Ebenaceae Extractives. Part 8.† The Structure of Diosquinone and Reactions of Related Quinone Epoxides

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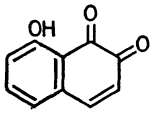
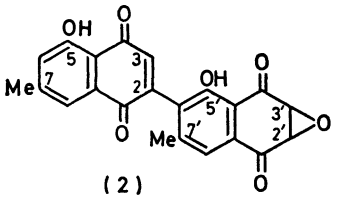
Diosquinone, from *Diospyros tricolor,* is shown to be the naphthoquinonylnaphthoquinone epoxide (2). Juglone epoxides react with chloroform and with ethanol with the formation of chloro- and chlorohydroxy-juglones and of ethoxy- and ethoxyhydroxy-juglones respectively.

THE bark of the West African tree *Diospyros tricolor* Hiern contains an orange pigment, diosquinone, which was originally formulated by Nogueira Prista [1] as the hydroxy-*o*-quinone (1). The failure of attempts [2] to synthesise a compound having this structure led us to re-examine the properties of diosquinone; these show [3] that it is, in fact, the (—)-enantiomer of the diospyrin epoxide (2). Thus, of the more abundant fragment ions in its



(1)



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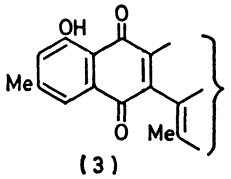

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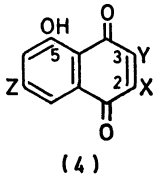
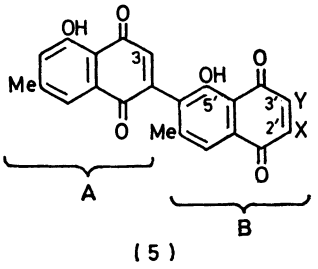


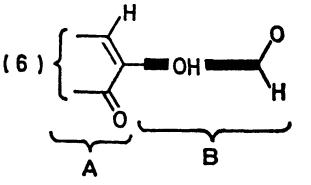
(4)

mass spectrum, those at *m/e* 374 (*i.e.* $M - 16$) and at *m/e* 163, 135, 134, and 106 indicate the presence of the epoxide function and of the part-structure (3),[4] respectively. The u.v.–visible light absorption spectrum closely resembles that of an equimolar mixture of 7-methyljuglone (4; X = Y = H, Z = Me) and 7-methyljuglone 2,3-epoxide, suggesting that diosquinone contains the chromophores of these compounds. Further, because the two conjugated systems do not interact significantly with each other, the C_{11} units appear to be



(5)

orthogonal. As would be expected those protons of diosquinone which are present in the part-structure (3) have chemical shifts which are almost identical with those [5] of the corresponding protons of diosyprin (5; X = Y = H). Similarly the chemical shifts and the coupling constants for the oxiran protons of diosquinone resemble closely those of the corresponding protons of 7-methyljuglone 2,3-epoxide. However the signals for the C-3 methine proton and the C-5′ hydroxy-proton of diosquinone appear as well-defined doublets at 0 °C which show partial coalescence at 50 °C, in contrast with the corresponding signals for diospyrin which are sharp singlets. Now, unlike isodiospyrin,[6] diospyrin is optically inactive and consequently free rotation of its two units, A and B, about the internuclear link must be possible. The two preferred conformations, those in which the units are orthogonal, are enantiomeric and as a result the C-3 methine proton has the same environment in both, as has the C-5′ hydroxy-proton. Because of the non-planarity of the epoxide system this is not the case with diosquinone. Here the two preferred conformations (6) and (7) are not equivalent and give rise to slightly



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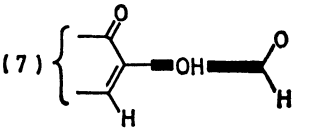


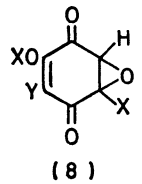
(7)

different chemical shifts for the protons concerned. The rate of interconversion of (6) and (7), even at 50 °C, appears to be relatively slow on the n.m.r. time-scale.

