Ebenaceae Extractives. Part 7.[1] Use of Hydroxy-proton Shifts of Juglone Derivatives in Structure Elucidation

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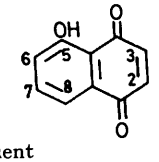
Substitution at one or more positions of juglone by bromo-, chloro-, hydroxy-, and methyl groups causes changes in the chemical shift of the hydroxy-proton which are additive and depend only on the nature and positions of the substituents. The hydroxy-proton signals of natural juglone derivatives show similar regularities and enable the structures of neodiospyrin (11), galpinone (8), and bisisodiospyrin (7) to be defined.

THE determination of the position of the linkage between the two units of a natural dimeric naphthoquinone such as diospyrin (1; X = H) presents some difficulty because of the problem of establishing which position on the quinone ring carries the substituent. This paper describes how the position of substitution may be deduced from the hydroxy-proton n.m.r. signals of the compound concerned.

TABLE 1

C-5 Hydroxy-proton shifts for substituted juglones [$\delta(CDCl_3)$]



Substituent						
C-2	C-3	C-6	C-7	C-8	Obs.	Calc.
H	H	H	H	H [a]	11.87	
Me	H	H	H	H [a]	11.93	
H	Me	H	H	H [b]	12.01	
H	H	Me	H	H [c]	12.22	
H	H	H	Me	H [a]	11.82	
Cl	H	H	H	H [d]	11.78	
H	Cl	H	H	H [d]	11.66	
OH	H	H	H	H [e]	12.28	
H	OH	H	H	H [e]	11.04	
H	H	H	H	OH [f]	12.38	
Me	Cl	H	H	H [g]	11.73	11.72
Me	H	H	H	Cl [h]	12.62	12.62
H	H	Me	H	Cl [c]	12.94	12.91
Cl	H	H	Me	H [i]	11.71	11.73
H	Cl	H	Me	H [i]	11.59	11.61
H	H	H	Me	Cl [j]	12.51	12.51
Me	OH	H	H	H [g]	11.08	11.10
Me	H	OH	H	H [h]	12.13	12.13
Me	H	H	H	OH [a]	12.42	12.44
					12.54 [k]	12.52 [k]
OH	Me	H	H	H [g]	12.39	12.42
H	Me	OH	H	H [h]	12.21	12.21
OH	H	H	Me	H [l]	12.23	12.23
H	OH	H	Me	H [l]	10.99	10.99
Cl	OH	H	H	H [e]	10.96	10.95
OH	Cl	H	H	H [e]	12.01	12.07
Br	OH	H	H	H [e]	10.95	10.95
OH	Br	H	H	H [e]	12.06	12.06
OH	OH	H	H	H [m]	11.32	11.45
Cl	Cl	H	Me	H [i]	11.55	11.52
H	Cl	H	Me	Cl [i]	12.26	12.30
OH	H	H	Me	Cl [i]	12.97	12.92
Cl	Cl	H	Me	Cl [i]	12.22	12.21
Cl	Cl	Cl	Me	Cl [i]	12.97	12.96

[a] R. H. Thomson, 'Naturally Occurring Quinones,' Academic Press, London, 2nd edn., 1971. [b] L. F. Fieser and J. T. Dunn, *J. Amer. Chem. Soc.*, 1936, **58**, 572. [c] Prepared by R. H. Thomson; see Experimental section. [d] Ref. 10. [e] R. H. Thomson, *J. Org. Chem.*, 1948, **13**, 870. [f] D. B. Bruce, A. J. S. Sorrie, and R. H. Thomson, *J. Chem. Soc.*, 1953, 2403. [g] R. H. Thomson, *J. Chem. Soc.*, 1949, 1277. [h] D. Skoyles, Ph.D. Thesis, Aberdeen, 1971. [i] Present work. [j] Ref. 12. [k] C-8 (OH). [l] Ref. 9. [m] J. F. Garden and R. H. Thomson, *J. Chem. Soc.*, 1957, 2483.

