aroylbenzyl-lithiums with furan-2(5H)-one. As a extension of this study we now describe a simple and general approach to the synthesis of naphtho[2,3-c]furan-1(3H)-one derivatives carrying a methoxy (or hydroxy) substituent at the 9-position and an aryl substituent at the 4-position, including natural lignans such as neojusticidin A **14** and neojusticidin B **15**, which is based on reactions of α-lithiated α-aryl-o-toluic acid derivatives with 2-furan-2(5H)-one and conceptually similar to that of Harrowven.[1c] These natural products were first isolated from *Justicia procumbens* Linn. var. *leucantha* Honda and characterized by Okigawa, Maeda and Kawano in 1970.[2] Few methods have been reported for the simple construction of this skeleton,[3] though a notable approach to neojusticidin B **15** from 3,4:3′,4′-bis(methylene-dioxy)benzophenone involving nine steps has been recorded by Horii, Tsujiuchi, Kanai and Momose,[3c] and a number of interesting methods have been reported to prepare other types of arylnaphthofuranone lignans.[1] So we have been aiming to develop a simple and general method to synthesize this class of compounds.

We envisioned two potential entries to this system by starting with readily available materials. One approach (Scheme 1), in which interaction of α-lithiated product of ethyl o-benzylbenzoate **1** with furan-2(5H)-one leading the dihydro derivative **2** followed by dehydrogenation should give us a rapid access to the system **3**, parallels the MIRC route to oxyaromatic compound utilizing *ortho*-toluate carbanions.[4] The second approach (Scheme 2) would involve treating 3-aryl-3-lithio-isobenzofuran-1(3H)-ones, lithio derivatives of 3-arylisobenzo-furan-1(3H)-ones **4–8**, with furan-2(5H)-one which would be expected to give the desired compounds **10–15** by the subsequent dehydration of the resulting 4-hydroxy derivatives **9**. Reactions of the benzylic anions of isobenzofuran-1(3H)-one[5] and its 3-substituted derivatives (such as CN[6] or SO₂Ph[7]) with Michael acceptors have been reported to give polycyclic compounds, some of which were elegantly elaborated to provide syntheses of useful natural products.[8] It is somewhat surprising that there have been so far few reports on the synthesis utilizing the benzylic anions of 3-arylisobenzofuran-1(3H)-ones.[9,10]
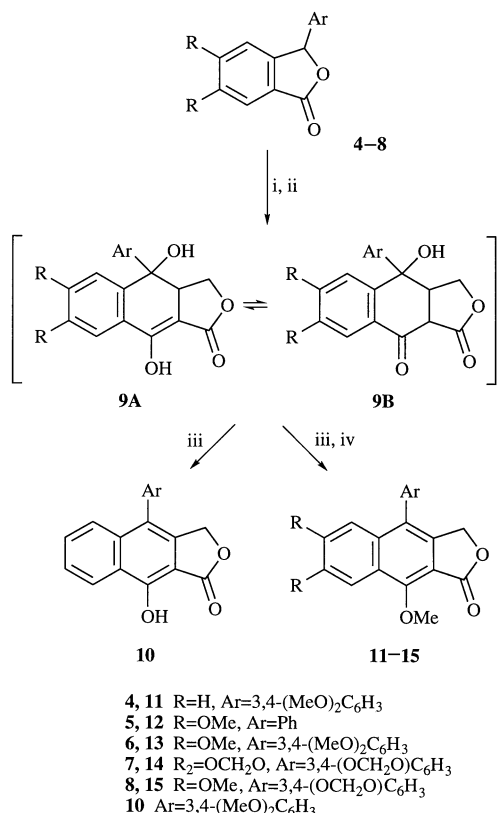
These approaches required the efficient preparation of the starting materials ethyl o-benzylbenzoate **1** and its substituted derivatives, and 3-arylisobenzofuranones **4–8**. Compound **1** was prepared by the normal esterification of commercially available o-benzylbenzoic acid. In order to obtain its substi-
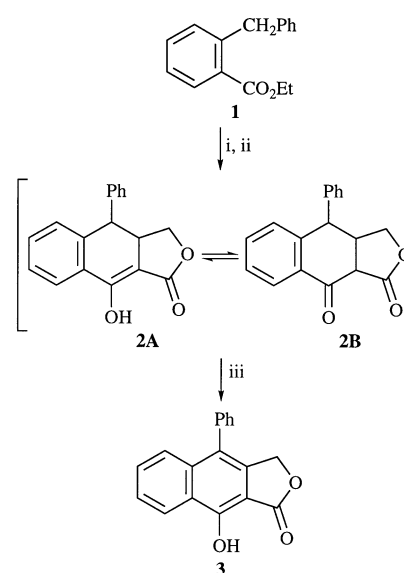
Scheme 1 *Reagents and conditions:* i, 2LDA, −78 °C, THF; ii, furan-2(5H)-one, −78 °C to RT; iii, 10% Pd–C, p-cymene, reflux

