# Syntheses of the Naturally Occurring Naphtho[2,3-*b*]pyran-5,10-quinones α-Caryopterone, Dihydro-α-caryopterone, and *O*-Methyldihydro-α-caryopterone [1]

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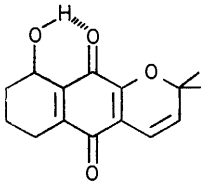
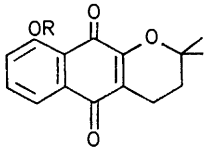
The title compounds have been prepared by appropriate alkylation of 3-hydroxy-5-methoxy-1,4-naphthoquinone, obtained from the adduct (6) derived by addition of 1-methoxycyclohexa-1,3-diene (4) to 2-methoxy-1,4-benzoquinone (5).

SEVERAL prenyljuglones have recently been discovered in nature. These include α-caryopterone (1),[2] dihydro-α-caryopterone (2),[3] and the *O*-methyl derivative of the latter, 9-methoxy-α-lapachone (3).[3] We describe here the synthesis of these three compounds from 3-hydroxy-5-methoxynaphthoquinone (10), conveniently synthesised by regiospecific addition of 1-methoxycyclohexa-1,3-diene (4) to 2-methoxy-1,4-benzoquinone (5).

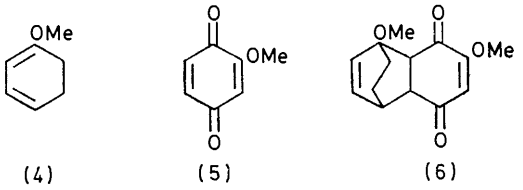


(1)

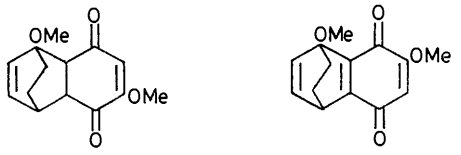


(2) R = H
(3) R = Me

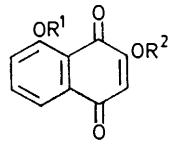
A Diels–Alder reaction between the diene (4) [4] and the quinone (5) [5] gave the adduct (6) in 60% yield; none of the alternative adduct (7) was detected. This regiospecificity is in accord with the expectation that the powerfully electron-donating methoxy-substituents should play a dominant role in determining the favoured transition state.[1] Structure (6) was assigned to the adduct since it could be converted into the known [6] 3,5-diacetoxy-1,4-naphthoquinone. This was accomplished by enolisation of the adduct (6) with potassium t-butoxide in tetrahydrofuran followed by oxidation of the resulting crude quinol to the quinone (8). This was pyrolysed with loss of ethylene to form the naphthoquinone (9). The quinonoid methoxy-group of this compound was hydrolysed by treatment with aqueous base; the aromatic methoxy-group was removed from the product (10) with boron tribromide and the derived dihydroxy-compound (11) was acetylated with pyridine and acetic anhydride. The m.p. (136°) of the diacetate showed it to be 3,5-diacetoxy-1,4-naphthoquinone (12) (lit.,[6] m.p. 137°) rather than its 2,5-isomer (lit.,[6] m.p. 152°).



(4) (5) (6)



(7) (8)



(9) $R^1 = R^2 = Me$
(10) $R^1 = Me, R^2 = H$
(11) $R^1 = R^2 = H$
(12) $R^1 = R^2 = COMe$
(18) $R^1 = Me, R^2 = COMe$

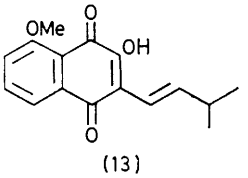
Two routes were established to the prenylated quinones from 3-hydroxy-5-methoxy-1,4-naphthoquinone (10); one afforded α-caryopterone and the other the dihydro-analogues (2) and (3). In the former case, the quinone (10) was subjected to a Hooker reaction with isovaleraldehyde in acetic acid. The product (13) was oxidatively cyclised by stirring at room temperature with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in benzene, from which the naphthopyranquinone (14)