The proton of the strongly hydrogen-bonded hydroxy-group of juglone, *i.e.* 5-hydroxy-1,4-naphthoquinone (2; W = X = Y = Z = H), gives rise, in deuteriochloroform solution, to a sharp signal at δ 11.87, the position of which is largely unaffected by changes in concentration. While examining the spectra of the bromo-, chloro-, hydroxy-, and methyl-juglones listed in Table 1 we noticed that, as with substituted naphthazarins,[2] the positions of the signals from their C-5 hydroxy-protons depend on the nature and location of the substituents present. The changes in chemical shift are substantial, ranging from +1.10 p.p.m. for the tetrachloromethyljuglone (3; W = X = Y = Z = Cl) to −0.92 p.p.m. for the bromohydroxyjuglone (2; W = Br, X = OH, Y = Z = H). Furthermore they appear to result essentially from the addition of the contributions from the individual substituents present. These contributions, which are summarised in Table 2, are obtained by subtracting the juglone hydroxy-proton shift from that of a monosubstituted juglone or, in some cases, the shift of a substituted juglone from that of a juglone with one more substituent group. Table 1 also shows the calculated values obtained by adding the appropriate contributions from Table 2 to that of juglone. With one exception the agreement is excellent, most of the calculated values being within 0.03 p.p.m. of those observed. The marked discrepancy (0.13 p.p.m.) between the two values for 2,3-dihydroxyjuglone is probably a consequence of the tautomerism which is possible with this compound. Because naphthazarin (2; W = X = Y = H, Z = OH) may be treated as if it contains two separate juglone systems, two calculated values are possible for 2-methylnaphthazarin; these agree well with the observed shifts.

TABLE 2

Contributions by substituents to the chemical shifts of C-5 hydroxy-protons in juglone derivatives

Substituent	Contribution (p.p.m., in $CDCl_3$) [a]				
	C-2	C-3	C-6	C-7	C-8
Me	+0.06	+0.14	+0.35	−0.05	
Cl	−0.09	−0.21	+0.75 [b]		+0.69 [b]
Br	−0.09 [b]	−0.22 [b]			
OH	+0.41	−0.83	+0.20 [b]		+0.51

[a] Calculated from shifts of monosubstituted juglones. [b] Calculated from shifts of polysubstituted juglones.

