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A facile synthesis of naturally occurring binaphthoquinones: efficient oxidative dimerization of 4-alkoxy-1-naphthols using silver(II) oxide–40% nitric acid

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Abstract—Oxidation of 4-alkoxy-1-naphthols with AgO–40% HNO_3 occurred along with a dimerization to give the corresponding bi-1,4-naphthoquinones. The oxidative dimerization required one hydroxyl group and took place at its *ortho* position. This reaction was applicable to syntheses of naturally occurring binaphthoquinones, bivitamin K_3 and 3,3′-bijuglone.

1. Introduction

Naturally occurring binaphthoquinones, such as bivitamin K_3,[1a] bilawsone,[1b] 3,3′-bijuglone,[1c] 3,3′-biplumbagin,[1d] biramentaceone,[1e] mamegakinone,[1f] dianellinone,[1g] 3,3′-bidiomelquinone A,[1h] and xanthomegnin,[1i] contain a bi-1,4-naphthoquinone moiety which is symmetrical 1,4-naphthoquinone. Usually, a synthesis of the bi-1,4-naphthoquinone skeleton requires two steps. For example, biramentaceone was prepared by oxidative coupling of 4-methoxy-1-naphthol compounds using lead dioxide,[2] or silver(I) oxide(Ag_2O),[3] followed by treatment with 65% HNO_3. Mamegakinone dimethyl ether was prepared by conversion of bromonaphthoquinone into a stannane derivative, followed by Stille-type coupling reaction with the bromonaphthoquinone in the presence of bis(triphenylphosphine) palladium(II) chloride.[4]

On the other hand, the oxidation of 1,4-dimethoxynaphthalene and *p*-dimethoxybenzene derivatives to the corresponding naphthoquinones and benzoquinones, respectively, has been accomplished using such oxidants as cerium(IV) ammonium nitrate[5] ($Ce(NH_4)_2(NO_3)_6$, CAN is used as the abbreviation hereafter), silver(II) oxide(AgO)–HNO_3,[6] and $(NH_4)_2S_2O_8$–$AgNO_3$.[7] In the course of our synthetic study of naphthoquinone derivatives, we have found that oxidation of 4-methoxy-1-naphthol with AgO–40% HNO_3 occurs along with a dimerization to give selectively 2,2′-bi-1,4-naphthoquinone in high yield in one step. The present paper describes oxidative dimerization of 4-alkoxy-1-naphthols using AgO–40% HNO_3 and its application to syntheses of bivitamin K_3 and 3,3′-bijuglone.

2. Results and discussion

Oxidation of 4-methoxy-1-naphthol (**1**) with various oxidants were carried out and the results are summarized in Table 1. Treatment of **1** with CAN (entry 1) or $(NH_4)_2S_2O_8$–$AgNO_3$ (entry 4) gave 1,4-naphthoquinone (**2**) as a main product. Interestingly, oxidation of **1** with AgO–40% HNO_3 in acetone at room temperature occurred along with a dimerization to give selectively 2,2′-bi-1,4-naphthoquinone (**3**) in 89% yield (entry 2a). When chloroform (entry 2c) or acetonitrile (2d) was the reaction solvent, the binaphthoquinone was also obtained in good yield.

In attempting to examine the oxidative dimerization using AgO–40% HNO_3, reaction of various naphthols and their derivatives with it were carried out and the results are summarized in Table 2. The oxidative dimerization required one hydroxyl group (entries 3, 4, 6 and 7) and proceeded with a methoxyl group (entry 6) or a methoxy methoxyl group (entry 7) in *para* position of the hydroxyl group, whereas no dimerization occurred in cases of 1-naphthol (entry 1), 1,4-dihydroxynaphthalene (entry 2) and 1,4-dimethoxynaphthalene (entry 8). On the basis of these results, we supposed the following reaction mechanism: electron-rich aromatic substrates having a hydroxyl group were oxidized by Ag(II)–HNO_3 system to generate an