tuted derivatives and compounds **4–8** we initially attempted the route developed by Arnold, Mellows and Sammes.[11] Unfortunately, we were not able to obtain these compounds in good isolated yields and a modifying procedure was therefore attempted. After several unsuccessful attempts, it was found that the use of the corresponding dimethyl acetals in place of 2-bromobenzaldehyde methylene acetals produced the desired compounds in satisfactory yields. Thus, bromine–lithium exchange between the appropriately substituted 2-bromobenzalde-hyde dimethyl acetals and butyllithium followed by *in situ* trapping of the resulting lithium compounds with aromatic aldehydes afforded the corresponding benzhydrol derivatives, which were transformed into the corresponding lactol derivatives upon exposure to aq. H₂SO₄. Oxidation of these lactols with Na₂Cr₂O₇ gave the desired lactones **4–8** (30–50% yields from o-bromobenzaldehydes), hydrogenolysis of which then afforded substituted o-(arylmethyl)benzoic acids (quantitative). Finally, the usual acidic esterification of these carboxylic acids afforded the corresponding esters (80–90%).

The o-toluate **1** was lithiated with 2 equivalents of lithium diisopropylamide (LDA) in THF at −78 °C to give a solution of the deep-red α-anion, which was then treated with furan-2(5H)-one. The characteristic colour disappeared immediately,

Scheme 2 *Reagents and conditions:* i, 2LDA, −78 °C, THF; ii, furan-2(5*H*)-one, −78 °C to RT; iii, I₂, CHCl₃, RT or SOCl₂, pyridine, RT; iv, CH₂N₂, 0 °C or K₂CO₃, MeI, acetone, reflux

4, 11 R=H, Ar=3,4-(MeO)₂C₆H₃
5, 12 R=OMe, Ar=Ph
6, 13 R=OMe, Ar=3,4-(MeO)₂C₆H₃
7, 14 R₂=OCH₂O, Ar=3,4-(OCH₂O)C₆H₃
8, 15 R=OMe, Ar=3,4-(OCH₂O)C₆H₃
10 Ar=3,4-(MeO)₂C₆H₃

Table 1 Preparation of 4-aryl-9-oxynaphtho[2,3-*c*]furan-1(3*H*)-one derivatives

Entry	Starting material	Dehydration conditions [a]	Methylation conditions [b]	Product (yield/%) [c]
1	**1**	—	—	**3** (56)
2	**4**	A	—	**10** (51)
3	**4**	A	A	**11** (51)
4	**5**	A	A	**12** (62)
5	**6**	A	A	**13** (56)
6	**7**	B	B	**14** (50) [d]
7	**8**	B	B	**15** (52) [e]

[a] A: I₂, CHCl₃, B: SOCl₂, pyridine. [b] A: CH₂N₂, Et₂O, B: MeI, K₂CO₃, acetone. [c] Yields refer to overall yields of purified products (preparative TLC on SiO₂) starting from **1** and **4–8**. [d] Neojusticin A (*i.e.*, justicidin D, ref. 2). [e] Neojusticin B (*i.e.*, justicidin C, ref. 2).

furanone carbonyls appeared to be rather sluggish at this temperature, and overnight stirring at room temperature was required to afford the corresponding dihydroxynaphthofuranone adducts **9** satisfactorily. Attempts to speed up the cyclization by the addition of co-solvent (TMEDA or HMPA) were met with a considerable lowering in the yield of the products. It was also found that the use of 2 equivalents of LDA was required for satisfactory production of the products. These products were also not further purified because of the reasons described for the adduct **2**. Their IR spectra (~3350, ~1780, ~1720 and ~1670 cm⁻¹) showed that each of these products was an equilibrium mixture of **9A** and **9B**. These were then immediately subjected to dehydration with iodine (followed by *O*-methylation with diazomethane for the preparation of **11–13**) to give the expected products **10–13** in reasonable isolated yields from the arylisobenzofuranones **4–6** (see Table 1, entries 2, 3, 4 and 7, respectively).