[1] Preliminary communication, R. G. F. Giles and G. H. P. Roos, *Tetrahedron Letters*, 1975, 4159.
[2] T. Matsumoto, C. Mayer, and C. H. Eugster, *Helv. Chim. Acta*, 1969, **52**, 808.
[3] H. Inouye, T. Okuda, and T. Hayashi, *Chem. and Pharm. Bull. (Japan)*, 1975, **23**, 384.
[4] A. J. Birch and K. P. Dastur, *J.C.S. Perkin I*, 1973, 1650.
[5] J. A. D. Jeffreys, *J. Chem. Soc.*, 1959, 2153.
[6] R. H. Thomson, *J. Org. Chem.*, 1948, **13**, 870.

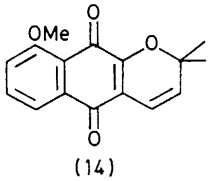
and the naphthofuranquinone (15) could be isolated in yields of 47 and 8%, respectively. In addition, a deep purple product, thought to be the *ortho*-quinone (16) (28%), was obtained but not characterised because of its ready conversion into the quinone (14) on warming with ethanol containing concentrated hydrochloric acid. The formation of compounds (14) and (16) can be rationalised in terms of cyclisation of the intermediate (17);[7] ring closure of (13) followed by oxidation would afford the product (15). When treated with boron tribromide in methylene chloride, the quinone (14) underwent demethylation to yield α-caryopterone, identical with the natural product.

The route to the lapachones involved initial acetylation of 3-hydroxy-5-methoxy-1,4-naphthoquinone (10). The derived acetate (18) was alkylated at the free quinonoid position with 4-methylpent-3-enoic acid in the presence of silver nitrate and ammonium peroxodisulphate to afford the prenylated product (19), which, upon hydrolysis with aqueous sodium carbonate, gave the methoxylapachol (20), isomeric with the product (13) of the Hooker reaction.

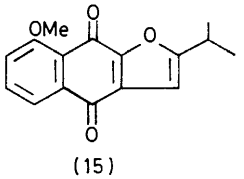
Cyclisation of the quinone (20) with hydrochloric acid in acetic acid yielded a mixture of the α- and β-methoxylapachones, (3) and (21), respectively. These were readily separable by column chromatography, and could be distinguished by their different colours and i.r. spectra. The former was identical with a sample of naturally occurring 9-methoxy-α-lapachone,[3] and the



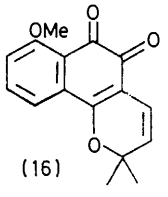
(13)



(14)



(15)



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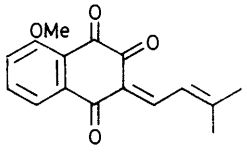
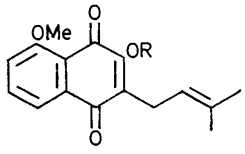
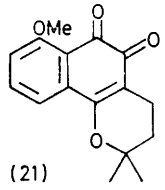


(17)

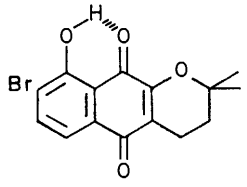
physical properties of and spectral data for the latter corresponded with those reported for *O*-methyldihydro-β-caryopterone, obtained by Eugster[2] by reduction, treatment with concentrated sulphuric acid, and methylation of naturally occurring α-caryopterone. This β-form (21) was readily isomerised to the α-lapachone (3) with concentrated hydrochloric acid in ethanol. Interestingly, attempted demethylation of the methyl ether (3) with boron trichloride effected its reverse transformation into the β-form (21). However, treatment of the methyl ether (3) with boron tribromide in methylene chloride at room temperature gave rise to dihydro-α-caryopterone (2), identical with the natural product.[3]



(19) R = COMe
(20) R = H



(21)



(22)

Under more vigorous conditions with an excess of boron tribromide, a second product (22), in addition to dihydro-α-caryopterone, was isolated in which the aromatic nucleus had undergone bromination. The position of bromination was indicated by its n.m.r. spectrum, which included two aromatic doublets at τ 2.16 and 2.53 (*J* 8 Hz).

