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# Cyclo-oligomerization of Quinones

## V.* The Acid Catalyzed Reactions of α-Naphthoquinone with Phenols

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In the presence of catalytic amounts of strong acid α-naphthoquinone reacts with several polyhydric phenols to yield at room temperature 2-(polyhydroxyphenyl)-1,4-naphthoquinones. At higher temperatures good yields of polyhydroxybenzo[b]naphtho[2,1-d]furans are formed.

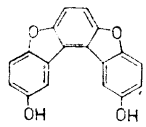
Many quinones readily undergo acid catalyzed condensations with phenols to give biphenyl derivatives or analogous compounds. The reaction products are often highly coloured hydroxyphenylquinones formed by oxidation of the primary phenolic condensation products by unchanged starting quinone. The reaction mixtures therefore also contain the hydroquinone corresponding to the original quinone.

Similar treatment of pure quinones frequently yields phenolic oligomers containing one or more dibenzofuran elements.[1–6] In these cases small amounts of the hydroquinone are obviously formed by some side reaction. This serves to start the condensation reactions which proceed to completion because the relevant hydroquinones are produced during the process. Therefore the condensation reactions are inhibited if oxidizing agents of sufficiently high oxidation potential are added to the reaction mixtures.[5] *p*-Benzoquinone gives, for example, small amounts of the tri- and tetramerization products *1* and *2* but 2,3-dialkylquinones and α-naphthoquinone give larger yields of analogous products.[4–6] It should be noted that during these reactions the condensation products are formed already at low temperatures and in the presence of small to moderate amounts of, *e.g.*, sulphuric acid. Under such conditions no dehydration of *o,o'*-dihydroxybiphenyls to dibenzofurans occurs. Much more drastic conditions, *e.g.*, prolonged boiling with strong hydrobromic acid, are normally required to bring about such ring closures. The relations between structure and ease of dibenzofuran formation have recently been studied in

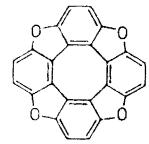
* Part IV: Ref. 6.

this laboratory by Stjernström.[7,8] Clearly the furan rings in the above quinone condensation products must have been formed in a quite different way.

In this paper we describe reactions during which either quinones or phenols containing dibenzofuran elements are formed depending upon the reaction conditions used.




1




2

Long ago Blumenfeld and Friedländer[9] noted that on addition of sulphuric acid to an acetic acid solution of α-naphthoquinone and resorcinol at room temperature a sparingly soluble, black product is formed. On heating, however, a colourless solution is obtained. The black product was easily obtained in an 80 % yield. The mass spectrum was in agreement with that expected for the quinone *4* contaminated with somewhat of the hydroquinone *3*. Recrystallization from ethanol in the presence of *p*-benzoquinone furnished the brown-red quinone *4*. The black product could be reduced to a tetraphenol (m.p. 169–171°) which gave a tetramethyl ether and a tetraacetate whose spectral properties (UV, NMR) clearly showed that *3* is the correct structure of the phenol. The quinone *4* dissolves in alkali giving a deep blue colour, typical for *o*- or *p*-hydroxyphenyl-1,4-naphthoquinones.[11] The UV and visible spectra of the quinone *4* in neutral or alkaline solution is shown in Fig. 1. The phenol,

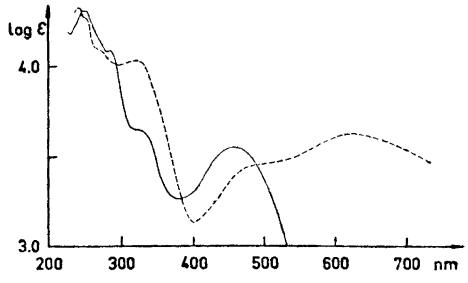



*Fig. 1.* UV and visible absorption curve of the quinone *4* in ethanol —— ($\lambda_{max}$/log $\varepsilon$ = 460/3.55) and in 1 % sodium carbonate solution in water – – – ($\lambda_{max}$/log $\varepsilon$ = 623/3.63).