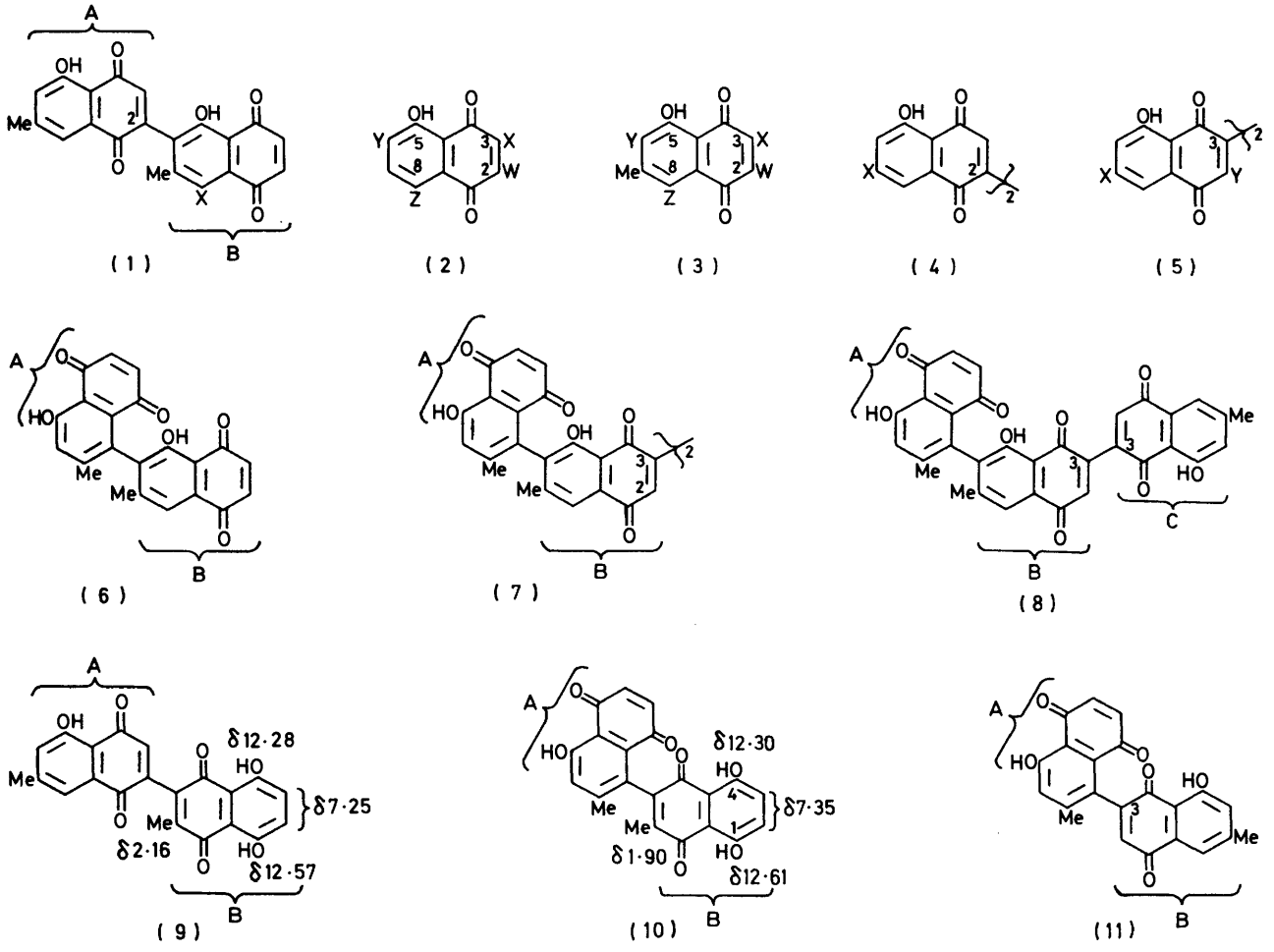
The additive nature of the shift contributions suggested

[1] Part 6, T. J. Lillie, O. C. Musgrave, and D. Skoyles, *J.C.S. Perkin 1*, 1976, 2546.

[2] R. E. Moore and P. J. Scheuer, *J. Org. Chem.*, 1966, **31**, 3272.

that the comparison of C-5 hydroxy-proton shifts would provide a reliable guide to the positions of substituents in more complex juglone derivatives such as the natural bisnaphthoquinones. Examination of the first four entries in Table 3, which records the n.m.r. signals for a number of natural and synthetic di-, tri-, and tetra-meric juglone derivatives, confirms that this is so. Thus the formal conversion of 2,2′- (4; X = H) and 3,3′-bijuglone (5; X = Y = H) into biramentaceone (4; X = Me) and mamegakinone (5; X = Me, Y = H), respectively, involves the introduction of two C-7 methyl groups. From Table 2, this should result in a change in the hydroxy-proton shift of −0.05 p.p.m. in each case, in excellent agreement with the observed values. Similarly the symmetrical biplumbagin (5; X = H, Y = Me)[3] isolated from *Plumbago zeylanica* shows a hydroxy-proton signal at δ 11.83, confirming that it is a 3,3′-bijuglone having two C-2 methyl groups (calculated shift δ 11.79), as proposed originally on biogenetic grounds, rather than a 2,2′-bijuglone with two C-3 methyl groups (calculated shift δ 11.98).

The hydroxy-proton shifts of the compounds discussed below establish the positions of their quinone–quinone or arene–quinone linkages. The tetrameric 7-methyljuglone derivative from *Diospyros lotus*, bisisodiospyrin (7),[4] is a symmetrical dimer derived from two molecules of isodiospyrin (6) linked to each other *via* C-2 or C-3 of unit B. Isodiospyrin and bisisodiospyrin each show two hydroxy-proton signals, at δ 12.40 and 12.02 and δ 12.40 and 11.90, respectively. We assign the signal at δ 12.40 to the hydroxy-proton of unit A in each case because, unlike unit B, this unit is not directly affected by the process of dimerisation. The signal at δ 12.02 from the hydroxy-proton in unit B of isodiospyrin is shifted by −0.12 p.p.m. to δ 11.90 in the spectrum of bisisodiospyrin. Now the dimerisation of 7-methyljuglone *via* C-2, to give biramentaceone (4; X = Me), leads to a shift in the hydroxy-proton signal of −0.02 p.p.m. while dimerisation *via* C-3, to give mamegakinone (5; X = Me, Y = H), results in a shift of −0.13 p.p.m. We conclude that bisisodiospyrin has the structure (7) in which the two B units are linked as in mamegakinone. Galpinone