We were unable to convert 9-methoxy-α-lapachone (3) into *O*-methyl-α-caryopterone by heating under reflux in dioxan in the presence of DDQ, a procedure which has been successful[8] for the conversion of α-lapachone to dehydro-α-lapachone. However, treatment of the methoxylapachol (20) with DDQ at room temperature in benzene afforded a mixture of quinones (14) and (16), which were separated. Crude (16) was converted into compound (14) wih ethanolic hydrochloric acid as before. This oxidative cyclisation presumably proceeds *via* the same intermediate (17) as thought to be implicated in the oxidation of the quinone (20).

## EXPERIMENTAL

Unless otherwise stated i.r. spectra were measured for solutions in carbon tetrachloride and n.m.r. spectra for solutions in [$^2$H]chloroform with tetramethylsilane as internal reference. N.m.r. spectra were recorded at 100 MHz with a Varian XL-100 spectrometer. Unless otherwise stated chromatography was carried out on dry columns with Merck Kieselgel 60 (70—230 mesh). Light petroleum refers to the fraction of b.p. 60—80°.

1,4,4a,8a-*Tetrahydro*-1,7-*dimethoxy*-1,4-*ethanonaphthalene*-5,8-*dione* (6).—The diene (4) (6.4 g) (containing *ca.* 20% of

[7] K. H. Dudley and R. W. Chiang, *J. Org. Chem.*, 1969, **34**, 120.

[8] A. R. Burnett and R. H. Thomson, *J. Chem. Soc.* (*C*), 1967 1261.

the isomeric 1,4-diene,[4] as determined by n.m.r. spectroscopy) was heated under reflux in benzene (100 ml) containing the methoxy-1,4-benzoquinone (5) (3 g) for 1.5 h, at which stage all the quinone had been consumed. The solvent was evaporated off and the residue chromatographed over a short dry column of neutral alumina (Merck) with benzene as eluant, to give the *product*, m.p. 117—119° (from benzene–light petroleum) (3.2 g; 60% based on quinone) (Found: C, 67.7; H, 6.6. $C_{14}H_{16}O_4$ requires C, 67.8; H, 6.4%), $\nu_{max.}$ (Nujol) 1 691, 1 650, and 1 612 $cm^{-1}$, $\tau$ 3.83 (1 H, d, *J* 2 Hz, 2-H), 3.87 (1 H, s, 3-H), 4.12 (1 H, s, 6-H), 6.27 (3 H, s, $OCH_3$), 6.55 (3 H, s, $OCH_3$), 6.67 (1 H, d, *J* 8 Hz, 8a-H), 6.88 (1 H, m, 4-H), 6.96 (1 H, dd, *J* 8 and 3 Hz, 4a-H), and 7.9—8.5 (4 H, m, $CH_2{\cdot}CH_2$).

1,4-*Dihydro*-1,7-*dimethoxy*-1,4-*ethanonaphthalene*-5,8-*quinone* (8).—The adduct (6) (1.0 g) in dry tetrahydrofuran (40 ml) was stirred with an excess of potassium t-butoxide (1.2 g) for 40 min. Water was added, followed by dilute hydrochloric acid until the solution was weakly acidic. The solution was extracted with ether; the extract was dried ($Na_2SO_4$), and silver(I) oxide (3 g) was added. The mixture was stirred for 3.5 h, filtered, and evaporated to yield the orange *quinone*, m.p. 118—118.5° (from benzene–light petroleum) (1.0 g, 100%) (Found: C, 68.4; H, 5.9. $C_{14}H_{14}O_4$ requires C, 68.3; H, 5.7%), $\nu_{max.}$ (Nujol) 1 671, 1 640, 1 611, and 1 579 $cm^{-1}$, $\tau$ 3.43 (1 H, dd, *J* 8 and 1 Hz, 2-H), 3.67 (1 H, dd, *J* 8 and 6 Hz, 3-H), 4.23 (1 H, s, quinone H), 5.7 (1 H, m, bridgehead H), 6.19 (3 H, s, $OCH_3$), 6.38 (3 H, s, $OCH_3$), and 8.0—8.8 (4 H, m, $CH_2{\cdot}CH_2$).