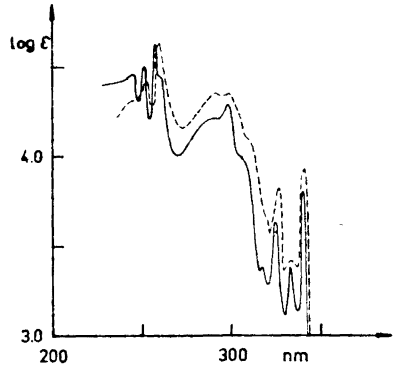
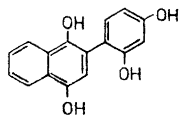
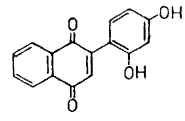



*Fig. 2.* UV absorption curve of α-brazan (*5*)[12] —— and of diacetoxybenzonaphthofuran (*6*, OAc instead of OH) – – – in ethanol. The latter is displaced 0.1 log $\varepsilon$ unit upwards.

m.p. 169–171°, is obviously identical with a product, m.p. 167°, obtained by Pummerer and Huppmann and assigned structure *3*.[9] So far we have not been able to repeat their experiment.

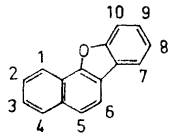



*3*

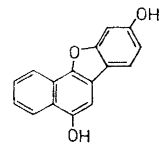



*4*

When naphtoquinone and an excess of resorcinol (1.5 mol) were similarly treated at reflux temperatures a colourless phenolic product (m.p. 210–211°) could be isolated in 70 % yield *via* its acetate. The UV-spectrum of the acetate was very similar to that of α-brazan (*5*) (Fig. 2).[12] The phenol, therefore, must be 5,9-dihydroxybenzo[b]naphtho[2,1-d]furan (*6*) and this conclusion is corroborated by the NMR investigation of its dimethyl ether.

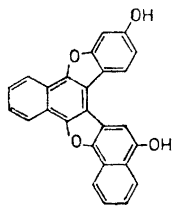



*5*

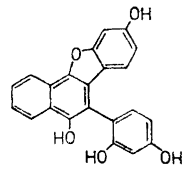



*6*

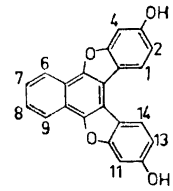
Two additional phenolic products A (about 2 %) and B (about 20 %) were isolated from the reaction mixture. Compound A was probably a condensation product of 2 mol of naphthoquinone and 1 mol of resorcinol minus 2 mol of water as evidenced by the MS ($m/e = 390$; $M^{+\cdot}$). One of the possible structures is *7*.




*7*



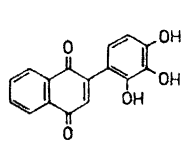

*8*



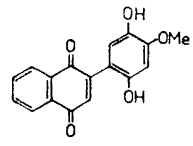

*9*

Compound B was obtained in almost quantitative yield by condensing the quinone *4* with resorcinol. Its structure, *8*, follows from its spectral properties and from the fact that it is dehydrated to a dihydric phenol when refluxed with hydrobromic acid. The NMR spectrum of this compound clearly shows that it must have the structure *9*.

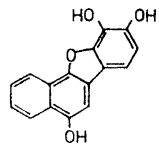
Pyrogallol and methoxyhydroquinone both react with naphthoquinone in the same way as resorcinol. At room temperature the quinones *10* and *11* were obtained but at reflux temperature compounds *12* and *13* were formed.



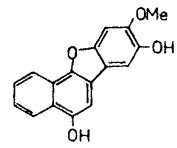

*10*




*11*



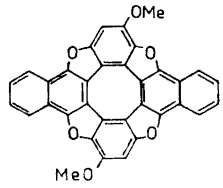

*12*



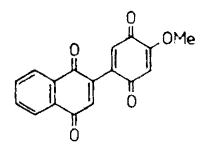

*13*

When introduced into a benzenesulphonic acid melt compound *11* underwent cyclodimerization to give a dimethoxydibenzotetraphenylenotetrafuran in 40 % yield ($m/e = 520$; $M^{+\cdot}$).