Keywords: binaphthoquinones; oxidative dimerization; alkoxynaphthols; silver(II) oxide.
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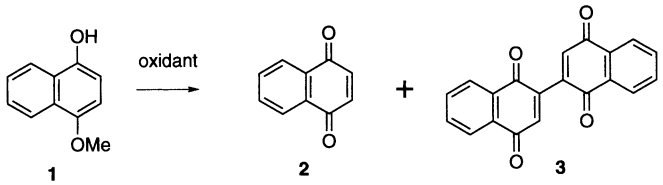
Table 1. Oxidation of 4-methoxy-1-naphthol (**1**) with various oxidants



Entry	Oxidant	Reaction conditions			Yield (%)[a]	
		Solvent	Temperature	Time (min)	**2**	**3**
1	$Ce(NH_4)_2(NO_3)_6$	$CH_3CN–H_2O$	Rt	30	71	27
2a	AgO–40% HNO_3	CH_3COCH_3	Rt	35	0	89
2b	AgO–40% HNO_3	CH_3COCH_3	0–5°C then rt	30 then 30	0	39
2c	AgO–40% HNO_3	$CHCl_3$	Rt	35	0	89
2d	AgO–40% HNO_3	CH_3CN	Rt	35	0	89
2e	AgO–40% HNO_3	THF	Rt	35	22	47
2f	AgO–40% HNO_3	dioxane	Rt	35	30	4
3	$TI(NO_3)_3·3H_2O$[b]	CH_3OH	Rt	40	7	40
4	$(NH_4)_2S_2O_8–AgNO_3$	$CH_3CN–H_2O$	Rt	23 h	69	18
5	65% HNO_3	–	Rt	2	40	16
6	Ag_2O–65% HNO_3	CH_3COCH_3	Rt	35	0	46

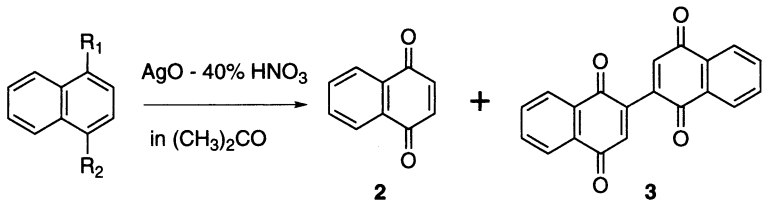
[a] Isolated yield.
[b] Ref. 8.

aromatic radical cation[9,10] and the subsequent radical–radical coupling[11] gave binaphthoquinones.

We next applied the oxidative dimerization to syntheses of naturally occurring binaphthoquinones. The starting material, 4-methoxy-3-methyl-1-naphthol (**8**) was prepared from vitamin K_3 (**4**) in four steps according to the literature procedures.[12–14] Oxidation of **8** with AgO–40% HNO_3 gave bivitamin K_3 (**9**)[15] in 59% yield as shown in Scheme 1. The compound **9** had been isolated before from the fern *Asplenium laciniatum* by Gupta and co-workers.[16] The binaphthoquinone **9** was also synthesized in 58% yield from **8** by the oxidative coupling of two steps using Laatsch's procedure.[3,17]