[3] G. S. Sidhu and A. V. B. Sankaram, *Tetrahedron Letters*, 1971, 2385.

[4] K. Yoshihira, M. Tezuka, and S. Natori, *Chem. and Pharm. Bull. (Japan)*, 1971, **19**, 2308.

(8),[5,6] which occurs in *Diospyros galpinii* and *Euclea natalensis*, is a trimeric naphthoquinone derived from 7-methyljuglone. Units A and B are joined as in isodiospyrin but the position of the quinone–quinone linkage between units B and C is unknown. All the n.m.r. signals for the protons of units A and B are almost identical with those of bisisodiospyrin, and it follows that unit B has a substituent at C-3. As the signals from unit C are virtually the same as those from mamegakinone, which contains two 7-methyljuglone units linked *via* C-3, galpinone must have the structure (8).

H) respectively, are −0.02 and −0.13 p.p.m., respectively, and we therefore assign the hydroxy-proton signals of the naphthazarin unit in 8′-hydroxydiospyrin as shown in structure (9). The suggested shift values are in keeping with the observation (see Table 2) that a substituent at C-2 in a juglone derivative, being further away from the C-5 hydroxy-group, has less effect on it and produces a smaller shift contribution than does a substituent at C-3. The related compound 8′-hydroxyisodiospyrin (10) [8] contains a similar methylnaphthazarin system but the attachment to this of unit A is *via* an

TABLE 3

N.m.r. signals for di-, tri-, and tetra-meric juglone derivatives

Compound	Unit	Observed chemical shift [δ ($CDCl_3$)] H-2	H-3	H-6	7-CH_3	H-8	5-(OH)
2,2′-Bijuglone (4; X = H) [a]			7.05	[b]	[b]	[b]	11.84
Biramentaceone (4; X = Me) [c]			7.01	7.13 [d]	2.44	7.50 [d]	11.80
3,3′-Bijuglone (5; X = Y = H) [a]		7.06		[b]	[b]	[b]	11.73
Mamegakinone (5; X = Me, Y = H) [e]		6.97		7.12 [d]	2.45	7.50 [d]	11.69
Diospyrin (1; X = H) [f]	A		6.89	7.12 [d]	2.45	7.50 [d]	11.85
	B	6.94	6.94		2.31	7.55	12.11
Isodiospyrin (6) [g]	A	6.72 [h]	6.91 [h]	7.30	2.03		12.40
	B	6.94	6.94		2.01	7.60	12.02
Bisisodiospyrin (7) [e]	A	6.71 [h]	6.91 [h]	7.29	2.04		12.40
	B	7.02			2.04	7.65	11.90
Galpinone (8) [i]	A	6.72 [h]	6.91 [h]	7.30	2.04		12.39
	B	7.01			2.04	7.67	11.88
	C	6.97		7.10 [d]	2.44	7.48 [d]	11.69
8′-Hydroxydiospyrin (9) [j]	A [k]		6.85	7.13 [d]	2.46	7.49 [d]	11.80
8′-Hydroxyisodiospyrin (10) [l]	A [k]	6.72 [h]	6.91 [h]	7.35 [m]	2.18		12.27
Neodiospyrin (11) [n]	A	6.77 [h]	6.93 [h]	7.25	2.30		12.28
	B	6.61		7.11 [d]	2.47	7.53 [d]	11.75

[a] B. C. Maiti, O. C. Musgrave, and D. Skoyles, in preparation. [b] Part of an ABX multiplet at δ *ca.* 7.30—7.70. [c] V. Krishnamoorthy and R. H. Thomson, *Phytochemistry*, 1969, **8**, 1591. [d] J_m *ca.* 1.5 Hz. [e] Ref. 4. [f] G. S. Sidhu and M. Pardhasaradhi, *Tetrahedron Letters*, 1967, 1313. [g] A. L. Fallas and R. H. Thomson, *J. Chem. Soc.* (*C*), 1968, 2279. [h] *J* 10 Hz. [i] Refs. 5 and 6. [j] Ref. 1. [k] For other signals see formula. [l] Ref. 8. [m] Multiplet. [n] Refs. 6 and 9.