Having established a simple and efficient route to 9-methoxy-4-arylnaphtho[2,3-*b*]furan-1(3*H*)-ones, we next turned our attention to the corresponding reactions using 3-(benzodioxolyl)isobenzofuran-1(3*H*)-ones **7** and **8** yielding natural lignans neojusticin A **14** and neojusticin B **15**, respectively. However, the reactions starting from compounds **7** and **8** under similar conditions described above gave rise to the desired products **14** and **15** only in considerably lower yields (*ca.* 15% yield each). The lower yield may be ascribed to the instability of the methylenedioxy moiety under these reaction conditions. We reasoned that dehydration of the corresponding adducts with thionyl chloride in pyridine, followed by the subsequent *O*-methylation with iodomethane in acetone in the presence of potassium carbonate, should not affect the methylenedioxy moiety and afford the desired products in good yields. As expected, dehydration and *O*-methylation under these modified conditions proceeded more cleanly than those under the initial ones to give compounds **14** and **15** in satisfactory yields (entries 5 and 6 in Table 1, respectively). IR and ¹H NMR data as well as melting points for these products are consistent with those reported in the literature.[2a]

The methodology described in this paper allows very rapid access to the 4-aryl-9-oxynaphtho[2,3-*c*]furan-1(3*H*)-one nucleus from readily available starting materials, and is applicable to the synthesis of natural lignans, neojusticin A and neojusticin B. Although the yields of the products are not so high, the convenience of this approach makes it attractive.

Experimental

The mps were recorded with a Laboratory Devices MEL-TEMP II melting point apparatus and are uncorrected. The IR spectra were determined for KBr disks with a Perkin-Elmer 1600 Series FT IR spectrometer. The ¹H NMR spectra were determined using SiMe₄ as an internal reference with a JEOL JNM-GX270 FT NMR spectrometer operating at 270 MHz in

indicating that the addition of the anion to furan-2(5*H*)-one in the manner of 1,4-addition was complete. The following intramolecular cyclization of the resulting enolate intermediate proceeded smoothly by allowing the reaction mixture to warm up to room temperature to afford the dihydronaphthofuranone adduct **2**. With 1 equivalent of LDA the sequence appeared to proceed not so cleanly as judged by TLC of the reaction mixture, and the product after dehydrogenation **3** (*vide infra*) was obtained only in a low yield. Every attempt to isolate this adduct in a pure form resulted in failure, because it was not only sparingly soluble in organic solvents, such as diethyl ether or dichloromethane, but also unstable under purification conditions. Therefore, after the production of compound **2** was briefly confirmed on the basis of its IR spectrum (3354, 1781, 1720 and 1671 cm⁻¹), which seemed to indicate that it was an equilibrium mixture of **2A** and **2B**, it was subjected to the next step without any purification. Dehydrogenation of **2** was successively achieved with 10% Pd on activated carbon in refluxing *p*-cymene to give 4-phenyl-9-hydroxynaphtho[2,3-*b*]furan-1(3*H*)-one **3** in a satisfactory yield (entry 1 in Table 1). We next subjected the derivatives of **1**, carrying methoxy substituents on the benzene rings, to this sequence. However, the reactions using these starting materials each gave an intractable mixture of products. Although we have no firm explanation at this point, this may be attributed to the lower reactivity of the toluate carbonyl group caused by the methoxy substituents. These results indicate that the strategy of Scheme 1 is unlikely to provide a general production of 4-aryl-9-oxynaphthofuranone derivatives, and we turned our attention to an alternative approach starting with 3-arylisobenzofuranones **4–8**.

The lithiation products of the 3-arylisobenzofuranones **4–6**, generated *in situ* by the treatment with 2 equivalents of LDA in THF at −78 °C, were also treated with furan-2(5*H*)-one. The addition of the anions to furan-2(5*H*)-one in the 1,4-addition manner proceeded smoothly. However, the intramolecular condensation of the resulting enolate intermediates with the benzo-

CDCl$_3$. J Values are given in Hz. Low-resolution mass spectra were recorded on a JEOL AUTOMASS 20 spectrometer or a JEOL JMS-AX505 HA spectrometer. Column chromatography was carried out on Merck Kieselgel 60 F$_{254}$. Thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 PF$_{254}$. All of the solvents used were dried over appropriate drying agents and distilled under argon prior to use. Furan-2(5H)-one was commercially available.