One of the two possible structures for this compound is *14*. The properties of the substance were very similar to those of similar quinone tetramers.[3,5,6] This cyclodimerization parallels the formation of the naphthoquinone tetramer from 2-(1,4-dihydroxy-2-naphthyl)-1,4-naphthoquinone.[5]




*14*




*15*

Sufficiently reactive phenol ethers also give condensation products with naphthoquinone. With resorcinol dimethyl ether it gave the red 2-(2,4-dimethoxyphenyl)-1,4-naphthoquinone (*4*, OMe instead of OH), identical with the product formed by chromic acid oxidation of the tetramethyl ether of the phenol *3*. Hydroxyhydroquinone trimethyl ether gave the deep blue 2-(2,4,5-trimethoxyphenyl)-1,4-naphthoquinone (*11*, OMe instead of OH) which on oxidation with nitric acid gave the diquinone *15* which is also formed upon similar oxidation of the quinone *11*.

In these condensation reactions the quinones, *e.g.* *4*, are formed as intermediates at higher temperatures. Samples withdrawn at early stages of the reaction displayed the intense absorption at 460 nm typical of compound *4*. At a lower temperature (50°) the quinone *4* first precipitated but slowly dissolved again to give a colourless solution from which a 20 % yield of furan *6*

could be isolated. There is certainly no mechanistic difference between the high and low temperature reactions. The reason why hydroxyphenylquinones can be isolated is obviously that, at low temperatures, they are insoluble in the reaction medium.

## EXPERIMENTAL

Melting points are uncorrected. Instruments: UV, Beckmann DK2; MS, LKB 9000 (ion source temp. 290°, 70 eV); NMR, Varian A-60A (TMS internal standard).

*2-(2,4-Dihydroxyphenyl)-1,4-naphthoquinone (4).* Naphthoquinone (15.8 g, 0.1 mol) was dissolved in acetic acid (400 ml) and a solution of resorcinol (6.1 g, 0.055 mol) in acetic acid (300 ml) was added. The light red solution was cooled to 20° and 2 M sulphuric acid (1 ml) was added. The reaction mixture immediately turned dark brown. It was cooled to 20° and the walls of the reaction flask were scratched with a glass rod to induce rapid crystallization. If cooling and scratching were omitted the yield was lowered. In some experiments the reaction was complicated by the coprecipitation of naphthoquinhydrone. After 2 h the mixture was filtered and the brownish-black product was washed with acetic acid and dried. Yield: 10.8 g, 80 %. The MS showed the product to be a 2:1 mixture of compounds *4* and *3*. The product was therefore recrystallized from ethanol containing enough benzoquinone to ensure complete oxidation to compound *4*. The brown-red product melted with decomposition at 202 – 204° (evacuated capillary). (Found: C 72.0; H 3.8. Calc. for $C_{16}H_{10}O_4$: C 72.2; H 3.8. Mw = 266). MS, $m/e = 266$ ($M^{+\cdot}$, base peak); 249 ($M^{+\cdot} - OH^{\cdot}$); 238 ($M^{+\cdot} - CO$); 104 ($C_6H_4CO^{+\cdot}$); 76 ($C_6H_5^+$). UV, see Fig. 1. With conc. sulphuric acid the compound gave an intense blue colour which slowly turned to green. The alkaline solution was deep blue (see Fig. 1 for absorption curve).

*2-(2,4-Dihydroxyphenyl)-4,4-naphthoquinone (3).* The quinone *4* (2 g) was boiled with a 20 % sodium dithionite solution (25 ml), charcoal was added and the solution filtered. On cooling colourless needles (1 g) separated. The compound was very sensitive to oxidation. Sublimed (150°/0.1 mm) material melted at 171 – 173° (Dec., evacuated capillary). (Found: C 71.0; H 4.5. Calc. for $C_{16}H_{12}O_4$ = C 71.6; H 4.5. Mw = 268). MS, $m/e = 268$ ($M^{+\cdot}$, base peak). Colour reaction with sulphuric acid, blue violet.

