Naturally Occurring Quinones. Part XXII.[1] Terpenoid Quinones in *Cordia* Spp.

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Cordiachromes A—F are terpenoid benzoquinones isolated from the heartwood of *Cordia millenii*. Cordiachrome C (3; R = H) has a benzogeijerene and A (1; R = H) and B (2; R = H) have a benzocogeijerene skeleton. Cordiachromes D—F are methoxy-derivatives of A—C, respectively. All six are optically inactive. Biogenetically they appear to be related to alkannin, which occurs in the same family (Boraginaceae). The distribution of cordiachromes in other *Cordia* spp. is surveyed.

CORDIA (Boraginaceae) is a genus of tropical trees, some of which yield valuable timber, but little is known of the wood extractives other than the presence of sesquiterpenes in *C. trichotoma* [2] and *C. chacoensis*.[3] From the heartwood of *C. millenii* we have now isolated six terpenoid benzoquinones, cordiachromes A—F.[4] We have also examined sixteen other *Cordia* spp. (see Table); all six pigments were found in *C. goeldiana* and *C. platythyrsa*, and cordiachromes A, B, and C in several other spp., but half of those examined contained no quinones at all. Most of the structural work was carried out on cordiachrome B and this is discussed first.

Cordiachrome B. This is a 2,3-dialkylbenzoquinone showing $\lambda_{max.}$ 250 and 350 nm, $\nu_{max.}$ 1650 and 1600 cm^{-1}, and τ 3·30 (2H, s); it has typical redox properties, gives a positive Craven test, and forms a leucodiacetate. As the molecular formula is $C_{16}H_{18}O_2$ the molecule must contain a benzoquinone ring fused to a $C_{10}H_{16}$ system containing three double-bond equivalents. That one of these is a terminal methylene group is evident from the formation of formaldehyde on ozonolysis, a strong i.r. band at 918 cm^{-1}, and broad singlets (each 1H) in the n.m.r. spectrum at τ 5·27 and 5·62. All of these signals disappear on hydrogenation, which gives (after re-oxidation with silver oxide) a dihydro-derivative. In the absence of further unsaturation the $C_{10}H_{16}$ system must comprise two rings, most probably in linear array to account for the formation, on zinc dust fusion, of a product showing u.v. absorption typical of an alkylanthracene. The remainder of the n.m.r. spectrum of cordiachrome B includes a singlet at τ 9·03 from a tertiary methyl, and multiplets at 7·0—8·2 (7H) and at 8·2—8·7 (4H). On this evidence we formulate cordia-

Distribution of cordiachromes in *Cordia* spp.

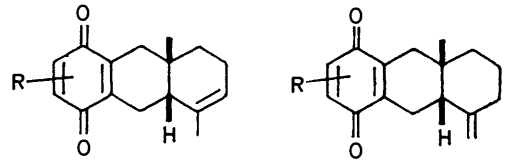
Species	Cordiachrome A	B	C	D	E	F
C. abyssinica R. Br.	++	++	++	−	−	−
C. alba (Jacq.) R. and S.	−	−	−	−	−	−
C. alliodora Ruiz. and Pav.	++	++	++	−	−	−
C. aubletii DC.	−	−	−	−	−	−
C. collococcas L.	−	−	−	−	−	−
C. cylindrostachya Kunth.	−	−	−	−	−	−
C. domestica Roth.	−	−	−	−	−	−
C. gerascanthus P. Br.	++	++	++	−	−	−
C. gharaf (Forsk) Ehr.	+	+	+	−	−	−
C. goeldiana Huber	+	+	+	+	+	+
C. millenii [a] Bak.	++	++	++	+	+	+
C. monoica [b] Roxb.	+	+	−	−	−	−
C. myxa L.	−	−	−	−	−	−
C. obliqua Willd.	−	−	−	−	−	−
C. oblongifolia Thw.	−	−	−	−	−	−
C. platythyrsa Bak.	++	++	++	+	+	+
C. sulcata DC.	−	−	−	−	−	−

[a] Also contains the quinols of cordiachromes A—C. [b] Also contains the quinols of cordiachromes A and B; one wood sample contained neither quinones nor quinols.