Ethyl *o*-benzylbenzoate 1 [12]

This compound was prepared by the acid-catalysed esterification of commercially available *o*-benzylbenzoic acid, bp 170–180 °C (bath temp.)/0.7 Torr; ν_{max}/cm^{-1} 1717; δ_H 1.29 (3 H, t, J 7.3), 4.28 (2 H, q, J 7.3), 4.38 (2 H, s), 7.2–7.3 (7 H, m), 7.41 (1 H, dd, J 7.6 and 1.5) and 7.88 (1 H, dd, J 7.6 and 1.5).

3-(3,4-Dimethoxyphenyl)isobenzofuran-1(3H)-one 4,[13] 5,6-dimethoxy-3-phenylisobenzofuran-1(3H)-one 5,[14] 5,6-dimethoxy-3-(3,4-dimethoxyphenyl)isobenzofuran-1(3H)-one 6, 7-(1,3-benzodioxol-5-yl)furo[3,4-*f*]-1,3-benzodioxol-5(7H)-one 7 [11] and 5,6-dimethoxy-3-(1,3-benzodioxol-5-yl)isobenzofuran-1(3H)-one 8 [9]

These compounds were prepared by a modification (using dimethyl acetals in place of ethylene acetals) of the method reported by Sammes *et al.*[11] Data for these compounds are as follows. Compound **4**: mp 145–146 °C (hexane–Et$_2$O) (lit.,[13] 148 °C); ν_{max}/cm^{-1} 1743; δ_H 3.81 (3 H, s), 3.88 (3 H, s), 6.36 (1 H, s), 6.68 (1 H, s), 6.86 (2 H, s), 7.33 (1 H, d, J 7.6), 7.56 (1 H, dd, J 7.6 and 7.3), 7.66 (1 H, dd, J 7.6 and 7.3) and 7.97 (1 H, d, J 7.6). Compound **5**: mp 137–137.5 °C (benzene–Et$_2$O) (lit.,[14] 112 °C); ν_{max}/cm^{-1} 1742; δ_H 3.88 (3 H, s), 3.96 (3 H, s), 6.28 (1 H, s), 6.68 (1 H, s) and 7.25–7.4 (6 H, m). Compound **6**: mp 180–181 °C (hexane–CH$_2$Cl$_2$) (Found: C, 65.2; H, 5.6. C$_{18}$H$_{18}$O$_6$ requires C, 65.45; H, 5.5%); ν_{max}/cm^{-1} 1750; δ_H 3.81 (3 H, s), 3.89 (6 H, s), 3.97 (3 H, s), 6.24 (1 H, s), 6.65–6.7 (2 H, m), 6.86 (1 H, d, J 8.8), 6.87 (1 H, d, J 8.8) and 7.35 (1 H, s). Compound **7**: mp 145–146 °C (MeOH) (lit.,[11] 146–147 °C). Compound **8**: mp 157–157.5 °C (hexane–CH$_2$Cl$_2$) (lit.,[9] 157.5–158 °C); ν_{max}/cm^{-1} 1761; δ_H 3.90 (3 H, s), 3.96 (3 H, s), 5.97 (2 H, s), 6.19 (1 H, s), 6.60 (1 H, s), 6.67 (1 H, s), 6.82 (2 H, br s) and 7.33 (1 H, s).

9-Hydroxy-4-phenylnaphtho[2,3-*c*]furan-1(3H)-one 3

To a stirred solution of LDA (2 mmol) in dry THF (2.5 cm^3) at −78 °C (cooling bath temperature) under argon, was added ethyl *o*-benzylbenzoate **1** (0.24 g, 1.0 mmol) dropwise *via* a syringe. The deep-red solution of the resulting carbanion was stirred for 5 min, after which furan-2(5H)-one (0.17 g, 2.0 mmol) was added dropwise to it *via* a syringe. The deep-red colour turned into yellow immediately. The reaction mixture was then allowed to warm to room temperature. Diethyl ether (10 cm^3) and saturated aqueous NH$_4$Cl (10 cm^3) were added to the mixture after which the layers were separated, and the aqueous phase was extracted with Et$_2$O (3 × 10 cm^3). The combined organic layers were washed with brine, dried (MgSO$_4$), and evaporated to give a residue (0.40 g). *p*-Cymene (8.0 cm^3) and 10% palladium-on-activated carbon (0.11 g, 1.0 mg) were added to the residue and the mixture was heated under reflux for 3 h. After cooling of the mixture to room temperature the catalyst was filtered off, and the solvent was removed under reduced pressure. Separation of the residue by preparative TLC on SiO$_2$ gave the 9-hydroxynaphthofuranone **3** (0.16 g, 56%) as a white solid: R_f 0.66 (1 : 3 EtOAc–hexane); mp 180 °C (decomp.) (hexane–CHCl$_3$) (Found: C, 78.25; H, 4.3. C$_{18}$H$_{12}$O$_3$ requires C, 78.25; H, 4.4%); ν_{max}/cm^{-1} 3424 and 1745; δ_H 5.27 (2 H, s), 7.35 (1 H, dd, J 7.9 and 1.6), 7.45–7.65 (6 H, m), 7.7–7.75 (1 H, m), 8.4–8.45 (1 H, m) and 8.65 (1 H, br); *m*/*z* 276 (M$^+$, 96%) and 202 (100).