2,8-*Dimethoxy*-1,4-*naphthoquinone* (9).—The quinone (8) (0.31 g), was heated at 120 °C and 8 mmHg under which conditions bubbling occurred as ethylene was eliminated. When bubbling ceased, sublimation at 140 °C (bath) and 0.5 mmHg afforded the light yellow product (0.27 g, 98%), m.p. 202—202.5° (from methanol) (lit.,[9] 195°) (Found: C, 66.0; H, 4.6. Calc. for $C_{12}H_{10}O_4$: C, 66.1; H, 4.6%), $\nu_{max.}$ (Nujol) 1 674, 1 642, 1 612, and 1 589 $cm^{-1}$; $\tau$ 2.2—2.5 (2 H, m, 5- and 6-H), 2.75 (1 H, dd, *J* 2 and 7 Hz, 7-H), 3.93 (1 H, s, quinonoid H), 6.00 (3 H, s, $OCH_3$), and 6.12 (3 H, s, $OCH_3$).

2-*Hydroxy*-8-*methoxy*-1,4-*naphthoquinone* (10).—The naphthoquinone (9) (1.00 g) was stirred with aqueous 1% base (20 ml) until it had dissolved. The solution was washed with ether and acidified with dilute hydrochloric acid. This was extracted with chloroform, and the extract was dried and evaporated to give the known [10,11] quinone, m.p. 209—211° (decomp.) [lit.,[11] 211° (decomp.)] (0.86 g, 92%), $\tau$ 2.18—2.40 (2 H, m, 5- and 6-H), 2.73 (1 H, dd, *J* 2 and 7 Hz, 7-H), 3.72 (1 H, s, quinonoid H), and 5.95 (3 H, s, $OCH_3$).

2,8-*Diacetoxy*-1,4-*naphthoquinone* (12).—The quinone (10) (0.17 g) in dry methylene chloride was treated at −78 °C with an excess of boron tribromide (1 g) in the same solvent. The solution was allowed to warm to room temperature and then hydrolysed with water, extracted with ether, and re-extracted with aqueous potassium hydroxide. This aqueous layer was finally acidified and extracted with ether, and the extract was dried and evaporated. The crude dihydroxyquinone so formed (0.15 g) was acetylated (pyridine–acetic anhydride) to yield the diacetate, which was purified over a short silica gel column (ethyl acetate–chloroform, 4 : 1). This gave pale yellow crystals, m.p. 136° (lit.,[6] 137°) (0.09 g, 42%), $\tau$ 1.95 (1 H, d, *J* 8 Hz, 5-H), 2.25 (1 H, t, *J* 8 Hz, 6-H), 2.63 (1 H, d, *J* 8 Hz, 7-H), 3.25 (1 H, s, quinonoid H), 7.56 (3 H, s, $COCH_3$), and 7.62 (3 H, s, $COCH_3$).

3-*Hydroxy*-5-*methoxy*-2-(3-*methylbut*-1-*enyl*)-1,4-*naphthoquinone* (13).—The quinone (10) (0.40 g) in hot (80 °C) glacial acetic acid (10 ml) was treated with concentrated hydrochloric acid (1 ml), followed immediately by isovaleraldehyde (1.25 ml). The dark solution was heated under gentle reflux for 1 h, then thrown into water (200 ml) and extracted with chloroform. The organic layer was dried and evaporated and the residue chromatographed over a short silica gel column with methylene chloride as eluant. This yielded the orange *product*, which was sublimed at 150 °C (bath) and 1.2 mmHg; m.p. 179.5—180° (0.45 g, 86%) (Found: C, 70.7; H, 6.0. $C_{16}H_{16}O_4$ requires C, 70.6; H, 5.9%), $\nu_{max.}$ 3 320, 1 736, 1 658, 1 618, and 1 584 $cm^{-1}$, $\tau$ 2.14—2.44 (2 H, m, 6- and 7-H), 2.79 (1 H, dd, *J* 2 and 8 Hz, 8-H), 3.02 (1 H, dd, *J* 7 and 16 Hz, 2′-H), 3.48 (1 H, d, *J* 16 Hz, 1′-H), 5.98 (3 H, s, $OCH_3$), 7.47 (1 H, octet, *J* 7 Hz, 3′-H), and 8.89 (6 H, d, *J* 7 Hz, $CH_3$).