[1] Part XXI, T. R. Erdman and R. H. Thomson, *J.C.S. Perkin I*, 1972, 1291.
[2] M. K. Seikel and J. W. Rowe, *Phytochemistry*, 1964, **3**, 27.
[3] J. Ramaldo and R. Yunes, *Rev. Fac. Ing. quim. Univ. nac. Litoral*, 1968, **37**, 109 (*Chem. Abs.*, 1970, **73**, 106,383).
[4] M. Moir, R. H. Thomson, B. M. Hausen, and M. H. Simatupang, *J.C.S. Chem. Comm.*, 1972, 363.

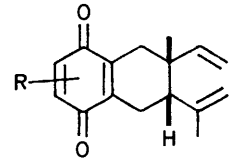
chrome B as (2) (stereochemistry is discussed later), and this structure is further supported by chemical degradation and mass spectroscopy.

Dihydrocordiachrome B (7) is a mixture of epimers, clearly revealed by overlapping methyl signals at τ 9·3 ($CDCl_3$) in the n.m.r. spectrum which separate into two sets of overlapping signals at τ 9·32 and 9·38 in C_6D_6. Oxidation of dihydrocordiachrome B with alkaline hydrogen peroxide, followed by methylation with

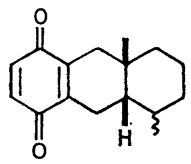


(1) R = H
(4) R = OMe

(2) R = H
(5) R = OMe



(3) R = H
(6) R = OMe



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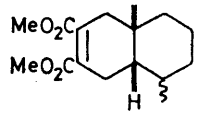

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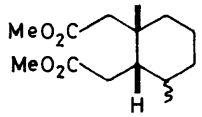

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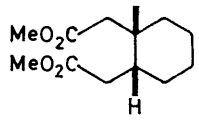

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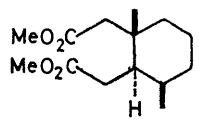

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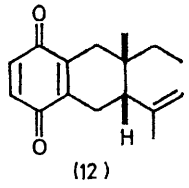

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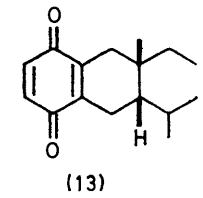
diazomethane, gave the bicyclic epimers (8), $C_{16}H_{24}O_4$, showing $\nu_{max.}$ 1725 and 1650 cm^{-1} (maleic ester [5]). The n.m.r. spectrum confirmed the presence of secondary and tertiary methyl groups, as well as two methoxy-groups, and two methylene groups adjacent to a double bond. Under electron bombardment the molecules fragment in several ways, two of which are suggested in Scheme 1 (all ions were accurately mass measured). Cleavage, as indicated, with hydrogen transfer to give the ions *a* and *b*, is evidently more important than simple retro-Diels–Alder fragmentation with formation of ions *c* and *d*.

[5] E. Dallwigk and E. Briner, *Helv. Chim. Acta*, 1958, **41**, 1033.

Similarly, cordiachrome B fragments predominantly at the alicyclic ring junction (Scheme 2) and, in contrast to



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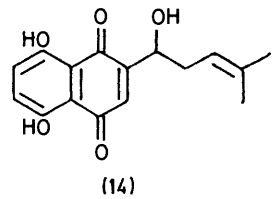

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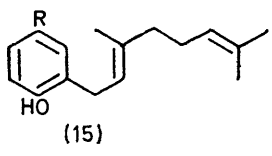

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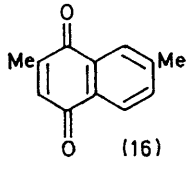

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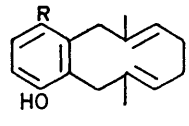