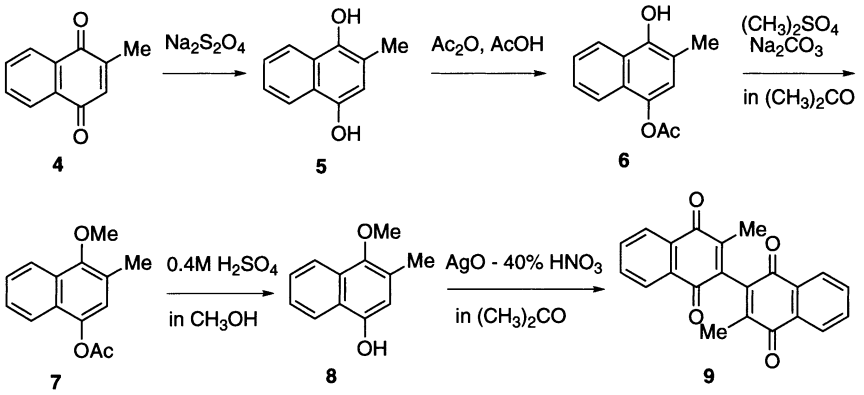
Since the dimerization using AgO–40% HNO_3 took place at an *ortho* position of a hydroxyl group, we examined whether the reaction occurs in compounds having a substituent group at the *ortho* position. Although the reaction of 2-formyl- and 2-hydroxymethyl-4-methoxy-1-naphthols resulted in destruction of the starting materials, interestingly, the oxidation of 4-methoxy-2-methyl-1-naphthol (**10**)[18] gave the dimer, 2,2′-(ethylene)bi-1,4-naphthoquinone (**11**) in 98% yield (Scheme 2). In order to compare our procedure with Laatsch's it, oxidative coupling of **10** using Laatsch's procedure was attempted to give **11** in 66% yield via the spiro compound **12** as shown in Scheme 3. The X-ray stereostructure of **12**, shown in Fig. 1, indicates that **12** has a spiro ring system.

Table 2. Oxidation of naphthols and their derivatives with AgO–40% HNO_3

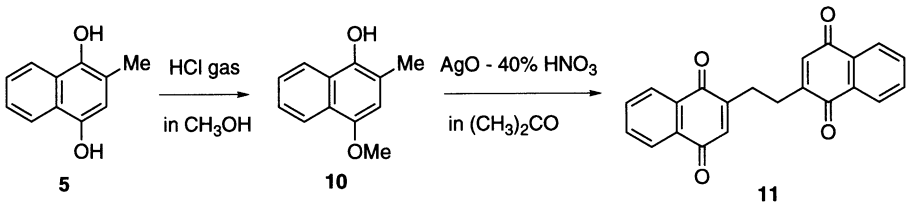


Entry	Substrate		Yield (%)[a]	
	R_1	R_2	**2**	**3**
1	OH	H	18	0
2	OH	OH	78	0
3	OH	Cl	0	27
4	OH	$NH_2·HCl$	20	6
5	OH	$OCOCH_3$	27	0
6	OH	OMe	0	89
7	OH	OCH_2OCH_3	9	83
8[b]	OMe	OMe	Quant	0
9	OMe	$OCOCH_3$	53	0
10	OMe	CHO	52	0

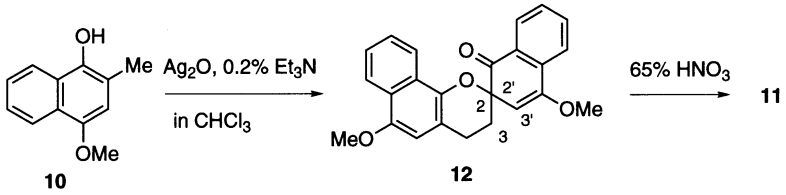
[a] Isolated yield.
[b] Ref. 6.



Scheme 1.



Scheme 2.



Scheme 3.