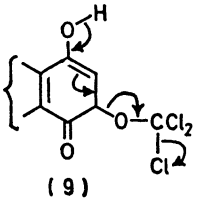
The optical activity of diosquinone establishes that the compound is a true natural product, not merely an artifact. Its chirality is associated with the unsymmetrically substituted quinone epoxide system and, as would be expected, the circular dichroism (c.d.) spectrum of diosquinone resembles that [7] of terreic acid (8; X = H, Y = Me) which contains a similar arrangement. Although several benzo- and naphtho-quinone epoxides are known to be produced by micro-organisms [8] we belive that diosquinone is the first quinone epoxide to be isolated from a higher plant. Diosquinone and the corresponding desoxy-compound, diospyrin, occur to-

† Part 7 is ref. 5.

gether in *Diospyros montana* [4] and it would seem reasonable that the biosynthesis of diosquinone should merely involve the epoxidation of diospyrin. However, we were unable to detect diospyrin in *D. tricolor*, our examination of the chloroform extract of the wood and bark from a young tree yielding only diosindigo A, isodiospyrin, mamegakinone, and diosquinone. We therefore consider that diospyrin is unlikely to be the precursor of diosquinone. Now the quinone epoxide (8; X = Me,



(8)



(9)

Y = OH) is known [9] to be an intermediate in the biosynthesis of the corresponding benzoquinone, fumigatin, and we suggest that, in a similar manner, diosquinone might be the precursor of diospyrin in *Diospyros* spp. It may be biogenetically significant that diosquinone itself can be formed, in principle, by the reaction of the aromatic nucleus of one molecule of 7-methyljuglone 2,3-epoxide with the epoxide ring of another followed by dehydration.

In the course of isolating diosquinone by t.l.c. we obtained traces of two other quinones which are isomeric with it. Both these, like diosquinone itself, undergo fragmentation in the mass spectrometer giving the relatively abundant ions *m/e* 163, 135, 134, and 106, and therefore [4] contain the part-structure (3). We established that the compounds are the hydroxydiospyrins (5; X = OH, Y = H) and (5; X = H, Y = OH) by synthesising them from diospyrin (5; X = Y = H). The latter, on treatment with acetic anhydride and sulphuric acid, underwent a Thiele reaction and the product, after hydrolysis and aerial oxidation, gave a mixture of the two hydroxy-compounds. In each case the position of the hydroxy-group follows from the chemical shift of the C-5′ hydroxy-proton of unit B. Thus the hydroxyquinone, m.p. 223—225°, shows a hydroxy-proton signal at δ 12.52, in excellent agreement with the value (δ 12.52) calculated [5] for 2′-hydroxydiospyrin, while the corresponding signal, at δ 11.24, for the isomer, m.p. 243—246°, establishes that the latter is 3′-hydroxydiospyrin (calculated, δ 11.28). The quinone, m.p. 243—245° (' Quinone II '), of unknown structure which Paris and Prista [10] isolated from *D. tricolor* is presumably 3′-hydroxydiospyrin.

For confirmation of the relationship between diosquinone and diospyrin the interconversion of the two compounds was desirable and we established suitable conditions for the reactions using simple juglone derivatives. Treatment of juglone 2,3-epoxide with a mixture of sodium iodide, zinc dust, sodium acetate, and acetic acid [11] gave mainly juglone and only a small amount of cleavage of the epoxide ring occurred with the formation of the corresponding hydroxyquinones. A similar reaction with diosquinone gave diospyrin and some 3′-hydroxydiospyrin. The oxidation of 7-methyljuglone with sodium perborate [12] afforded the corresponding 2,3-epoxide in good yield provided that the solution was adjusted only to pH 5 with hydrochloric acid during the working-up; when the solution was kept at pH 3—4 for 10 min considerable cleavage of the epoxide ring occurred with the formation of the corresponding chloro- and hydroxy-quinones. The epoxidation of diospyrin in this way gave (±)-diospyrin epoxide and a little 2′-hydroxydiospyrin. The former shows mass and u.v. spectra which are identical with those of diosquinone but the solid-state properties of the two substances differ. The (±)-product is less soluble and has a higher m.p., and its i.r. spectrum is not completely identical with that of diosquinone; it must therefore be a racemic compound and not a racemic mixture.