9-*Methoxy*-2,2-*dimethylnaphtho*[2,3-b]*pyran*-5,10-*quinone* (14) *and* 2-*Isopropyl*-8-*methoxynaphtho*[2,3-b]*furan*-4,9-*quinone* (15).—The quinone (13) (300 mg) in benzene (50 ml) was added to a solution of DDQ (300 mg) in benzene (100 ml). This was stirred at room temperature overnight. The precipitate ($H_2$DDQ) was filtered off and washed with benzene. The solution was evaporated and the residue chromatographed (eluant methylene chloride). A pale yellow band afforded the *naphthofuranquinone* (15), which was sublimed [150 °C (bath) and 2.2 mmHg]; m.p. 157—158.5° (25 mg, 8%) (Found: C, 71.1; H, 5.2. $C_{16}H_{14}O_4$ requires C, 71.1; H, 5.2%), $\nu_{max.}$ 1 726 and 1 668 $cm^{-1}$, $\tau$ 2.10—2.56 (2 H, m, 6- and 7-H), 2.72 (1 H, dd, *J* 2 and 8 Hz, 8-H), 3.49 (1 H, s, 3-H), 5.99 (3 H, s, $OCH_3$), 6.90 (1 H, septet, *J* 7 Hz, $CHMe_2$), and 8.65 (6 H, d, *J* 7 Hz, $CH_3$). An orange-yellow band gave the naphthopyranquinone (14), which was sublimed [150 °C (bath) and 2 mmHg], m.p. 132—134° (140 mg, 47%) (Found: C, 71.1; H, 5.6. $C_{16}H_{14}O_4$ requires C, 71.1; H, 5.2%), $\nu_{max.}$ 1 727, 1 677, 1 650, and 1 636 $cm^{-1}$, $\tau$ 2.18—2.50 (2 H, m, 6- and 7-H), 2.78 (1 H, dd, *J* 2 and 8 Hz, 7-H), 3.39 (1 H, d, *J* 9 Hz, 3-H), 4.35 (1 H, d, *J* 9 Hz, 4-H), 6.01 (3 H, s, $OCH_3$), and 8.46 (6 H, s, $CH_3$). Further fractions afforded a red crystalline material, assumed to be the *ortho*-quinone (16) (85 mg, 28%), which was converted into the quinone (14) with concentrated hydrochloric acid (1 ml) in ethanol (10 ml) on warming on a water-bath.

α-*Caryopterone* (9-*Hydroxy*-2,2-*dimethylnaphtho*[2,3-b]-*pyran*-5,10-*quinone*) (1).—The quinone (14) (300 mg) in methylene chloride (5 ml) was treated at −78 °C with an excess of boron tribromide (500 mg) in methylene chloride (10 ml). Work-up as described before afforded crude material which was chromatographed (methylene chloride). This gave α-*caryopterone* (160 mg, 55%), which was recrystallised from toluene–light petroleum. A sample obtained by p.l.c. with 10% ethyl acetate–light petroleum had m.p. and mixed m.p. 170—172° (decomp.), with darkening at 143° [lit.,[1] 143.5—145° (decomp.)] (Found: C, 70.2; H, 5.0. $C_{15}H_{12}O_4$ requires C, 70.3; H, 4.7%), identical (i.r. and n.m.r. spectra and t.l.c.) with the natural material.

[9] G. R. Birchall and A. H. Rees, *Canad. J. Chem.*, 1974, **52**, 610.

[10] A. C. Baillie and R. H. Thomson, *J. Chem. Soc.* (*C*), 1966, 2184.