4-(3,4-Dimethoxyphenyl)-9-hydroxynaphtho[2,3-*c*]furan-1(3H)-one 10

To a stirred solution of LDA (3.0 mmol) in THF (3.8 cm^3) at −78 °C (cooling bath temperature), under an argon atmosphere, was added a solution of the benzofuranone **4** (0.41 g, 1.5 mmol) in THF (2.2 cm^3). After 5 min, furan-2(5H)-one (0.25 g, 3.0 mmol) was added dropwise *via* a syringe to the deep red solution of the resulting carbanion; the solution turned orange immediately and was allowed to warm to room temperature. Stirring was continued overnight, after which time the reaction mixture was worked up in a similar manner as described above. The crude product was dissolved in CHCl$_3$ (9 cm^3) containing iodine (75 mg, 0.30 mmol) and the mixture was stirred for 10 h under an argon atmosphere. The resulting mixture was diluted with CHCl$_3$ (30 cm^3), washed successively with aqueous Na$_2$S$_2$O$_3$ and brine, dried (MgSO$_4$), and evaporated to yield a yellow solid. Purification of this by preparative TLC on SiO$_2$ afforded the 9-hydroxynaphthofuranone **10** (0.26 g, 51%) as a white solid: R_f 0.48 (1 : 2, EtOAc–hexane); mp 173–173.5 °C (Et$_2$O–CHCl$_3$) (Found: C, 71.15; H, 4.8. C$_{20}$H$_{16}$O$_5$ requires C, 71.4; H, 4.8%); ν_{max}/cm^{-1} 3407 and 1729; δ_H 3.88 (3 H, s), 3.97 (3 H, s), 5.28 (1 H, d, J 14.6), 5.30 (1 H, d, J 14.6), 6.85 (1 H, d, J 1.8), 6.87 (1 H, dd, J 8.3 and 1.8), 7.02 (1 H, dd, J 1.8), 7.55–7.65 (2 H, m), 7.75–7.8 (1 H, m), 8.4–8.5 (1 H, m) and 8.61 (1 H, s); *m*/*z* 336 (M$^+$, 79%) and 262 (100).

4-(3,4-Dimethoxyphenyl)-9-methoxynaphtho[2,3-*c*]furan-1(3H)-one 11

The hydroxynaphthofuranone **10** (0.13 g, 0.4 mmol) was treated with diazomethane (25 mmol) in Et$_2$O (20 cm^3) at 0 °C for 3 h to give, after purification by preparative TLC on SiO$_2$, the 9-methoxynaphthofuranone **11** in almost quantitative yield, R_f 0.69 (1 : 1, EtOAc–hexane); mp 219–221 °C (Et$_2$O–CHCl$_3$) (Found: C, 71.95; H, 5.2%. C$_{21}$H$_{18}$O$_5$ requires C, 72.0; H, 5.2%); ν_{max}/cm^{-1} 1765; δ_H 3.87 (3 H, s), 3.98 (3 H, s), 4.42 (3 H, s), 5.18 (1 H, d, J 12.5), 5.21 (1 H, d, J 12.5), 6.85 (1 H, d, J 1.8), 6.90 (1 H, dd, J 8.3 and 1.8), 7.03 (1 H, d, J 8.3), 7.55–7.6 (2 H, m), 7.7–7.8 (1 H, m) and 8.45–8.55 (1 H, m); *m*/*z* 350 (M$^+$, 100%).