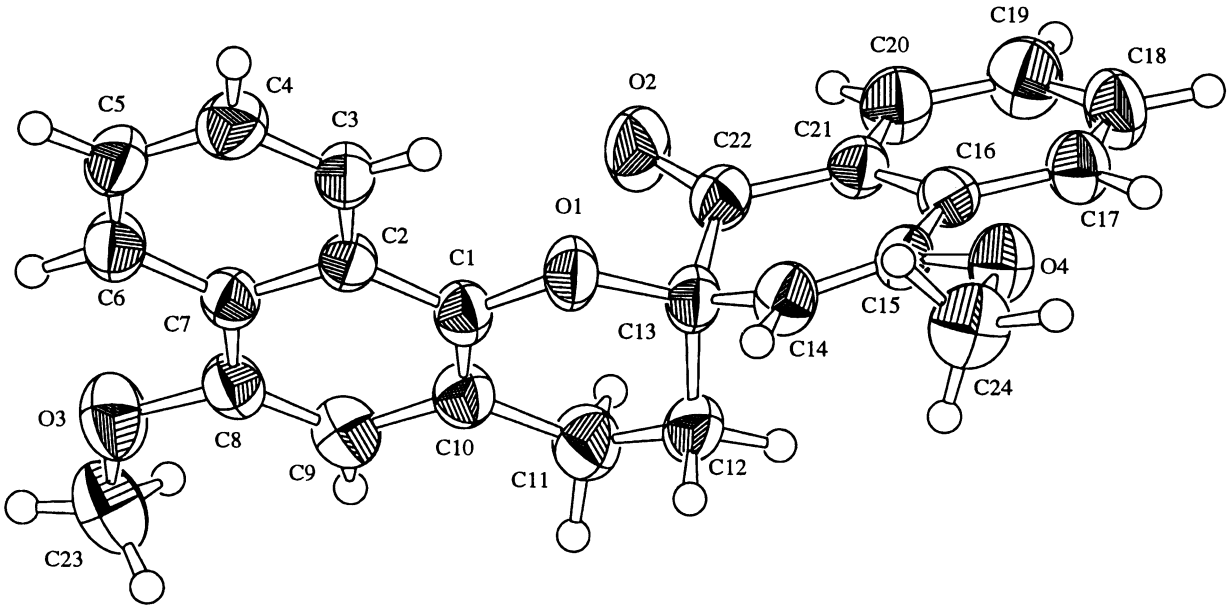
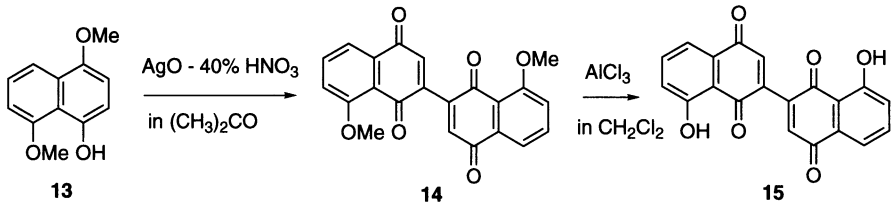


Figure 1. X-Ray determined structure of **12**.



13 14 15

Scheme 4.

We chose 3,3′-bijuglone which had been isolated from the root bark of *Juglans regia*,[19] as a second target compound. According to the established procedure,[20] the starting material **13** was prepared in four steps from 1,5-dihydroxynaphthalene. Oxidation of **13** with AgO–40% HNO_3 gave the dimer, 3,3′-bijuglone dimethyl ether (**14**) in 71% yield along with 5-methoxy-1,4-naphthoquinone[20] in 3% yield. At this point we encountered difficulties in demethylation of **14**. Attempts employing BBr_3,[21] Me_3SiI[21] and $AlCl_3$–Et_2S[22] resulted in destruction of **14** to give complex products. Fortunately 3,3′-bijuglone (**15**) was obtained in 64% yield using 10 molar equiv. of $AlCl_3$[23] in dichloromethane at room temperature for 22 h as shown in Scheme 4.

In summary, we found that oxidation of 4-alkoxy-1-naphthols with AgO–40% HNO_3 occurs along with a dimerization. The oxidative dimerization required one hydroxyl group and took place at its *ortho* position. The dimerization was applicable to synthese of naturally occurring binaphthoquinones to give bivitamin K_3 and 3,3′-bijuglone.[24]