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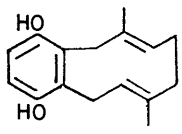

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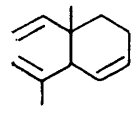

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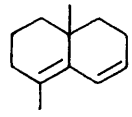

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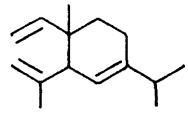
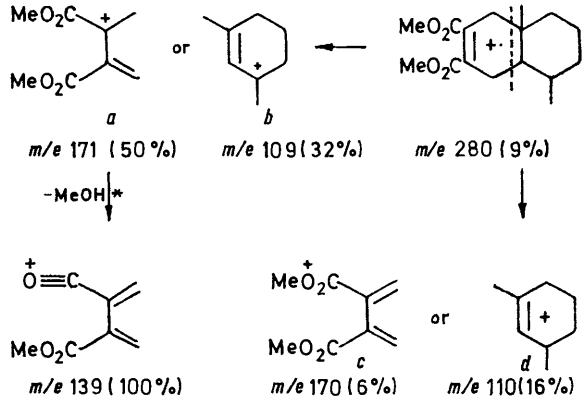


(21)

normal quinone mass spectra, M^+— CO and M^+— 2CO ions are not formed. The peak at *m/e* 186, regarded initially as M^+— 2CO, was shown by accurate mass measurement to be $C_{12}H_{10}O_2$.

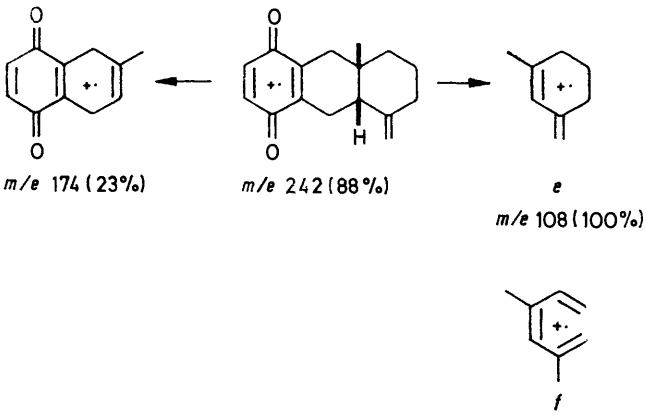
Ozonolysis of dihydrocordiachrome B, followed by oxidation with acidic hydrogen peroxide, and then



SCHEME 1

methylation, gave epimeric diesters (ν_{CO} 1745 cm^{-1}) containing a secondary and a tertiary methyl group (n.m.r.). These are regarded as having structure (9),

although the molecular ion (*m/e* 256) was absent from the mass spectrum, the highest peak at *m/e* 225 corresponding to $C_{13}H_{21}O_3^+$. As the diesters must contain four oxygen atoms, *m/e* 225 is evidently $M^+ -$ MeO. For comparison the *cis*-diester (10) was prepared from the diacid,[6] and, allowing for a difference of 14 mass



SCHEME 2

units between corresponding peaks, the mass spectra of (9) and (10) are virtually identical, the molecular ion also being absent from the spectrum of (10). The n.m.r. spectra of these esters are very similar, both showing methoxy-resonances at τ 6·35 and 6·37, and a tertiary methyl signal at τ 8·95. This indicates that (9) also has *cis*-stereochemistry, which was confirmed by comparison with the known *trans*-isomer (11) prepared [7] by degradation of dihydroeudesmol. The i.r. and mass spectra of (9) and (11) are virtually identical and the compounds are nearly indistinguishable by t.l.c. and g.l.c. However, the n.m.r. spectra are different; in the spectrum of (11) the methoxy-signals coincide at τ 6·36, and the tertiary methyl group resonates at τ 9·07. We conclude that (9) is *cis* as shown, and accordingly formulate cordiachrome B as (2).