Among the compounds which we have isolated [4] from a different species of *Diospyros*, *D. montana*, are several which appear to be artefacts derived from the diosquinone which is also present. These are 2′- and 3′-chlorodiospyrin, 3′-chloro-2′-hydroxydiospyrin (5; X = OH, Y = Cl), and a chromenonecarboxylic acid and its ethyl ester. We suggested that the three chlorine-containing compounds might result from reactions involving the chloroform used in the isolation procedure and have now obtained evidence which supports this view. Prolonged boiling in chloroform solution partly converted 7-methyljuglone epoxide into the 3-chloroquinone (4; X = H, Y = Cl, Z = Me), and the 2-chloro-3-hydroxyquinone (4; X = Cl, Y = OH, Z = Me). The orientation of the substituents at C-2 and C-3 in the latter compound follows from the chemical shift (δ 10.91) observed for the C-5 hydroxy-proton which is in excellent agreement with the value (10.90) calculated.[5] The chlorinated compounds clearly originate from the cleavage of the epoxide ring by hydrogen chloride followed by dehydration or oxidation. It seems likely that part of the quinone epoxide is reduced by the chloroform *via* an adduct such as (9) which decomposes as shown to give the parent quinone, phosgene, and hydrogen chloride; more hydrogen chloride results from the reaction of the phosgene with the ethanol present as stabiliser in the chloroform. We did not, however, obtain any evidence of chromenone formation in the reaction of juglone epoxide with boiling ethanol. The products were those expected from the reaction of ethanol with the epoxide ring, followed by dehydration or oxidation, namely 3-ethoxyjuglone (4; X = Z = H, Y = OEt) and 2-ethoxy-3-hydroxyjuglone (4; X = OEt, Y = OH, Z = H). The water produced in the reaction was responsible for the formation of the other products, 2- and 3-hydroxyjuglone, and 2,3-dihydroxyjuglone. We obtained authentic samples of the monohydroxyjuglones by treating juglone 2,3-epoxide with sulphuric acid. The locations of the substituents in the two ethoxyquinones follow from the chemical shifts of their C-5 hydroxy-protons. Although the contributions of ethoxy-groups to such shifts have not been measured we can assume

that they will be similar to those of methoxy-groups, for which the values, measured at 60 MHz,[13] are +0.30 (at C-2) and −0.23 p.p.m. (at C-3). The chemical shifts calculated [5] for the hydroxy-proton shifts of 2- and 3-methoxyjuglone are δ 12.17 and 11.64 respectively; the latter agrees the more closely with the value (11.77) observed for the ethoxyjuglone. The corresponding values calculated for 2-ethoxy-3-hydroxy- and 3-ethoxy-2-hydroxy-juglone are δ 11.34 and 12.05, respectively, of which the former is the closer to that observed (δ 11.20).

EXPERIMENTAL

General instructions are given in Parts 4 [14] and 5.[4] Unless stated otherwise t.l.c. was performed on silica gel G (Merck) which had been washed with 3% aqueous oxalic acid, with chloroform for development. U.v.–visible absorption spectra were measured for solutions in methanol.