*2-(2,4-Diacetoxyphenyl)-1,4-diacetoxynaphthalene (3,* OAc instead of OH). On reductive acetylation ($Ac_2O$, Zn, traces of pyridine) the above crude condensation product gave the acetate of *3* in a quantitative yield. M.p. 155 – 156° (EtOH). (Found: C 65.9; H 4.8. Calc. for $C_{24}H_{20}O_8$: C 66.1; H 4.6. Mw = 436). MS, $m/e = 436$ ($M^{+\cdot}$). UV (ethanol) $\lambda_{max}$ (nm)/log $\varepsilon$ = 242/4.60; 283/3.92. The UV spectrum was very similar to that of 2-phenylnaphthalene.[13]

*2-(2,4-Dimethoxyphenyl)-1,4-dimethoxynaphthalene (3,* OMe instead of OH). The phenol *3* was methylated with excess dimethyl sulphate and alkali. Needles m.p. 120 – 121° (EtOH). (Found: C 73.9; H 6.2. Calc. for $C_{20}H_{20}O_4$: C 74.1; H 6.2. Mw = 324). MS, $m/e$ = 324 ($M^{+\cdot}$, base peak). NMR ($CDCl_3$), $\delta$ (ppm) = 3.52, 3.68, 3.75, and 3.86 (12 H, four $-OCH_3$); 6.42 – 7.86 (3 H, complex multiplets, ArH *ortho* to $-OCH_3$); 7.20 – 7.60 (3 H, complex multiplets, ArH); 8.05 – 8.35 (complex multiplets, 2 H, ArH).

*5,9-Diacetoxybenzo[b]naphtho[2.1-d]furan (6,* OAc instead of OH). A solution of naphthoquinone (3.2 g) and resorcinol (3.3 g) in acetic acid (10 ml) was heated to boiling. Addition of sulphuric acid (2 M, 1 ml) started a strongly exothermal reaction. A deep brown colour developed which faded within a couple of minutes. A sample withdrawn immediately after addition of acid was diluted with ethanol and the resulting solution displayed the typical absorption maximum of the quinone *4* at 460 nm. After refluxing for 1 h the mixture was poured into water (0.5 l). The precipitate was collected and washed with water (1 l). The product (4.4 g) was acetylated ($Ac_2O$, pyridine). From the hot reaction mixture 0.1 g of crystals separated (filtrate = A). The MS of the collected acetate indicated that it had the structure *7* (OAc instead of OH) or isomer ($m/e = 474$ ($M^{+\cdot}$); 432; 390 (base peak). (Calc. for $C_{30}H_{18}O_5$: **Mw = 474**)). After cooling the filtrate A deposited the diacetate of compound *6*. Colourless needles (3.5 g, 60 %). M.p. 202 – 204° (HOAc). (Found: C 71.7; H 4.2. Calc. for $C_{20}H_{14}O_5$: C 71.8; H 4.2.) MS: $m/e = 334$ ($M^{+\cdot}$); 292; 250 (base peak). UV, see Fig. 2. The mother liquors were poured into water and the solid collected was dissolved in the smallest possible amount of ethanol. After some

days the product that had separated (0.35 g) was recrystallized from acetic acid. This product was identical (MS, m.p.) with the acetate of compound *8* (see below).

In a similar experiment the reaction mixture was directly acetylated and filtered while hot to give the acetate of compound *7* or isomer (2 %). The filtrate was poured into water. The solid was collected and chromatographed on silica gel. Methylene chloride eluted the acetate of compound *6* (66 %) and chloroform/methylene chloride (1/3) eluted the acetate of compound *8* (17 %).

*5,9-Dihydroxybenzonaphthofuran (6).* The diacetate was refluxed with acidified ($H_2SO_4$) aqueous methanol. M.p. 210 – 211° (dilute ethanol). (Found: C 76.8; H 4.0. Calc. for $C_{16}H_{10}O_3$: C 76.8; H 4.0. Mw = 250). MS, *m/e* = 250 ($M^{+\cdot}$, base peak); 222 ($M^{+\cdot} - CO$, metastable peak at *m/e* = 197.3, calc. for 250 – 222: *m/e* = 197.1); 221; 164; 125 ($M^{2+}$). Colour reaction with sulphuric acid, intense red-violet.

*5,9-Dimethoxybenzonaphthofuran* (*6*, OMe instead of OH). The phenol *6* was methylated ($Me_2SO_4$, NaOH). M.p. 111 – 111.5° (ethanol). (Found: C 77.8; H 5.1. Calc. for $C_{18}H_{14}O_3$: C 77.6; H 5.1. Mw = 278). MS, *m/e* = 278 ($M^{+\cdot}$, base peak). NMR ($CDCl_3$), $\delta$ (ppm) = 3.80 and 4.94 (6 H, two $-OCH_3$); 6.87 ($H_8$, quartet, $J_{7-8} = 8.5$ cps, $J_{8-10} = 2.5$ cps); 7.01 ($H_6$, singlet); 7.09 ($H_{10}$, doublet, $J_{8-10} = 2.5$ cps); 7.64 ($H_7$, doublet, $J_{7-8} = 8.5$ cps); 7.4 – 7.8 ($H_2$ and $H_3$, complex multiplets); 8.15 – 8.40 ($H_1$ and $H_4$, complex multiplets).