Cordiachrome A. This is an isomer of cordiachrome B and on hydrogenation gives a product indistinguishable from dihydrocordiachrome B. All spectroscopic parameters for A and B are very similar except for n.m.r., the spectrum of A showing a broad methyl singlet at τ 8·27 coupled to a vinylic multiplet (1H) at τ 4·69 which collapses to a narrow triplet (*J* 3 Hz) when the methyl frequency is irradiated. Accordingly, cordiachrome A must have structure (1). When first isolated cordiachrome A is contaminated with a red pigment having the same R_F value in all chromatographic systems tried but separable on a column of alumina. Unfortunately the red compound ($\lambda_{max.}$ 485 nm) was irreversibly adsorbed. [A similar red compound is associated with cordiachrome D (4).]

Cordiachrome C. This is also a 2,3-dialkylbenzoquinone isomeric with A and B and its n.m.r. spectrum reveals the presence of five vinylic protons (in addition to the quinone H), five protons adjacent to centres of unsaturation (τ 7·10—7·90), a vinylic methyl, and a tertiary methyl group. Intense i.r. absorption at 990 cm^{-1} suggests the presence of a vinyl group, confirmed in the n.m.r. spectrum by an AMX system centred at τ 4·08 (1H, dd, *J* 11 and 17 Hz), 4·98 (1H, dd, *J* 1 and 11 Hz), and 5·10 (1H, dd, *J* 1 and 17 Hz). Hydrogenation in ethyl acetate (and reoxidation of the quinol) gave a dihydro-derivative in which the vinyl group had been saturated. Both cordiachrome C and its dihydro-derivative show a strong i.r. band at 895 cm^{-1} characteristic of a *gem*-disubstituted olefin, and the n.m.r. spectra of both compounds include signals from terminal methylene protons (2H) and a vinylic methyl group. Hydrogenation of cordiachrome C in acetic acid gave (after reoxidation) a tetrahydro-derivative which was fully saturated, apart from the quinone ring. As cordiachrome C has two olefinic double bonds in addition to the quinone system it follows from the molecular formula ($C_{16}H_{18}O_2$) that a second ring must be present, and we formulate this quinone as (3). The *cis*-stereochemistry is suggested by analogy but has not been established. Di- and tetra-hydrocordiachrome C have structures (12) and (13), respectively. In the mass spectrum of cordiachrome C the base peak is at $M -$ Me and the ion *m/e* 108 (*f* or *e*) is relatively weak.

Cordiachromes D—F. Cordiachrome D shows $\lambda_{max.}$ 276 and 365 nm, $\nu_{max.}$ 1677, 1660, and 1615 cm^{-1}, and the n.m.r. spectrum differs from that of cordiachrome A only in the upfield shift of one quinonoid proton signal to τ 4·14 and replacement of the other by a methoxy-singlet at τ 6·20. Cordiachrome D has thus one of the two structures (4), consistent with all the other spectroscopic data. Cordiachromes E and F have structures (5) and (6), respectively, and are the corresponding methoxy-derivatives of cordiachromes B and C (see Experimental section). A yellow oil identical (R_F and i.r.) with cordiachrome F was obtained by heating cordiachrome C with zinc chloride in methanol; it was probably a mixture of the 5- and 6-methoxy-derivatives but could not be resolved. However the natural and synthetic quinones were indistinguishable by g.l.c. and the possibility remains that cordiachrome F (and hence D and E) is also a mixture of isomers.

Cordiachrome quinols. T.l.c. of the chloroform extract of *C. millenii* revealed a colourless band which was intensely blue in u.v. light and slowly turned red when left on the plate exposed to daylight. When eluted and shaken with silver oxide it yielded a red oil, shown by t.l.c. on silica gel–silver nitrate plates to be a mixture of cordiachromes A (with its red impurity), B, and C. When the fluorescent band was rapidly removed from the plate and kept in acetic anhydride–pyridine a mixture of the three leucodiacetates was obtained. From the relative weights, cordiachromes A, B, and C appear to

[6] R. P. Linstead, A. F. Millidge, and A. L. Walpole, *J. Chem. Soc.*, 1937, 1140; *cf.* G. Stork and S. D. Darling, *J. Amer. Chem. Soc.*, 1960, **82**, 1512.