Diospyrin (1; X = H) contains an arene–quinone linkage the location [7] of which has been questioned.[8] The following arguments support the view that the linkage involves C-2 rather than C-3 of unit A. First, 8′-hydroxydiospyrin (1; X = OH) [1] exists in solution in the tautomeric form (9) in which the quinone ring of unit B carries two substituents.[2] Of its three hydroxy-proton signals (Table 3) that at δ 11.80 has the same shift as does the corresponding group in biramentaceone (4; X = Me) and must result from the hydroxy-proton of a 7-methyljuglone unit (unit A) which has a quinonoid substituent at C-2. As the carbon skeleton of 8′-hydroxydiospyrin is the same as that of diospyrin,[1] unit A of the latter must also carry a substituent at C-2. Secondly, the hydroxy-proton signals from unit B of 8′-hydroxydiospyrin (at δ 12.57 and 12.28) are displaced by +0.03 and −0.14 p.p.m. respectively from those (at δ 12.54 and 12.42) of the C-8 and the C-5 hydroxy-protons of 2-methylnaphthazarin (2; X = Y = H, W = Me, Z = OH). Now the shift contributions of a quinonoid substituent at C-2 and at C-3 of juglone, obtained by subtracting the 7-methyljuglone shift from those of biramentaceone and mamegakinone (5; X = Me, Y = arene–quinone bond instead of a quinone–quinone bond. The different type of substituent appears to have little effect on the signals (at δ 12.61 and 12.30) from the hydroxy-protons of unit B, which resemble those of 8′-hydroxydiospyrin. Accordingly we assign these signals as in structure (10). The subtraction from these values of the corresponding shifts for the hydroxy-protons of 2-methylnaphthazarin gives +0.07 and −0.12 p.p.m. as the contributions of the aryl substituent, *i.e.* of unit A, to the shifts of the unit B hydroxy-protons at C-1 and C-4. The same shift contributions will clearly be applicable to the hydroxy-proton signals of juglones carrying aryl substituents at C-2 and C-3 respectively. The addition of the contribution from a C-2 aryl substituent (+0.07 p.p.m.) to the observed shift (δ 11.82) of the hydroxy-proton of 7-methyljuglone gives δ 11.89 as the value expected for structure (1; X = H), which is in good agreement with the shift (δ 11.85) observed for diospyrin. The attachment of an aryl substituent at C-3 of 7-methyljuglone would lead to a hydroxy-proton shift of δ 11.70.

Neodiospyrin (11),[6,9] which occurs in *Diospyros kaki*

[5] M. A. Ferreira, A. Correia Alves, M. Aurea Cruz Costa, and M. I. Paul, submitted to *Phytochemistry*.

[6] K. W. Gerritsma and L. M. van der Vijver, unpublished work; L. M. van der Vijver, Ph.D. Thesis, Amsterdam, 1975.

[7] G. S. Sidhu and M. Pardhasaradhi, *Indian J. Chem.*, 1970, **8**, 569.

[8] M. Tezuka, C. Takahashi, M. Kuroyanagi, M. Satake, K. Yoshihira, and S. Natori, *Phytochemistry*, 1973, **12**, 175.

[9] M. Tezuka, M. Kuroyanagi, K. Yoshihira, and S. Natori, *Chem. and Pharm. Bull.* (*Japan*), 1972, **20**, 2029.

and *D. rotundifolia*, contains two 7-methyljuglone units linked *via* an arene–quinone bond, but the position of substitution on the quinonoid ring has not been established. The chemical shift (δ 11.75) of the hydroxy-proton of unit B agrees well with that (δ 11.70) derived above for a 7-methyljuglone carrying an aryl substituent at C-3 and accordingly we formulate neodiospyrin as (11).