Extraction of Diospyros tricolor *Hiern.*—(*a*) A portion (0.27 g) of the crude extract from which diosquinone was originally isolated [10] was separated by t.l.c. (dichloromethane) into (i) *diosquinone* (2) (R_F 0.85) which crystallised from methanol and then from carbon tetrachloride in orange needles (0.16 g), m.p. 200—200.5° (lit.,[10] 198—199°) (Found: *M*, 390.0740. $C_{22}H_{14}O_7$ requires *M*, 390.0739), $\nu_{max.}$ 1 701 (aryl carbonyl C=O), 1 656 (sh), 1 639, and 1 607 cm^{-1} (quinone and H-bonded aryl ketone C=O and C=C), $\lambda_{max.}$ 248 (log ε 4.40) and 375 nm (3.81), $\lambda_{infl.}$ 289 (log ε 3.86) and 422 nm (3.74), δ (0°) 2.28 and 2.44 (each 3 H, s, 7′- and 7-Me), 3.97 and 4.01 (2 H, AB q, *J* 4 Hz, H-3′ and -2′), 6.85 and 6.87 (1 H, d, H-3), 7.13br (1 H, s, H-6), 7.49br (2 H, s, H-8 and -8′), 11.46 and 11.48 (1 H, d, 5′-OH), and 11.84 (1 H, s, 5-OH), $[\alpha]_D^{20}$ −106° (*c* 0.1, $CHCl_3$), c.d. $\lambda_{max.}$($CHCl_3$) 283 (Δε −0.90), 292 (−0.87), 323 (+4.26), and 372 nm (−3.76), $\lambda_{infl.}$ 334 nm (Δε +3.43), *m/e* 392 [11%, $(M + 2H)^{+\cdot}$], 390 (100, $M^{+\cdot}$), 375 [21, $(M - Me)^+$], 374 [43, $(M - O)^{+\cdot}$], 362 [20, $(M - CO)^{+\cdot}$], 361 [28, $(M - CHO)^+$], 345 (20, 374 − CHO), 163 [25, $(C_9H_7O_3)^+$], 135 [40, $(C_8H_7O_2)^+$], 134 [40, $(C_8H_6O_2)^{+\cdot}$], and 106 [64, $(C_7H_6O)^{+\cdot}$]; (ii) *2′-hydroxydiospyrin* (5; X = OH, Y = H) (R_F 0.47) which, after column chromatography on acid-washed silica gel (benzene), crystallised from dichloromethane as orange crystals (1 mg), m.p. 222° (decomp.) (Found: *M*, 390.0735. $C_{22}H_{14}O_7$ requires *M*, 390.0739); and (iii) a trace of *3′-hydroxydiospyrin* (5; X = H, Y = OH) (R_F 0.32) (see below).

(*b*) The finely ground wood and bark (1.26 kg) from the branches of a young tree from the Yapo Forest, Ivory Coast, was extracted (Soxhlet) successively for 24 h periods with light petroleum and with chloroform. Evaporation of the chloroform solution and separation of the residue (0.83 g) by t.l.c. gave (i) diosindigo A [14] (1 mg), (ii) diosquinone (6 mg), which crystallised from light petroleum as orange needles, m.p. 199—200°, (iii) isodiospyrin [6] (2 mg), and (iv) mamegakinone [15] (8 mg).

Deoxygenation of Quinone Epoxides.—(*a*) A mixture of 2,3-epoxy-2,3-dihydrojuglone [12] (40 mg), anhydrous sodium acetate (35 mg), sodium iodide (100 mg), zinc powder (100 mg), and acetic acid (1 ml) was stirred for 1.5 h at room temperature and filtered. The residue was washed with acetic acid and the filtrates were combined and diluted with water. Extraction with ether gave a solid which was separated by t.l.c. into juglone (12 mg, 33%), m.p. 154° (decomp.), and traces of 2,5- and 3,5-dihydroxy-1,4-naphthoquinone.

(*b*) A similar reaction with diosquinone (20 mg) gave diospyrin (2 mg, 10%), m.p. 256—257° (lit.,[16] 258°), $[\alpha]_D^{22}$ 0°, and 3′-hydroxydiospyrin (1 mg).