[7] L. Ruzicka, P. A. Plattner, and A. Fürst, *Helv. Chim. Acta*, 1942, **25**, 1364; P. A. Plattner, A. Fürst, and J. Hellerbach, *ibid.*, 1947, **30**, 2158.

be accompanied by larger amounts of the corresponding quinols in *C. millenii*.

Biogenesis. As the cordiachromes occur in heartwood it is difficult to establish their mode of biogenesis by experiment but their relationship with the other quinones in the Boraginaceae is of interest. These [8] are few in number, alkannin (14) occurring most widely, and the others have the same carbon skeleton with variations in the side chain. Recently, Schmid and Zenk [9] have shown that ring A in alkannin originates from *p*-hydroxybenzoic acid, the remaining ten carbon atoms being derived from mevalonic acid. This suggests that the biogenetic route proceeds by interaction of a phenolic precursor with geranyl pyrophosphate to form (15), which subsequently undergoes oxidative cyclisation, reminiscent of the biogenesis of chimaphilin (16).[8,10] This may involve oxidation at an allylic methyl group and the most attractive route to the cordiachromes is a similar cyclisation which proceeds *via* oxidation of a terminal allylic group in (15) to give a *trans,trans*-cyclodecatriene (17; R probably OH). Acid-catalysed cyclisation of (17), folded in boat conformation (18), can then lead to cordiachromes A and B with *cis*-stereochemistry, while a ' biogenetic Cope rearrangement ' would produce the carbon skeleton of cordiachrome C. The intermediacy of an optically-inactive precursor (17) would explain why *all these quinones are optically inactive* (over the range 260—500 nm). A similar situation has been observed in *Geijera parviflora*,[11] where geijerene (19) and cogeijerene (20) occur together, and in *Dysoxylon frazeranum*,[12] which contains δ-elemene (21), all three hydrocarbons being racemic. (As all the cordiachromes can be isolated by cold extraction with organic solvents they must be natural compounds and not artefacts.) Analogous cyclisations are well known in sesquiterpene biogenesis [13] although *cis*-ring junctions are rare.

EXPERIMENTAL

Spectra were measured for solutions in EtOH (u.v.), for KBr discs (i.r.), and for solutions in $CDCl_3$ (n.m.r.), and t.l.c. and p.l.c. were carried out on layers of silica gel, unless otherwise stated. Petroleum used had b.p. 60—80°.

Extraction of Cordia millenii.—Finely ground heartwood (600 g) of *C. millenii* was extracted (Soxhlet) successively with petroleum (3 l) and chloroform (3 l). Evaporation of the chloroform extract left a dark brown oil (25 g) which was chromatographed on a column of silica gel in chloroform to give a mixture of quinones as an orange oil (5 g). This was separated into three fractions by p.l.c. in hexane–butanone (4 : 1).

Fraction 1 (R_F 0·8). This orange oil (2 g) was rechromatographed on silica gel–10% $AgNO_3$ plates in benzene to give three coloured bands, listed in descending order of R_F.

Band (i). The red oil from this band was passed down a column of neutral alumina in benzene to give *cordiachrome A* (1) (800 mg) as a yellow oil (Found: M^+, 242·1304. $C_{16}H_{18}O_2$ requires M, 242·1307), $\lambda_{max.}$ 250 and 356 nm (log ε 4·19 and 3·22), $\nu_{max.}$ (film) 1652 and 1603 cm^{-1}, τ 3·30 (2H, s, quinone-H), 4·69 (1H, m, –CH=), 6·95—8·80 (9H, m, CH and CH_2), 8·27br (3H, s, MeC=), and 8·96 (3H, s, tertiary Me), *m/e* (%) 242(100), 227(46), 186(35), 174(18), 136(27), 108(87), 93(65), 91(28), and 77(19).