6,7,9-Trimethoxy-4-phenylnaphtho[2,3-*c*]furan-1(3H)-one 12

This compound was prepared from the benzofuranone **5** as described for the preparation of the 9-methoxynaphthofuranone **11** without isolation of the corresponding 9-hydroxy derivative; R_f 0.61 (1 : 1, EtOAc–hexane); mp 147–148 °C (Et$_2$O–CHCl$_3$) (Found: C, 71.7; H, 4.9. C$_{21}$H$_{18}$O$_5$ requires C, 72.0; H, 5.2%); ν_{max}/cm^{-1} 1749; δ_H 3.79 (3 H, s), 4.06 (3 H, s), 4.39 (3 H, s), 5.12 (2 H, s), 6.95 (1 H, s), 7.35–7.4 (2 H, m), 7.45–7.6 (3 H, m) and 7.7–7.75 (1 H, m); *m*/*z* 350 (M$^+$, 100%).

4-(3,4-Dimethoxyphenyl)-6,7,9-trimethoxynaphtho[2,3-*c*]furan-1(3H)-one 13

This compound was prepared from the benzofuranone **7** as described for the preparation of the 9-methoxynaphthofuranone **11** without isolation of the corresponding 9-hydroxy derivatives; R_f 0.43 (1 : 1, EtOAc–hexane); mp 131–132 °C (Et$_2$O–CH$_2$Cl$_2$) (Found: C, 67.1; H, 5.4. C$_{23}$H$_{22}$O$_7$ requires C, 67.3; H, 5.4%); ν_{max}/cm^{-1} 1756; δ_H 3.81 (3 H, s), 3.88 (3 H, s), 4.07 (3 H, s), 4.39 (3 H, s), 5.14 (1 H, d, J 12.0), 5.16 (1 H, d, J 12.0), 6.8–6.95 (2 H, m), 7.0–7.05 (2 H, m) and 7.71 (1 H, s); *m*/*z* 410 (M$^+$, 100%).

9-(1,3-Benzodioxol-5-yl)-5-methoxyfuro[3′,4′:6,7]naphtho-[2,3-*d*]-1,3-dioxol-6(8H)-one (Neojusticin A) 14

The benzofuranone **7** (0.15 g, 0.50 mmol) was lithiated, treated with furan-2(5H)-one (84 mg, 1.00 mmol) and the mixture worked up in a manner similar to that described for the preparation of the 9-hydroxynaphthofuranone **10**. The crude product (0.17 g) was dissolved in THF (5 cm^3) containing pyridine (0.3 cm^3) under an argon atmosphere. SOCl$_2$ (0.12 g, 1.0 mmol) was then added to the mixture and stirring was continued for 18 h at room temperature. The mixture was evaporated under reduced pressure. A solution of the residue (0.17 g) in acetone (12 cm^3)

containing K_2CO_3 (1.6 g, 12 mmol) and MeI (1.6 g, 11 mmol) was heated under reflux for 11 h after which it was filtered and the filtrate was evaporated. The residue was partitioned between water and $CHCl_3$ (20 cm³ each). The organic layer was separated, dried ($MgSO_4$) and evaporated to give a yellow solid. Purification of this by preparative TLC gave neojusticidin A **14** (95 mg, 50%) as a white solid, R_f 0.47 (1:1, EtOAc–hexane); mp 271–272 °C (Et_2O–$CHCl_3$) (lit.,[2a] 273–275 °C); v_{max}/cm⁻¹ 1761; δ_H 4.33 (3 H, s), 5.11 (1 H, d, J 14.9), 5.12 (1 H, d, J 14.9), 6.05–6.1 (4 H, m), 6.75 (1 H, dd, J 8.7 and 1.8), 6.77 (1 H, s), 6.95 (1 H, d, J 8.7), 6.99 (1 H, s) and 7.71 (1 H, s); m/z 378 (M⁺, 100%).

4-(1,3-Benzodioxol-5-yl)-6,7,9-trimethoxynaphtho[2,3-*c*]furan-1(3*H*)-one (Neojusticin B) 15

This compound was prepared from the benzofuranone **8** as described for the preparation of neojusticidin A **14**. Data for **15**, R_f 0.58 (1:1, EtOAc–hexane); mp 265–268 °C (Et_2O–$CHCl_3$) (lit.,[2a] 262–265 °C); v_{max}/cm⁻¹ 1754; δ_H 3.84 (3 H, s), 4.06 (3 H, s), 4.38 (3 H, s), 5.13 (2 H, s), 6.06 (1 H, d, J 1.5), 6.09 (1 H, d, J 1.5), 6.80 (1 H, dd, J 8.7 and 1.8), 6.81 (1 H, s), 6.97 (1 H, d, J 8.7), 6.99 (1 H, s) and 7.70 (1 H, s); m/z 394 (M⁺, 100%).

Acknowledgements

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