*6-(2,4-Dihydroxyphenyl)-5,9-dihydroxybenzonaphthofuran (8).* To a boiling solution of resorcinol (5.0 g) in acetic acid (50 ml) containing sulphuric acid (2 M, 2 ml) the quinone *4* (2.7 g) was added in portions. After each addition a deep brown-red colour developed which soon faded. After boiling for 10 min the solution was poured into water and the precipitate was collected. Yield: 3.2 g, 90 %. M.p. after sublimation 275 – 278° (Dec., evacuated capillary). (Found: C 74.3; H 3.8. Calc. for $C_{22}H_{14}O_5$: C 73.7; H 3.9. Mw = 358). MS, *m/e* = 358 ($M^{+\cdot}$, base peak); 249.

*6-(2,3-Diacetoxyphenyl)-5,9-diacetoxybenzonaphthofuran* (*8*, OAc instead of OH) was obtained from the preceding phenol. Prisms m.p. 201 – 202° (HOAc). (Found: C 68.4; H 4.2. Calc. for $C_{30}H_{22}O_9$: C 68.4; H 4.2. Mw = 526). MS, *m/e* 526 ($M^{+\cdot}$). UV (ethanol): $\lambda_{max}$ (nm)/log $\varepsilon$ = 263/4.81; 290/4.33; 300/4.28; 329/3.62; 344/3.66.

*6-(2,4-Dimethoxyphenyl)-5,9-dimethoxybenzonaphthofuran* (*8* OMe instead of OH) was obtained by methylation of the phenol *7*, in the usual way. Prisms m.p. 170 – 171° (HOAc). (Found: C 75.2; H 5.4. Calc. for $C_{26}H_{22}O_5$. C 75.3; H 5.4. Mw = 414). MS, *m/e* = 414 ($M^{+\cdot}$, base peak). NMR ($CDCl_3$): $\delta$ (ppm) = 3.56, 3.61, 3.73, and 3.82 (12 H, four $-OCH_3$ groups); 6.50 – 7.71 (8 H, complex multiplets, aromatic H); 8.02 – 8.38 (2 H, complex multiplets, aromatic H). The singlet at $\delta$ = 7.02 ppm observed in the spectra of the 5-methoxybenzonaphthofurans described here and arising from $H_6$ was not present in this spectrum.

*3,12-Dihydroxynaphtho[1,2-b:4,3-b']bisbenzofuran (9).* The phenol (*7*) (3 g) was refluxed with constant boiling hydrobromic acid (50 ml) and acetic acid (20 ml) for 60 h under nitrogen. The product (2.7 g) was sublimed (270°/0.1 mm) and did not melt below 360°. (Found: C 77.9; H 3.5. Calc. for $C_{22}H_{12}O_4$: C 77.6; H 3.6. Mw = 340). MS, *m/e* = 340 ($M^{+\cdot}$, base peak). NMR (DMSO $d_6$), $\delta$ (ppm) = 7.19 ($H_2$ and $H_{13}$, quartet, $J_{2-1} = 8.5$ cps, $J_{2-4} = 2.0$ cps); 7.31 ($H_4$ and $H_{11}$, doublet, $J_{2-1} = 2.0$ cps); 7.51 – 7.74 ($H_7$ and $H_8$, quartet); 8.28 ($H_1$ and $H_4$, doublet, $J_{1-2} = 8.5$ cps); 8.21 – 8.45 ($H_6$ and $H_9$, quartet); 10.10 (two phenolic H; singlet).

*3,12-Diacetoxynaphthobisbenzofuran* (*9*, OAc instead of OH) was obtained from the phenol *8*. M.p. 261 – 262° (pyridine). (Found: C 73.9; H 3.6. Calc. for $C_{16}H_{16}O_6$ = C 73.6; H 3.8. Mw = 424). MS, *m/e* = 424 ($M^{+\cdot}$). UV (ethanol), $\lambda_{max}$ (nm)/log $\varepsilon$ = 281/4.84; 347/3.82; 365/3.90. Absolute intensities slightly uncertain due to low solubility.