Accurate values for the hydroxy-proton shifts are essential if arguments based on shift differences are to lead to reliable conclusions. We obtained all the spectra described in Tables 1 and 3 for dilute solutions using the same 100 MHz spectrometer and measured the shifts either relative to the chloroform signal at δ 7.25 or, better, by using a frequency counter. We consider the values by either method to be reproducible to within ±0.02 p.p.m. The use of the conventional, uncalibrated, sweep-offset procedure is not sufficiently accurate and can give erroneous results.

The hydroxy- and the new chloro-juglones described in the Experimental section were prepared by standard procedures. The chlorination of 7-methyljuglone (3; W = X = Y = Z = H) gave mainly the 3-chloro-derivative, as expected,[10] together with a little of the 2-chloro-isomer. Further chlorination of 3-chloro-7-methyljuglone afforded the 2,3-dichloro-compound. Similar reactions with 8-chloro-7-methyljuglone (3; W = X = Y = H, Z = Cl) produced the corresponding 3,8-dichloro-, 2,3,8-trichloro-, and 2,3,6,8-tetrachloro-derivatives.

EXPERIMENTAL

General instructions are given in Parts 4 [11] and 5.[1] N.m.r. spectra were measured at 30 ± 0.5 °C for solutions in deuteriochloroform with a Varian HA-100D spectrometer (tetramethylsilane as internal standard). The hydroxy-proton signal of juglone appeared at δ 11.83, 11.85, and 11.87 at concentrations of 17.0, 7.0, and 1.7% w/v, respectively. All other measurements were made at concentrations <1.7% w/v. U.v.–visible spectra were measured for methanolic solutions.

8-Chloro-5-hydroxy-6-methyl-1,4-naphthoquinone (R. H. Thomson).—Prepared from 4-chloro-2-methylphenol and maleic anhydride by the method [12] previously used for the 7-methyl isomer, this *chloroquinone* (24%) crystallised from light petroleum (b.p. 100—120°) as orange-red needles, m.p. 159—160° (Found: *M*, 222.0080. $C_{11}H_7{}^{35}ClO_3$ requires *M*, 222.0084).

5-Hydroxy-6-methyl-1,4-naphthoquinone (R. H. Thomson).—Prepared from the above 8-chloroquinone by the sequence [12] previously used for the 7-methyl isomer this *quinone* (35%) crystallised from light petroleum (b.p. 80—90°) as orange needles, m.p. 108° (Found: *M*, 188.0472. $C_{11}H_8O_3$ requires *M*, 188.0473).

2- and 3-Chloro-5-hydroxy-7-methyl-1,4-naphthoquinone.—A mixture of 5-hydroxy-7-methyl-1,4-naphthoquinone [12] (140 mg), chlorine (40 mg), and glacial acetic acid (10 ml) was shaken for 15 h and then poured into water. Extraction with chloroform gave 2,3-dichloro-2,3-dihydro-5-hydroxy-7-methyl-1,4-naphthoquinone (152 mg), which separated from chloroform as yellow needles, m.p. 137—139°, $\nu_{max.}$ 1 705 and 1 645 (aryl C=O and hydrogen-bonded aryl C=O), and 1 608 cm^{-1} (C=C), $\lambda_{max.}$ 244 (log ε 4.27), 277 (4.16), and 365 nm (3.66), δ 2.52 (3 H, s, 7-CH_3), 4.28 (2 H, s, H-2 and -3), 7.22br (1 H, s, H-6), 7.52br (1 H, s, H-8), and 11.40 (1 H, s, 5-OH), and which underwent oxidation in air to give 2,3-dichloro-5-hydroxy-7-methyl-1,4-naphthoquinone. A solution of the dichlorodihydro-compound (150 mg) in ethanol (50 ml) was boiled for 1 h and evaporated. Crystallisation of the residue from light petroleum gave *3-chloro-5-hydroxy-7-methyl-1,4-naphthoquinone* (65 mg) as orange needles, m.p. 193—194° (Found: *M*, 222.0085. $C_{11}H_7{}^{35}ClO_3$ requires *M*, 222.0084), $\nu_{max.}$ 1 660 and 1 639 (quinone C=O), and 1 593 cm^{-1} (C=C), $\lambda_{max.}$ 278 (log ε 4.03) and 429 nm (3.57), $\lambda_{infl.}$ 256 nm (log ε 3.91).