[11] J. W. MacLeod and R. H. Thomson, *J. Org. Chem.*, 1960, **25**, 36.

3-*Acetoxy*-5-*methoxy*-2-(3-*methylbut*-2-*enyl*)-1,4-*naphtho*-*quinone* (19).—The quinone (10) (0.96 g) was acetylated with acetic anhydride (5 ml) containing concentrated sulphuric acid (0.2 ml) to give 2-acetoxy-8-methoxy-1,4-naphthoquinone (0.65 g, 53%), $\tau$ 2.2—2.5 (2 H, m, 5- and 6-H), 2.6—2.8 (1 H, m, 7-H), 3.36 (1 H, s, quinonoid H), 6.01 (1 H, s, $OCH_3$), and 7.62 (3 H, s, $COCH_3$). Because of its ready hydrolysis, the crude acetate was alkylated directly with 4-methylpent-3-enoic acid (0.30 g) and silver nitrate (0.30 g) in acetonitrile (12 ml) and water (15 ml), to which was added a solution of ammonium peroxodisulphate (1.2 g) in water (10 ml) at 60—65 °C with vigorous stirring over 1 h. The mixture was neutralised with solid sodium hydrogen carbonate and extracted with ether, and the organic layer was dried and evaporated. The residue was eluted through a short silica gel column with methylene chloride to give the *quinone* (0.65 g, 75%). A sample prepared by p.l.c. with methylene chloride had m.p. 103—104° (Found: C, 68.8; H, 5.9. $C_{18}H_{18}O_5$ requires C, 68.8; H, 5.7%), $\nu_{max.}$ 1 785, 1 727, 1 675, and 1 650 $cm^{-1}$, $\tau$ 2.16—2.50 (2 H, m, 7- and 8-H), 2.66—2.83 (1 H, m, 6-H), 4.92 (1 H, t, *J* 8 Hz, 2′-H), 6.02 (3 H, s, $OCH_3$), 6.76 (2 H, d, *J* 8 Hz, $CH_2$), 7.62 (3 H, s, $COCH_3$), 8.25 (3 H, s, $CH_3$), and 8.32 (3 H, s, $CH_3$).

3-*Hydroxy*-5-*methoxy*-2-(3-*methylbut*-2-*enyl*)-1,4-*naphtho*-*quinone* (20).—The acetate (19) (0.65 g) was heated under gentle reflux with M-sodium carbonate (50 ml) until all material was dissolved. The solution was cooled in ice, acidified with concentrated hydrochloric acid, and extracted with methylene chloride. The organic layer was dried and evaporated and the residue chromatographed over a short silica gel column with methylene chloride. A small quantity of starting material was eluted first, followed by the product (0.25 g, 55% based on starting material consumed). This was sublimed [130 °C (bath) and 1.3 mmHg]; m.p. 155.5—156.5° (Found: C, 70.8; H, 6.1. $C_{16}H_{16}O_4$ requires C, 70.6; H, 5.9%), $\nu_{max.}$ 3 360, 1 728, and 1 653 $cm^{-1}$, $\tau$ 2.1—2.5 (2 H, m, 7- and 8-H), 2.79 (1 H, dd, *J* 2 and 8 Hz, 6-H), 4.79 (1 H, t, *J* 8 Hz, 2′-H), 5.98 (3 H, s, $OCH_3$), 6.72 (2 H, d, *J* 8 Hz, $CH_2$), 8.21 (3 H, s, $CH_3$), and 8.31 (3 H, s, $CH_3$).