*3,12-Dimethoxynaphthobisbenzofuran* (*9* OMe instead of OH). The methylated phenol *9* melted at 236 – 237° (pyridine). (Found: C 78.3; H 4.3. Calc. fo $C_{24}H_{16}O_4$: C 78.3; H 4.4. Mw = 368). MS, *m/e* = 368 ($M^{+\cdot}$, base peak).

*2-(2,3,4-Trihydroxyphenyl)-1,4-naphthoquinone (10).* Naphthoquinone and pyrogallol were treated at 20° as above. A brown-black material separated in 80 % yield which was shown by MS to consist of a 4/1 mixture of quinone *10* and the corresponding hydroquinone. Recrystallization from acetic acid containing benzoquinone gave the deep brown-red quinone *10*, which undergoes a phase transition at 129 – 130° and finally melts at 172 – 173° (Dec., evacuated capillary). (Found: C 67.8; H 3.6. Calc. for $C_{16}H_{10}O_5$: C 68.1; H 3.7. Mw = 282). MS, *m/e* = 282 ($M^{+\cdot}$, base peak), 266, 265, 244, 237, 226, 197,

104, 76. UV (ethanol), $\lambda_{max}$ (nm)/log $\varepsilon$ = 248/4.26; 327/3.74; 454/3.42. Colour reaction with sulphuric acid, olive green.

*2-(2,3,4-Triacetoxyphenyl)-1,4-diacetoxynaphthalene* was obtained from the quinone *10* ($Ac_2O$, Zn dust, trace of pyridine). M.p. 143 – 145° (HOAc). (Found: C 63.3; H 4.6. Calc. for $C_{26}H_{22}O_{16}$: C 63.1; H 4.5. Mw = 494). MS, *m/e* = 494 (M+·).

*2-(2,3,4-Trimethoxyphenyl)-1,4-dimethoxynaphthalene.* The preceding acetate was saponified (MeOH, trace $H_2SO_4$ under $N_2$, reflux 2 h) and after neutralization of the solution (NaOAc) it was methylated ($Me_2SO_4$, NaOH) as above. The product was distilled at reduced pressure and recrystallized from acetic acid. M.p. 117 – 118°. (Found: C 70.8; H 6.2. Calc. for $C_{21}H_{22}O_5$: C 71.2; H 6.2. Mw = 354). MS, *m/e* = 354 (M+·, base peak). NMR ($CDCl_3$), $\delta$ (ppm) = 3.56; 3.71; 3.81; 3.88, and 3.91 (15 H of 5 $-OCH_3$ groups); 6.66 (1 H, doublet, position 3 of phenyl group, $J_{2-3}$ = 8.8 cps); 6.76 (1 H, position 3 of the naphthyl group); 7.11 (1 H, doublet, position 2 of the phenyl group, $J_{2-3}$ = 8.8 cps); 7.32 – 7.58 (2 H, positions 6 and 7 of the naphthyl group); 8.03 – 8.37 (2 H, positions 5 and 8 of the naphthyl group).

*5,9,10-Triacetoxybenzo[b]naphtho[2,1-d]furan* (*12*, OAc instead of OH). Naphthoquinone (6.3 g) and pyrogallol (7.6 g) were refluxed with a mixture of acetic acid and sulphuric acid. The phenolic product obtained on acetylation as described above gave three acetates: (a) A sparingly soluble triacetate (0.26 g) [probably the triacetate of the pyrogallol analogue of compound *7* as judged by its MS, *m/e* = 532 (M+·) (calc. for $C_{32}H_{20}O_8$: Mw = 532)]. (b) The triacetate of compound *12* (5.3 g, 34 %). M.p. 174 – 175°, resolidifying and finally melting at 191 – 193° (HOAc). (Found: C 67.4; H 4.1. Calc. for $C_{22}H_{10}O_6$: C 67.3; H 4.1. Mw = 392). MS, *m/e* = 392 (M+·); 350; 308; 266. UV (ethanol). $\lambda_{max}$ (nm)/log $\varepsilon$ = 245/4.55, 254/4.66; 262/4.90; 295/4.26; 326/3.76; 334/4.48; 3.41/3.87. This spectrum is very similar to that of α-brazan [12] and to that of the diacetate of compound *6*. (c) The hexaacetate of the pyrogallol analogue of compound *8* ((*m/e* = 644 (M+·) and peaks corresponding to successive losses of 6 $CH_2CO$ groups (calc. for $C_{32}H_{26}O_{13}$: Mw = 644)].