Evaporation of the mother liquor gave a solid which after repeated t.l.c. (light petroleum–dichloromethane) gave *2-chloro-5-hydroxy-7-methyl-1,4-naphthoquinone* (4 mg) as yellow needles (from light petroleum), m.p. 105° (Found: *M*, 222.0083. $C_{11}H_7{}^{35}ClO_3$ requires *M*, 222.0084), $\nu_{max.}$ 1 682 and 1 642 (quinone C=O), and 1 590 cm^{-1} (C=C), $\lambda_{max.}$ 279 (log ε 3.91) and 434 nm (3.49), $\lambda_{infl.}$ 261 nm (log ε 3.82).

2,3-Dichloro-5-hydroxy-7-methyl-1,4-naphthoquinone. — A mixture of 3-chloro-5-hydroxy-7-methyl-1,4-naphthoquinone (30 mg), chlorine (50 mg), and glacial acetic acid (10 ml) was boiled under reflux for 30 min and then poured into water. Extraction with chloroform gave the *dichloroquinone* as yellow needles (22 mg) (from light petroleum), m.p. 174—175° (Found: *M*, 255.9701. $C_{11}H_6{}^{35}Cl_2O_3$ requires *M*, 255.9694), $\nu_{max.}$ 1 678 and 1 632 (quinone C=O), and 1 577 cm^{-1} (C=C), $\lambda_{max.}$ 253 (log ε 3.75), 291 (3.94), and 433 nm (3.50).

3,8-Dichloro-5-hydroxy-7-methyl-1,4-naphthoquinone.—8-Chloro-5-hydroxy-7-methyl-1,4-naphthoquinone [12] (200 mg) was shaken for 15 h with a solution of chlorine (64 mg) in glacial acetic acid (10 ml) and the mixture was then poured into water. Extraction with chloroform gave a yellow solid which was boiled for 20 min with ethanol. Evaporation, and crystallisation of the residue from light petroleum gave the *dichloroquinone* (130 mg) as orange needles, m.p. 179° (Found: *M*, 255.9699. $C_{11}H_6{}^{35}Cl_2O_3$ requires *M*, 255.9694), $\nu_{max.}$ 1 654, 1 638 (quinone C=O), and 1 605 cm^{-1} (C=C), $\lambda_{max.}$ 258 (log ε 4.04), 282 (4.04), and 439 nm (3.66).

2,3,8-Trichloro- and 2,3,6,8-Tetrachloro-5-hydroxy-7-methyl-1,4-naphthoquinone.—A mixture of the above dichloroquinone (50 mg), chlorine (65 mg), and glacial acetic acid (15 ml) was boiled under reflux for 1 h and then poured into water. Extraction with chloroform gave a solid which crystallised from light petroleum to give the *trichloroquinone* as orange needles (32 mg), m.p. 183° (Found: *M*, 289.9302. $C_{11}H_5{}^{35}Cl_3O_3$ requires *M*, 289.9304), $\nu_{max.}$ 1 678 and 1 629 (quinone C=O), and 1 588 cm^{-1} (C=C), $\lambda_{max.}$ 258 (log ε 3.85), 289 (3.95), and 439 nm (3.69). Evaporation of the mother liquor gave a solid which, after repeated t.l.c. (dichloromethane), gave more of the trichloroquinone (8 mg) and the *tetrachloroquinone*, which crystallised from light petroleum as orange prisms (7 mg), m.p. 163—165° (Found: *M*, 323.8904. $C_{11}H_4{}^{35}Cl_4O_3$ requires *M*, 323.8914), $\nu_{max.}$ 1 674 and 1 629 (quinone C=O), and 1 594 cm^{-1} (C=C), $\lambda_{max.}$ 256 (3.73), 296 (3.61), and 435 nm (3.25).