O-*Methyldihydro*-α-*caryopterone* (3,4-*Dihydro*-9-*methoxy*-2,2-*dimethylnaphtho*[2,3-b]*pyran*-5,10-*quinone*) (3) *and* 3,4-*Dihydro*-7-*methoxy*-2,2-*dimethylnaphtho*[1,2-b]*pyran*-5,6-*quinone* (21).—The quinone (20) (210 mg) in acetic acid (5 ml) and concentrated hydrochloric acid (0.75 ml) was heated on a water-bath for 75 min. The solution was cooled, water was gradually added, and the whole was extracted with methylene chloride. The organic layer was dried and evaporated, and the residue was chromatographed (methylene chloride) to give starting material (4 mg), followed by the *quinone* (3) (101 mg, 49%), which was sublimed [150—155 °C (bath) and 1.8 mmHg], m.p. and mixed m.p. 165—167° (lit.,[3] 168—169°) (Found: C, 70.5; H, 6.0. $C_{16}H_{16}O_4$ requires C, 70.6; H, 5.9%), $\nu_{max.}$ ($CHCl_3$) 1 671, 1 640, 1 623, and 1 587 $cm^{-1}$, $\tau$ 2.22—2.54 (2 H, m, 6- and 7-H), 2.82 (1 H, dd, *J* 2 and 8 Hz, 8-H), 6.04 (3 H, s, $OCH_3$), 7.43 (2 H, t, *J* 7 Hz, 4-$H_2$), 8.20 (2 H, t, *J* 7 Hz, 3-$H_2$), and 8.59 (6 H, s, $CH_3$). The synthetic and natural materials had the same $R_F$ value on t.l.c. A third band afforded the *ortho*-quinone (21) (100 mg, 49%), m.p. 160—161° (lit.,[2] 162—163°). The i.r. and n.m.r. data are identical with those recorded.[2] The quinone (21) was quantitatively converted into the quinone (3) by treatment with concentrated hydrochloric acid in hot ethanol.

*Dihydro*-α-*caryopterone* (3,4-*Dihydro*-9-*hydroxy*-2,2-*dimethylnaphtho*[2,3-b]*pyran*-5,10-*quinone*) (2).—(*a*) The quinone (3) (30 mg) in dry methylene chloride (10 ml) was treated at −78 °C with boron tribromide (1.5 mol. equiv.) in the same solvent (10 ml). This was allowed to warm to room temperature and was stirred overnight. Water was cautiously added, and the solution extracted with chloroform. The contents of the organic layer were purified by p.l.c. (benzene), affording the *product* (2) (17 mg, 60%), which was sublimed [100—110 °C (bath) and 2.7 mmHg], m.p. 119°, mixed m.p. 119—120° (lit.,[3] 120—122°)(Found: C, 69.45; H, 5.6. $C_{15}H_{14}O_4$ requires C, 69.75; H, 5.45%). The synthetic and natural materials had the same $R_F$ values, and an n.m.r. spectrum consistent with that reported.

(*b*) In an initial experiment designed to afford the above product, the quinone (3) was treated with an excess (3 mol. equiv.) of boron tribromide at room temperature in methylene chloride and the solution was heated under reflux for 20 min. Work-up and p.l.c. as above yielded, in addition to (2), a preponderance of 8-*bromo*-3,4-*dihydro*-9-*hydroxy*-2,2-*dimethylnaphtho*[2,3-b]*pyran*-5,10-*quinone*, which had the higher $R_F$ value. This was sublimed [145—150 °C (bath) and 4 mmHg], m.p. 180—181° (Found: C, 54.0; H, 4.2. $C_{15}H_{13}BrO_4$ requires C, 53.45; H, 3.9%), $\tau$ −2.48 (1 H, s, OH), 2.16 (1 H, d, *J* 8 Hz, 6-H), 2.53 (1 H, d, *J* 8 Hz, 7-H), 7.38 (2 H, t, *J* 7 Hz, 4-$H_2$), 8.18 (2 H, t, *J* 7 Hz, 3-$H_2$), and 8.56 (6 H, s, $CH_3$).

9-*Methoxy*-2,2-*dimethylnaphtho*[2,3-b]*pyran*-5,10-*quinone* (14).—The quinone (20) (175 mg) and DDQ (215 mg) were stirred together in benzene (100 ml) at room temperature for 5 h. The precipitate ($H_2$DDQ) was filtered off and washed with benzene and the solution evaporated. The residue was chromatographed (methylene chloride) to afford starting material (10 mg), followed by the quinone (14) (60 mg), identical with that obtained from compound (13). A final band gave rise to compound (16) which could be converted into the quinone (14) as described earlier.

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