Band (ii). Elution gave *cordiachrome B* (2) as a yellow oil which crystallised from petroleum in golden needles, m.p. 64—65° (500 mg) (Found: M^+, 242·1304. $C_{16}H_{18}O_2$ requires M, 242·1307), $\lambda_{max.}$ 250 and 350 nm (log ε 4·13 and 2·87), $\nu_{max.}$ 1650, 1600, and 918 cm^{-1}, τ 3·30 (2H, s, quinone-H), 5·27 and 5·62 (each 1H, s, $=CH_2$), 7·00—8·16 (7H, m, quinone-CH_2 and CH–C=), 8·16—8·70 (4H, m, CH and CH_2), and 9·03 (3H, s, tertiary Me), *m/e* (%) 242(88), 227(31), 186(64), 174(23), 173(29), 172(29), 108(100), 93(55), 91(26), 79(22), and 77(22).

Band (iii). This material was passed through a column of silica gel in benzene to give *cordiachrome C* (3) (500 mg) as a yellow oil (m.p. 21—22°) (Found: M^+, 242·1307. $C_{16}H_{18}O_2$ requires M, 242·1307), $\lambda_{max.}$ 247 and 343 nm (log ε 4·13 and 2·87), $\nu_{max.}$ (film) 1657, 1604, 990, 913, and 895 cm^{-1}, τ 3·30 (2H, s, quinone-H), 4·08 (1H, dd, *J* 11 and 17 Hz, $-CH{=}CH_2$), 4·98 (1H, dd, *J* 1 and 11 Hz, $-CH{=}CH_2$ *cis*), 5·10 (1H, dd, *J* 1 and 17 Hz, $-CH{=}CH_2$ *trans*), 5·08 and 5·22 (each 1H, s, $>C{=}CH_2$), 7·10—7·90 (5H, m, CH and CH_2), 8·23 (3H, s, MeC=), and 8·87 (3H, s, tertiary Me), *m/e* (%) 242(52), 227(100), 213(29), 200(30), 187(44), 186(29), 174(33), 161(25), 160(25), 115(30), 108(23), 93(39), and 77(35).

Fraction 2 (R_F 0·4). This orange oil (200 mg) was rechromatographed on silica gel–10% $AgNO_3$ plates in chloroform to give three coloured bands, listed in descending order of R_F.

Band (i). Elution gave a red oil (40 mg). A trace of red material was removed by t.l.c. in benzene–chloroform (1 : 3), with multiple development, to give *cordiachrome D* (4) (20 mg) as a yellow oil (Found: M^+, 272·1411. $C_{17}H_{20}O_3$ requires M, 272·1413), $\lambda_{max.}$ 276 and 340—370 nm (log ε 4·07 and 2·59), $\nu_{max.}$ (film) 1677, 1660, 1640, 1615, and 1230 cm^{-1}, τ 4·14 (1H, s, quinone-H), 4·70 (1H, m, –CH=), 6·20 (3H, s, OMe), 6·86—8·80 (9H, m, CH and CH_2), 8·29br (3H, s, MeC=), and 8·98 (3H, s, tertiary Me), *m/e* (%) 272(80), 257(25), 216(15), 108(85), 93(16), 91(33), 85(77), and 83(100).

Band (ii). The yellow oil from this zone crystallised from petroleum–dichloromethane to give *cordiachrome E* (5) (40 mg) as lemon-yellow needles, m.p. 124—126° (Found: M^+, 272·1413. $C_{17}H_{20}O_3$ requires M, 272·1413), $\lambda_{max.}$ 275 and 350—370 nm (log ε 4·07 and 2·61), $\nu_{max.}$ 1669, 1652, 1634, 1610, 1225, and 890 cm^{-1}, τ 4·13 (1H, s, quinone-H), 5·28 and 5·62 (each 1H, s, $=CH_2$), 6·20 (3H, s, OMe), 6·98—8·16 (7H, m, quinone-CH_2 and CH–C=), 8·16—8·80 (4H, m, CH and CH_2), and 9·04 (3H, s, tertiary Me), *m/e* (%) 272(91), 257(26), 216(31), 203(19), 108(91), 93(65), 91(32), 85(65), and 83(100).