3. Experimental

3.1. General

^1H (500 MHz) and ^{13}C NMR (125 MHz) spectra were taken on a JEOL JNM-A500 spectrometer in $CDCl_3$ solutions using Me_4Si and $CDCl_3$ as an internal standard. EI mass spectra were performed with a JEOL JMS-SX 102A mass spectrometer. Infrared spectra were recorded on a Shimadzu IR 470 spectrometer. Melting points were observed with a Yanaco MS-S3 micro melting point apparatus (hot-plate type). Elemental analyses were determined with a Yanaco CHN Corder MT-3. X-Ray crystallography was measured on a Rigaku automated four-circle diffractometer AFC7R with graphite monochromatized Mo Kα radiation (λ=0.71069 Å), the ω–2θ scan technique being employed. For preparative column chromatography, Wakogel C-200 silica gel was employed. Naphthols and their derivatives except 4-acetoxy-1-naphthol, 4-methoxy-1-naphthol and 4-acetoxy1-1-methoxynaphthalene in Table 2 were purchased from Tokyo Kasei Kogyo. 4-Acetoxy-1-methoxynaphthalene was prepared by treatment of 4-methoxy-1-naphthol with acetic anhydride in pyridine.

3.1.1. 4-Acetoxy-1-naphthol. Acetic anhydride (204 mg, 2.0 mmol) was added to a solution of 1,4-dihydroxynaphthalene (320 mg, 2.0 mmol) in pyridine (4 ml) and stirred at room temperature for 3 h. After concentration under reduced pressure, the crude product was chromatographed on silica-gel to give 4-acetoxy-1-naphthol (262 mg, 65% yield) along with 1,4-diacetoxynaphthalene (84 mg, 17% yield). Recrystallization of the monoester from hexane–ethyl acetate (3:1) gave an analytical sample as light mud yellow solid, mp 126–127°C; IR (KBr) 3420 (OH), 1737 (C=O), 1583, 1230, 1064 cm^{-1}; ^1H NMR δ 2.44 (s, 3H, CH_3), 5.62 (broad, 1H, OH), 6.45 (d, J=8.2 Hz, 1H, ArH), 6.91 (d, J=8.2 Hz, 1H, ArH), 7.43 (m, 1H, ArH), 7.49 (m, 1H, ArH), 7.72 (d, J=8.2 Hz, 1H, ArH), 8.06 (d, J=8.2 Hz, 1H, ArH); ^{13}C NMR δ 20.97 (CH_3), 107.68, 117.84, 120.74, 122.31, 124.98, 125.16, 125.49, 126.83, 127.30, 139.61, 149.85, 170.82; MS *m/z* (rel. intensity, %) 202 (M^+, 16), 160 (100), 154 (12), 131 (15), 69 (22); HRMS calcd for $C_{12}H_{10}O_3$ M 202.0630, found 202.0589.

3.1.2. 4-Methoxymethoxy-1-naphthol. To a stirred and cooled (0°C) solution of 1,4-dihydroxynaphthalene (500 mg, 3.12 mmol) in DMF (10 ml) was added sodium hydride (125 mg, 68% in paraffin, 3.12 mmol) under a nitrogen atmosphere. After 10 min, chloromethyl methyl ether (251 mg, 3.12 mmol) was added and stirring was continued overnight. The reaction mixture was poured into water and extracted with chloroform. The extracts were washed with brine, dried over Na_2SO_4 and evaporated. The residue was purified by silica-gel chromatography to give 4-methoxymethoxy-1-naphthol (161 mg, 25 % yield) as oil; IR (neat) 3380 (OH), 1595, 1269, 1148, 1059 cm^{-1}; ^1H NMR δ 3.55 (s, 3H, OCH_3), 5.31 (s, 2H, CH_2), 5.39 (broad, 1H, OH), 6.67 (d, J=8.1 Hz, 1H, ArH), 6.91 (d, J=8.1 Hz, 1H, ArH), 7.50 (m, 2H, ArH), 8.12 (m, 1H, ArH), 8.20 (m, 1H, ArH); ^{13}C NMR δ 56.14 (CH_3), 95.46 (CH_2), 107.95, 108.61, 121.60, 121.88, 125.21, 125.70, 125.96, 126.91, 146.23, 147.02; MS *m/z* (rel. intensity, %) 204 (M^+, 100), 174 (50), 159 (88), 131 (25), 115 (16), 103 (20), 77 (25); HRMS calcd for $C_{12}H_{12}O_3$ M 204.0786, found 204.0781.