Preparation of Quinone Epoxides.—(*a*) A solution of sodium perborate [12] (115 mg) in water (14 ml) at 0 °C was added to a solution of 7-methyljuglone (50 mg) in ethanol (20 ml) at 0 °C. After 2 min the solution was adjusted to pH 5.0 with 2M-hydrochloric acid and a saturated solution of sodium chloride was added. Extraction with ether gave a solid which, after purification by t.l.c. (dichloromethane), crystallised from light petroleum to give *2,3-epoxy-2,3-dihydro-7-methyljuglone* as pale brown prisms (35 mg), m.p. 94—95° (Found: *M*, 204.0424. $C_{11}H_8O_4$ requires *M*, 204.0423), $\nu_{max.}$ 1 694, 1 659, and 1 620 cm^{-1} (aryl ketone C=O), $\lambda_{max.}$ 242 (log ε 4.19), 289 (3.69), and 365 nm (3.69), δ 2.44 (3 H, s, 7-Me), 3.95 and 3.99 (2 H, AB q, *J* 3.5 Hz, H-3 and -2), 7.09br and 7.37br (each 1 H, s, H-6 and -8), and 11.19 (1 H, s, OH), *m/e* 204 (100%, $M^{+\cdot}$), 203 [14, $(M - H)^+$], 176 [15, $(M - CO)^{+\cdot}$], 148 (15, 176 − CO), 135 (44), 134 (23), 119 (15, 134 − Me), and 106 (15).

(*b*) A similar reaction mixture was kept at pH 3—4 for 10 min at 5 °C and then treated with saturated aqueous sodium chloride. The resulting precipitate was separated by t.l.c. into (i) 3-chloro-5-hydroxy-7-methyl-1,4-naphthoquinone (5 mg), m.p. 189—191° (lit.,[5] 193—194°), (ii) 2,3-epoxy-2,3-dihydro-7-methyljuglone (15 mg), (iii) 2,5-dihydroxy-7-methyl-1,4-naphthoquinone (5 mg), m.p. 206—210° (decomp.) [lit.,[5] 208—210° (decomp.)], and (iv) 3,5-dihydroxy-7-methyl-1,4-naphthoquinone (2 mg), m.p. 217° (lit.,[5] 217°).

(*c*) An oxidation of diospyrin (50 mg) as in (*a*), for 4 min, gave (i) (±)-*2′,3′-epoxy-2′,3′-dihydrodiospyrin* (2) as orange plates (16 mg), m.p. 236° (decomp.) (Found: *M*, 390.0735. $C_{22}H_{14}O_7$ requires *M*, 390.0739), $\nu_{max.}$ 1 702, 1 654 (sh), 1 642, and 1 615 cm^{-1} (quinone and aryl ketone C=O), $\lambda_{max.}$ 249 (log ε 4.40) and 376 nm (3.81), $\lambda_{infl.}$ 291 (log ε 3.90) and 423 nm (3.73), and (ii) 2′-hydroxydiospyrin (2 mg).

2′- and 3′-Hydroxydiospyrin.—A solution of diospyrin (100 mg) in acetic anhydride (40 ml) and concentrated sulphuric acid (2.5 ml) was stirred at room temperature for 18 h and then poured onto ice. Extraction with ether gave a residue which was boiled for 15 min with methanol (20 ml) and 2M-hydrochloric acid (30 ml) before being again extracted with ether. Air was bubbled through the ethereal solution for 2 h, and the solvent was evaporated off. The residue was separated by t.l.c. into (i) the faster-moving component, *2′-hydroxydiospyrin* (5; X = OH, Y = H) which crystallised from light petroleum as orange crystals (3 mg), m.p. 223—225° (decomp.) (Found: *M*, 390.0743. $C_{22}H_{14}O_7$ requires *M*, 390.0739), $\nu_{max.}$ 1 678 (sh), 1 648, and 1 612 cm^{-1} (quinone C=O), $\lambda_{max.}$ 292 (log ε 3.92) and 437 nm (3.58), $\lambda_{infl.}$ 249 nm (log ε 4.22), δ 2.29 and 2.45 (each 3 H, s, 7′- and 7-Me), 6.28 and 6.88 (each 1 H, s, H-3′ and -3), 7.12br and 7.48br (each 1 H, s, H-6 and -8), 7.59 (1 H, s, H-8′), and 11.83 and 12.52 (each 1 H, s, 5- and 5′-OH), *m/e* 392 [10%, $(M + 2H)^{+\cdot}$], 390 (100, $M^{+\cdot}$), 375 [19, $(M - Me)^+$], 362 [20, $(M - CO)^{+\cdot}$], 344 [19, $(M - H_2O - CO)^{+\cdot}$], 163 (15), 135 (24), 134 (16), and 106 (22), and (ii) *3′-hydroxydiospyrin* (5; X = H, Y = OH) (2 mg) which crystallised from light petroleum in orange crystals, m.p. 243—246° (decomp.) (Found: *M*, 390.0747. $C_{22}H_{14}O_7$ requires *M*, 390.0739), $\nu_{max.}$ 1 670(sh), 1 643, and 1 617 cm^{-1} (quinone C=O), $\lambda_{max.}$ 430 nm (log ε 3.81), $\lambda_{infl.}$ 232 (log ε 4.48), and 263 nm (4.34), δ 2.31 and 2.45 (each 3 H, s, 7′- and 7-Me), 6.33 and 6.89 (each 1 H, s, H-2′ and -3), 7.12br and 7.49br (each