*5,9,10-Trihydroxybenzonaphthofuran (12)* was obtained from the acetate ($MeOH/H_2O$, trace $H_2SO_4$, reflux 2 h). M.p. 267 – 269° after sublimation (evacuated capillary). (Found: C 72.3; H 3.7. Calc. for $C_{16}H_{10}O_4$: C 72.2; H 3.8. Mw = 266). MS, *m/e* = 266 (M+·). Colour reaction sulphuric acid, red-violet.

*5,9,10-Trimethoxybenzonaphthofuran* (*12*, OMe instead of OH). M.p. 119.5 – 120° (EtOH). (Found: C 74.0; H 5.2. Calc. for $C_{19}H_{16}O_4$: C 74.0; H 5.2. Mw = 308). MS, *m/e* = 308 (M+·). NMR ($CDCl_3$), $\delta$ (ppm) = 3.89, 3.96, and 4.25 (9 H, three $-OCH_3$ groups); 6.85 ($H_8$, doublet, $J_{7-8}$ = 8.5 cps); 7.00 ($H_6$ singlet); 7.34 ($H_7$, doublet, $J_{7-8}$ = 8.5 cps); 7.40 – 7.70 ($H_3$ and $H_7$); 8.28 – 8.42 ($H_1$ and $H_4$).

*2-(2,5-Dihydroxy-4-methoxyphenyl)-1,4-naphthoquinone (11).* 1,4-Naphthoquinone (3.2 g) and methoxyhydroquinone (1.7 g) were treated as above at 20°. After recrystallization from ethanol reddish brown prisms (2.0 g) were obtained. M.p. 230 – 233° (Dec., evacuated capillary). (Found: C 68.9; H 4.0. Calc. for $C_{17}H_{12}O_5$: C 68.9; H 4.1. Mw = 296). MS, *m/e* = 296 (M+·, base peak); 281, 279; 268; 253; 225; 211; 104; 76; 69. UV (ethanol), $\lambda_{max}$ (nm)/log $\varepsilon$ = 246/4.30; 302/4.11/ 503/3.32. Colour reaction with sulphuric acid, green.

*2-(2,5-Diacetoxy-4-methoxyphenyl)-1,4-diacetoxynaphthalene.* Needles from acetic acid. M.p. 160 – 161° (HOAc). (Found: C 64.5; H 4.7. Calc. for $C_{25}H_{22}O_9$: C 64.4; H 4.8).

*2-(2,4,5-Trimethoxyphenyl)-1,4-dimethoxynaphthalene* was obtained from the quinone *11* by reduction with sodium dithionite in methanol. After filtering, the phenol solution was treated directly with dimethyl sulphate and alkali. M.p. 99 – 101° (ethanol). (Found: C 70.6; H 6.2. Calc. for $C_{21}H_{22}O_5$: C 71.3; H 6.3).

*5,8-Diacetoxy-9-methoxybenzo[b]naphtho[2,1-d]furan* (*13*, OAc instead of OH). Naphthoquinone (7.9 g) and methoxyhydroquinone (10.5 g) were refluxed in acetic acid/sulphuric acid, worked up and acetylated as described above. Three products were obtained: (a) A diacetate in low yield [*m/e* = 504 (M+·). Calc. for $C_{34}H_{26}O_{13}$: Mw = 504] probably corresponding to the acetate of compound *7*. (b) A tetraacetate in low yield [*m/e* = 586 (M+·). Calc. for $C_{32}H_{26}O_{11}$: Mw = 586) corresponding to the methoxyhydroquinone analogue of compound *8*. (c) The diacetate of compound *13* (5.0 g, 28 %). Needles m.p. 178 – 179° (HOAc). (Found: C 69.1; H 4.4. Calc. for $C_{21}H_{16}O_6$: C 69.2; H 4.4. Mw = 364). MS, *m/e* = 364 (M+·); 322; 280 (base peak); 265.