Band (iii). Crystallisation of the product from this band afforded *cordiachrome F* (6) (50 mg) as golden yellow needles, m.p. 106—107° (Found: M^+, 272·1414. $C_{17}H_{20}O_3$ requires

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M, 272·1413), $\lambda_{max.}$ 275 and 360—370 nm (log ε 4·13 and 2·70), $\nu_{max.}$ 1670, 1650, 1630, 1612, 1240, 1015, 914, and 895 cm^{-1}, τ 4·08 (1H, dd, *J* 11 and 17 Hz), 4·11 (1H, s, quinone-H), 4·80—5·30 (4H, m, $-CH{=}CH_2$ and $>C{=}CH_2$), 6·19 (3H, s, OMe), 7·10—7·90 (5H, m, CH and CH_2), 8·22 (3H, s, $MeC{=}$), and 8·87 (3H, s, tertiary Me), *m/e* (%) 272(49), 257(100), 225(30), 217(22), 189(18), 115(13), 93(15), 91(24), 85(17), 83(27), and 69(27).

Fraction 3 (R_F 0·10). This was colourless but showed an intense blue u.v. fluorescence. It turned red when left on the plate. Elution then gave a red oil (2·2 g) containing cordiachromes A, B, and C, identified by co-t.l.c. on silica gel–10% $AgNO_3$ plates. Another sample of fraction 3 was rapidly scraped into acetic anhydride (25 ml) and pyridine (10 ml) while still colourless. After 4 days under nitrogen the mixture was poured on ice (100 g) and water (100 ml) and extracted with ether. The extracts were washed, dried ($MgSO_4$), and evaporated, and the residual oil (140 mg) was chromatographed on a column of silica gel. Elution with benzene gave a colourless oil (100 mg), $\nu_{max.}$ (film) 1770 cm^{-1}, shown (n.m.r.) to be a mixture of cordiachrome A, B, and C leucodiacetates in the approx. ratio 1 : 3 : 3. The leucodiacetates were prepared separately, as colourless oils, from each quinone in the usual way, each showing *inter alia* $\nu_{max.}$ 1770 cm^{-1}, τ 3·11 (2H, s, ArH) and 7·70 (6H, s, 2 × OAc).

Cordiachrome F from Cordiachrome C.—Cordiachrome C (30 mg) was heated with anhydrous zinc chloride (50 mg) in methanol (3 ml) for 3 h, poured into water, and extracted with ether. Evaporation of the dried extract left an oil which separated (t.l.c. in chloroform) into starting quinone (15 mg) and a yellow oil (8 mg). The latter would not crystallise, but was identical with cordiachrome F [t.l.c. (two systems) and i.r. spectra (CCl_4)].