1 H, s, H-6 and -8), 7.59 (1 H, s, H-8′), and 11.24 and 11.84 (each 1 H, s, 5′- and 5-OH), *m/e* 392 [20%, $(M + 2H)^{\cdot+}$], 390 (100, $M^{\cdot+}$), 375 [25, $(M - Me)^+$], 344 [24, $(M - H_2O - CO)^{\cdot+}$], 316 (14, 344 − CO), 163 (16), 135 (24), 134 (14), and 106 (23).

Reaction of 2,3-*Epoxy*-2,3-*dihydro*-7-*methyljuglone with Chloroform.*—A solution of the epoxide (100 mg) in chloroform (AnalaR, containing 7% ethanol) was boiled under reflux for 2 days and evaporated. Separation of the residue by t.l.c. gave (i) 3-chloro-5-hydroxy-7-methyl-1,4-naphthoquinone (6 mg), (ii) unchanged starting epoxide (42 mg), and (iii) 2-*chloro*-3,5-*dihydroxy*-7-*methyl*-1,4-*naphthoquinone* (4; X = Cl, Y = OH, Z = Me) (10 mg) which crystallised from light petroleum as yellow needles, m.p. 210—211° (Found: *M*, 238.0032. $C_{11}H_7O_4{}^{35}Cl$ requires *M*, 238.0033), $\nu_{max.}$ 3 290 (hydrogen-bonded H–O), and 1 664 and 1 631 cm^{-1} (quinone C=O), $\lambda_{max.}$ 236 (log ε 3.97), 294 (3.95), and 410 nm (3.51), $\lambda_{infl.}$ 247 nm (log ε 3.95), δ 2.44 (3 H, s, 7-Me), 7.07br and 7.57br (each 1 H, s, H-6 and -8), and 10.91 (1 H, s, 5-OH), *m/e* 238 (100%, $M^{\cdot+}$), 210 [79, $(M - CO)^{\cdot+}$], 175 (75, 210 − Cl), 147 (38, 175 − CO), 135 (45), 119 (34, 147 − CO), and 106 (21).