*5,8-Dihydroxy-9-methoxybenzonaphthofuran* (*13*) was obtained from the acetate. M.p. 226–227°. (Found: C 72.8; H 4.3. Calc. for $C_{17}H_{12}O_4$: C 72.8; H 4.3. Mw = 280). MS, *m/e* = 280 (M+·, base peak); 265.

*5,8,9-Trimethoxybenzonaphthofuran* (*13*, OMe instead of OH) was obtained from the phenol *13*. M.p. 142–143° (EtOH). (Found: C 74.2; H 5.3. Calc. for $C_{21}H_{16}O_6$: C 74.0; H 5.2). NMR ($CDCl_3$), $\delta$ (ppm) = 3.81, 3.84, and 3.86 (9 H, 3 $-OCH_3$ groups); 6.82 ($H_7$ or $H_{10}$, singlet); 6.93 ($H_{10}$ or $H_7$, singlet); 7.02 ($H_6$, singlet); 7.30–7.60 ($H_2$ and $H_3$); 8.05–8.30 ($H_1$ and $H_4$).

*Dimethoxydibenzotetraphenylenotetrafuran* (*14* or isomer). The quinone *11* (1.0 g) was dissolved in a benzenesulphonic acid melt at 60°. From the intensely green solution a product soon precipitated. After 10 min ethanol was added and the solid collected by centrifugation. After washing with ethanol and pyridine the product (0.4 g, 40 %) was sublimed (400°/0.01 mm) to give a slightly yellow product, no m.p. below 360°. (Found: C 78.6; H 3.2. Calc. for $C_{34}H_{16}O_6$: C 78.5; H 3.1. Mw = 520). MS, *m/e* = 520 (M+·, base peak); 505; 490; 260.0 ($M^{2+}$); 252.5; 245. This compound exhibits a greenish yellow fluorescence in UV light.

*2-(4-Methoxybenzoquinonyl)-1,4-naphthoquinone* (*15*). 2-(2,5-Dihydroxy-4-methoxyphenyl)-1,4-naphthoquinone and 2-(2,4,5-trimethoxyphenyl)-1,4-naphthoquinone were treated with conc. nitric acid. As soon as the reaction mixtures turned yellow, water was added. The products were recrystallized from $Ac_2O$. Yellow needles charring at 326–330°. The IR and MS of the two products were identical. The substance could be sublimed under reduced pressure. (Found: C 69.2; H 3.4. Calc. for $C_{17}H_{10}O_5$: C 69.4; H 3.4. Mw = 294). MS, *m/e* = 294 (M+·, base peak).

*2-(2,4,5-Trimethoxyphenyl)-1,4-naphthoquinone* (*11*, OMe instead of OH). Naphthoquinone (3.2 g) in acetic acid (15 ml) was mixed with a solution of hydroxyhydroquinone trimethyl ether (1.7 g) in acetic acid (5 ml) and sulphuric acid (2 M in $H_2O$, 10 ml) was added. After 8 h the product was collected. Yield: 90 %. Blue dimorphous needles from ethanol. M.p. 168–169° and 183–184°. (Found: C 70.0; H 4.9. Calc. for $C_{19}H_{14}O_4$: C 70.3; H 5.0.) UV (ethanol), $\lambda_{max}$ (nm)/log $\varepsilon$ = 246/4.49; 294/4.24; 468/3.18. Colour reaction with sulphuric acid, green.

*2-(2,4-Dimethoxyphenyl)-1,4-naphthoquinone* (*4*, OMe instead of OH). Naphthoquinone (3.2 g) and resorcinol dimethyl ether (4 ml) in acetic acid (30 ml) were treated with sulphuric acid (2 M, 1.0 ml) in water (15 ml). After 8 h the red product (1.0 g, 36 %) was collected. Recrystallization and sublimation gave bright red needles. M.p. 160–160.5°. (Found: C 73.6; H 4.8. Calc. for $C_{18}H_{14}O_4$: C 73.5; H 4.8). UV (ethanol), $\lambda_{max}$ (nm)/log $\varepsilon$ = 246/4.37; 252/4.37; 329/3.65; 425/3.45. Colour reaction with sulphuric acid, green.

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