3.2. General procedure for the oxidative dimerization

Reaction of 4-methoxy-1-naphthol (**1**) is described as a typical example. To a mixture of **1** (100 mg, 0.574 mmol) and AgO (711 mg, 5.74 mmol) in acetone (10 ml) was added 40% HNO_3 (3 ml) over 5 min. After stirring at room temperature for 30 min, the reaction mixture was diluted with water and extracted with chloroform. The extracts were washed with brine, dried over Na_2SO_4 and evaporated. The crude product was purified by silica-gel chromatography to give 2,2′-bi-1,4-naphthoquinone (**3**) (81 mg, 89% yield).

3.2.1. 2,2′-Bi-1,4-naphthoquinone (3). Light mud yellow solid; mp 264–267°C (lit.[25] 260–265°C); IR (KBr) 1663 (C=O), 1589, 1337, 1304, 1254, 1227, 772 cm^{-1}; ^1H NMR δ 7.08 (s, 2H, ArH), 7.58–8.30 (m, 8H, ArH); MS *m/z* (rel. intensity, %) 314 (M^+, 100), 297 (68), 258 (15), 230 (15), 202 (37).

3.2.2. Bivitamin K_3 (9). Mud yellow prisms (from acetonitrile); mp 249–251°C (lit.[16] 243–246°C); IR (KBr) 1661 (C═O), 1593, 1284 cm^{-1}; ^1H NMR δ 2.07 (s, 6H, CH_3), 7.76 (m, 4H, ArH), 8.09 (m, 2H, ArH), 8.17 (m, 2H, ArH); ^{13}C NMR δ 14.36 (CH_3), 126.63, 126.66, 131.93, 132.10, 133.88, 133.94, 140.54, 145.77, 182.62 (C═O), 184.43 (C═O); MS *m/z* (rel. intensity, %) 342 (M^+, 100), 327 (72), 313 (30), 300 (40), 285 (22), 271 (13), 239 (15), 228 (14), 215 (20), 152 (20), 104 (35), 76 (40). Anal. Calcd for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12. Found: C, 77.08; H, 4.18.

3.2.3. 2,2′-(Ethylene)bi-1,4-naphthoquinone (11). Light mud yellow solid (from chloroform–ethyl acetate (10:1)); mp 248–249°C; IR (KBr) 1662 (C═O), 1616, 1592, 1303 cm^{-1}; ^1H NMR δ 2.89 (s, 4H, CH_2), 6.83 (s, 2H, quinone H), 7.75 (m, 4H, ArH), 8.07 (m, 2H, ArH), 8.10 (m, 2H, ArH); ^{13}C NMR δ 28.43 (CH_2), 126.18, 126.70, 132.06, 132.16, 133.81, 133.87, 135.43, 149.81, 184.83 (C═O), 184.92 (C═O); MS *m/z* (rel. intensity, %), 342 (M^+, 100), 325 (20), 313 (10), 297 (16), 115 (39), 76 (33). Anal. Calcd for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12. Found: C, 76.76; H, 4.13.

3.2.4. 3,3′-Bijuglone dimethyl ether (14). Yellow plates (from acetonitrile); mp ~256°C (dec.) (lit.[19] mp 250°C); IR (KBr) 1658 (C═O), 1585, 1316, 1279, 1215, 1022 cm^{-1}; ^1H NMR δ 3.99 (s, 6H, OCH_3), 6.95 (s, 2H, quinone H), 7.33 (m, 2H, ArH), 7.73 (m, 4H, ArH); ^{13}C NMR δ 56.45 (OCH_3), 118.14, 119.06, 119.79, 134.19, 134.81, 135.27, 146.78, 160.05, 182.10 (C═O), 184.43 (C═O); MS *m/z* (rel. intensity, %) 374 (M^+, 100), 357 (91), 236 (23), 189 (16), 76 (52). Anal. Calcd for $C_{22}H_{14}O_6$: C, 70.59; H, 3.77. Found: C, 70.38; H, 3.80.