2,5- and 3,5-Dihydroxy-7-methyl-1,4-naphthoquinone.—A mixture of 5-hydroxy-7-methyl-1,4-naphthoquinone (350 mg), acetic anhydride (10 ml), and concentrated sulphuric acid (0.3 ml) was kept at room temperature overnight and

[10] R. H. Thomson, *J. Org. Chem.*, 1948, **13**, 377.
[11] O. C. Musgrave and D. Skoyles, *J.C.S. Perkin I*, 1974, 1128.
[12] R. G. Cooke and H. Dowd, *Austral. J. Chem.*, 1953, **6**, 53.

then poured onto ice. Extraction with ether gave a solid which was boiled with methanolic 2M-hydrochloric acid for 15 min. Extraction of this mixture with ether gave a solid which was separated by t.l.c. (chloroform) into two bands. The faster-moving band gave the 2,5-dihydroxyquinone (85 mg) as orange plates (from chloroform), m.p. 208—210° (decomp.) (lit.,[9] 196—200°) (Found: *M*, 204.0421. Calc. for $C_{11}H_8O_4$: *M*, 204.0423), $\nu_{max.}$ 1 666sh, 1 642, and 1 616 cm^{-1} (quinone C=O and C=C), $\lambda_{max.}$ 249 (log ε 4.00), 292 (3.96), and 429 nm (3.49).

A mixture of the 2,5-dihydroxyquinone (20 mg), anhydrous sodium acetate (10 mg), acetic anhydride (5 ml), and zinc dust (20 mg) was boiled under reflux for 20 min and then poured into water. Extraction with chloroform and crystallisation of the product from light petroleum gave 1,2,4,5-*tetra-acetoxy*-7-*methylnaphthalene* (25 mg), m.p. 148—149° (Found: *M*, 374.1000. $C_{19}H_{18}O_8$ requires *M*, 374.1002), $\nu_{max.}$ 1 760 (aryl acetate C=O), 1 641 and 1 618 cm^{-1} (C=C), δ 2.29, 2.35, 2.36, 2.44, and 2.48 (each 3 H, s, ArOAc and ArMe), 7.00br (1 H, s, H-6), 7.05 (1 H, s, H-3), and 7.52br (1 H, s, H-8).

The slower-moving band afforded the 3,5-dihydroxyquinone (43 mg) as yellow needles (from chloroform), m.p. 217° (lit.,[9] 190—207°) (Found: *M*, 204.0421. Calc. for $C_{11}H_8O_4$: *M*, 204.0423), $\nu_{max.}$ 1 657sh, 1 640sh, and 1 626 cm^{-1} (quinone C=O and C=C), $\lambda_{max.}$ 287 (log ε 3.92) and 402 nm (3.48). Reductive acetylation as for the 2,5-isomer gave 1,3,4,5-*tetra-acetoxy*-7-*methylnaphthalene*, m.p. 178° (Found: *M*, 374.1000. $C_{19}H_{18}O_8$ requires *M*, 374.1002), $\nu_{max.}$ 1 765 (aryl acetate C=O) and 1 618 cm^{-1} (C=C), δ 2.30, 2.36, 2.36, 2.44, and 2.49 (each 3 H, s, ArOAc and ArMe), 7.05br (1 H, s, H-6), 7.25 (1 H, s, H-2), and 7.57br (1 H, s, H-8).

8-*Chloro*-2,5-*dihydroxy*-7-*methyl*-1,4-*naphthoquinone*. — A similar reaction between 8-chloro-5-hydroxy-7-methyl-1,4-naphthoquinone, acetic anhydride, and concentrated sulphuric acid gave, as the major product, the *chlorodihydroxyquinone*, which crystallised from chloroform as orange plates, m.p. 195—197° (Found: *M*, 238.0034. $C_{11}H_7{}^{35}ClO_4$ requires *M*, 238.0033), $\nu_{max.}$ 1 660, 1 654sh, and 1 622 cm^{-1} (quinone C=O and C=C).

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