Reaction of 2,3-*Epoxy*-2,3-*dihydrojuglone with Ethanol.*—A solution of 2,3-epoxy-2,3-dihydrojuglone [12] (500 mg) in redistilled ethanol (100 ml) was heated in a sealed tube on a steam-bath for 3 days and then evaporated. The residue was separated by repeated t.l.c. into (i) 3-*ethoxy*-5-*hydroxy*-1,4-*naphthoquinone* (4; X = Z = H, Y = OEt) (27 mg) which crystallised from light petroleum as yellow prisms, m.p. 150—151° (Found: *M*, 218.0578. $C_{12}H_{10}O_4$ requires *M*, 218.0579), $\nu_{max.}$ 1 640 and 1 600 cm^{-1} (quinone C=O and C=C), $\lambda_{max.}$ 283 (4.06) and 416 nm (3.51), $\lambda_{infl.}$ 240 nm (log ε 3.96), δ 1.54 (3 H, t, *J* 7.5 Hz, CH_3CH_2OR), 4.10 (2 H, q, *J* 7.5 Hz, CH_3CH_2OR), 6.12 (1 H, s, H-2), *ca.* 7.2 and 7.59—7.64 (3 H, m, H-6, -7, and -8), and 11.77 (1 H, s, OH), *m/e* 218 (56%, $M^{\cdot+}$), 174 [100, $(M - C_2H_4O)^{\cdot+}$], and 173 (20, 174 − H), (ii) 2,5-dihydroxy-1,4-naphthoquinone (34 mg), m.p. 217° (decomp.), (iii) 2-*ethoxy*-3,5-*dihydroxy*-1,4-*naphthoquinone* (4; X = OEt, Y = OH, Z = H) (60 mg) which crystallised from light petroleum in orange needles, m.p. 125—127° (Found: *M*, 234.0529. $C_{12}H_{10}O_5$ requires *M*, 234.0528), $\nu_{max.}$ 3 225 (hydrogen-bonded H–O), 1 666, 1 637, 1 625, and 1 596 cm^{-1} (quinone C=O and C=C), $\lambda_{max.}$ 229 (log ε 4.21), 255 (4.11), 282 (4.14), and 410 nm (3.66), δ 1.41 (3 H, t, *J* 7 Hz, CH_3CH_2OR), 4.52 (2 H, q, *J* 7 Hz, CH_3CH_2OR), 7.13—7.66 (3 H, m, H-6, -7, and -8), and 11.20 (1 H, s, 5-OH), *m/e* 234 (75%, $M^{\cdot+}$) and 178 [100, $(M - C_2H_4 - CO)^{\cdot+}$], (iv) 3,5-dihydroxy-1,4-naphthoquinone (41 mg), m.p. 216° (decomp.), and (v) 2,3,5-trihydroxy-1,4-naphthoquinone (5 mg) which crystallised from chloroform as red prisms, m.p. 260° (decomp.) [lit.,[17] 234° (decomp.)] (Found: *M*, 206.0214. $C_{10}H_6O_5$ requires *M*, 206.0215), $\nu_{max.}$ 3 320 (hydrogen-bonded H–O), 1 673, 1 645, and 1 607 cm^{-1} (quinone C=O), $\lambda_{max.}$ 228 (log ε 3.90), 283 (3.87), and 403 nm (3.50), δ 6.77 and 6.85 (each 1 H, s, 2- and 3-OH), 7.07—7.74 (3 H, m, H-6, -7, and -8), and 11.32 (1 H, s, 5-OH), *m/e* 206 (100%, $M^{\cdot+}$) and 178 [89, $(M - CO)^{\cdot+}$].

2,5- *and* 3,5-*Dihydroxy*-1,4-*naphthoquinone.*—A solution of juglone 2,3-epoxide (100 mg) in concentrated sulphuric acid (2 ml) was kept for 30 min and added to ice–water (20 ml). Extraction with ether gave a solid which was separated by t.l.c. (dichloromethane) into a faster-moving component which crystallised from chloroform to give the 2,5-dihydroxyquinone (35 mg) as orange cubes, m.p. 217—219° (decomp.), [lit.,[18] 220° (decomp.)], $\nu_{max.}$ 3 190 (hydrogen-bonded H–O), 1 680, 1 658, and 1 620 cm^{-1} (quinone C=O), $\lambda_{max.}$ 242 (log ε 4.10), 284 (4.08), and 414 nm (3.59), δ 6.29 (1 H, s, H-3), 7.35—7.65 (3 H, m, H-6, -7, and -8), and 12.28 (1 H, s, 5-OH), and a slower-moving component which crystallised from chloroform to give the 3,5-dihydroxyquinone (19 mg) as orange cubes, m.p. 216° (decomp.) [lit.,[18] 218—220° (decomp.)], $\nu_{max.}$ 3 210 (hydrogen-bonded H–O), 1 655(sh), 1 637, 1 618, and 1 594 (sh) (quinone C=O and C=C), $\lambda_{max.}$ 230 (log ε 4.32), 271 (4.21), and 410 nm (3.65), $\lambda_{infl.}$ 292 nm (log ε 3.99), δ 6.33 (1 H, s, H-2), 7.24—7.66 (3 H, m, H-6, -7, and -8), and 11.04 (1 H, s, OH).

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