3.2.5. Demethylation of 14. To a solution of **14** (87 mg, 0.231 mmol) in dichloromethane (30 ml) was added $AlCl_3$ (308 mg, 2.31 mmol). After stirring at room temperature for 22 h, the reaction mixture was decomposed with 5% aqueous oxalic acid (20 ml), extracted with chloroform, washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica-gel chromatography to give 3,3′-bijuglone (**15**) (51 mg, 64% yield). Orange solid; mp 265–267°C (dec.) (lit.[3] 270°C); IR (KBr) 1663 (C═O), 1627 (C═O), 1454, 1293 cm^{-1}; ^1H NMR δ 7.04 (s, 2H, quinone H), 7.34 (m, 2H, ArH), 7.70 (s, 4H, ArH), 11.76 (s, 2H, OH); MS *m/z* (rel. intensity, %) 346 (M^+, 100), 329 (22), 289 (25), 262 (23), 234 (18), 205 (19), 120 (23), 92 (40); HRMS calcd for $C_{20}H_{10}O_6$ M 346.0478, found 346.0462.

3.3. Oxidative dimerization of two steps by Laatsch's method[3,17]

3.3.1. Synthesis of 11 from 10. To a solution of **10** (100 mg, 0.531 mmol) in chloroform (10 ml) was added triethylamine (0.02 ml) and Ag_2O (616 mg, 2.66 mmol). The mixture was stirred at room temperature for 24 h and filtered off. The filtrate was evaporated in vacuo to give the crude product **12**, which was used for the following reaction without purification. To the crude **12** was added 65% HNO_3 (4 ml). The mixture was stirred at room temperature for 3 min and diluted with water and extracted with chloroform. The extracts were washed with brine and dried over Na_2SO_4. After evaporation of the solvent, chromatographic purification (chloroform) gave the dimer **11** (60 mg, 66% yield). In order to determine the structure of **12**, the other crude product of **12** was purified by silica-gel chromatography eluting with chloroform, followed by recrystallization from hexane–ethyl acetate (10:1). **12**: Yellow prisms; mp 131–132°C; IR (KBr) 1690 (C═O), 1596, 1385, 1267, 1101, 764 cm^{-1}; ^1H NMR δ 2.13 (m, 1H, H–C–*H*), 2.25 (m, 1H, *H*–C–H), 2.94 (m, 2H, CH_2), 3.76 (s, 3H, OCH_3-4′), 3.96 (s, 3H, OCH_3-6), 5.35 (s, 1H, H-3′), 6.51 (s, 1H, ArH-5), 7.44 (m, 3H, ArH), 7.65 (m, 1H, ArH), 7.73 (d, *J*=7.3 Hz, 1H, ArH), 8.02 (dd, *J*=7.6 and 0.9 Hz, 1H, ArH), 8.17 (m, 2H, ArH); ^{13}C NMR δ 22.53 (CH_2), 31.33 (CH_2), 55.15 (OCH_3), 55.70 (OCH_3), 78.96, 100.97, 104.91, 113.32, 121.56 (2C), 122.65, 125.15, 125.42, 125.86, 126.11, 127.37, 128.67, 128.90, 134.52, 134.57, 141.98, 149.06, 150.81, 197.81 (C═O); MS *m/z* (rel. intensity, %) 372 (M^+, 42), 370 (100), 355 (52), 187 (62), 186 (56). Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.11; H, 5.40.

Single crystals of **12** were grown from hexane–ethyl acetate (3:1) and were monoclinic space group $P2_1/n$, a=6.5 (1) Å, b=27.1 (2) Å, c=10.6 (1) Å, β=93 (1)°, V=1877 (49) $Å^3$, Z=4, Rint=0.063, R=0.114, Rw=0.105, $R1$=0.047.

Crystallographic data for **12** has been deposited with the Cambridge Crystallographic Data Center as the deposition number CCDC 164999. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.cam.ac.uk).

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