Dihydrocordiachromes.—Cordiachrome A (40 mg) in acetic acid (25 ml) was hydrogenated over 10% palladised charcoal (20 mg) for 3 h at room temperature. The solution was filtered into water and extracted with ether, and the extracts were washed with water and saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated. The oily quinol in ether (50 ml) was shaken with silver oxide (1 g) and magnesium sulphate (1 g) for 15 min; the solution was filtered and evaporated, and the residual quinone was chromatographed in benzene on a column of silica gel to give *dihydrocordiachrome A* * (7) (35 mg) as a yellow oil (Found: M^+, 244·1468. $C_{16}H_{20}O_2$ requires *M*, 244·1463), $\lambda_{max.}$ 250 and 347 nm, $\nu_{max.}$ (film) 1655 and 1605 cm^{-1}, τ 3·32 (2H, s, quinone-H), and 9·12—9·14 (6H, overlapping *Me*CH and tertiary Me), *m/e* (%) *inter alia* 244(100), 229(37), 109(74), and 95(97). Similarly cordiachrome B was hydrogenated in ethyl acetate and treated as above to give dihydrocordiachrome B * as a yellow oil identical (t.l.c., g.l.c., and u.v., i.r., n.m.r., and mass spectra) with dihydrocordiachrome A. Hydrogenation of cordiachrome C in ethyl acetate and reoxidation gave *dihydrocordiachrome C* (12) as a yellow oil (Found: M^+, 244·1462. $C_{16}H_{20}O_2$ requires *M*, 244·1463), $\nu_{max.}$ (film) 1655, 1603, and 895 cm^{-1}, τ 3·30 (2H, s, quinone-H), 5·12 and 5·30 (each 1H, s, $=CH_2$), 7·30—8·80 (7H, m, CH and CH_2), 8·25br (3H, s, $MeC{=}$), and 9·00—9·35 (6H, m, $MeCH_2$ and tertiary Me).

Tetrahydrocordiachrome (13).—Dihydrocordiachrome C (35 mg) (or cordiachrome C) was hydrogenated over palladised charcoal in acetic acid and reoxidised as above to give *tetrahydrocordiachrome C* (30 mg) as a yellow oil (Found: M^+, 246·1629. $C_{16}H_{22}O_2$ requires *M*, 246·1620), $\nu_{max.}$ (film) 1655 and 1603 cm^{-1}, τ 3·30 (2H, s, quinone-H), 7·40—8·80 (8H, m, CH and CH_2), and 8·90—9·30 (12H, m, 4 × Me).

Zinc Dust Fusion [14] *of Cordiachrome B.*—An intimate mixture of cordiachrome B (30 mg), zinc dust (600 mg), zinc chloride (1·2 g), and sodium chloride (300 mg) was heated in a Pyrex tube at 290—300° for 20 min. The cooled tube was crushed in 3M-hydrochloric acid (20 ml) and the insoluble material was collected, dried, and extracted with hot benzene. Evaporation left a residue which was chromatographed (t.l.c.) in petroleum revealing a band with intense blue u.v. fluorescence and showing $\lambda_{max.}$ (C_6H_{12}) 248·5, 260, 332, 350, 367, and 386·5 nm [*cf.* 3,9-dimethylanthracene,[15] $\lambda_{max.}$ (EtOH) 260, 332, 350, 367, and 387 nm].

Degradation of Dihydrocordiachrome B.—(a) *With alkaline hydrogen peroxide.* To dihydrocordiachrome B (170 mg) in methanol (10 ml) and 2M-sodium hydroxide (10 ml) was added 30% (100 vol.) hydrogen peroxide (3 ml). The solution was heated on a steam-bath for 15 min, with further additions of peroxide (1 ml) and 2N-sodium hydroxide (2 ml). The cooled mixture was then acidified with 5N-hydrochloric acid and extracted with ether. The extract was washed, dried ($MgSO_4$), and evaporated. The residual dark oil (150 mg) in ether (10 ml) was treated with an excess of diazomethane at 0°. After removal of solvent the crude ester was passed through a column of alumina in benzene yielding an oil (50 mg), the major component of which was isolated by preparative g.l.c. to give the *maleate ester* (8) * as a liquid (Found: M^+, 280·1674. $C_{16}H_{24}O_4$ requires *M*, 280·1674), $\nu_{max.}$ (film) 1725, 1650, and 1260 cm^{-1}, τ 6·25 (6H, s, 2 × OMe), 7·20—7·61 (4H, m, 2 × $CH_2{\cdot}C{=}$), 8·05—8·82 (8H, m, CH and CH_2), and 9·07 (6H, m, *Me*CH and tertiary Me), *m/e* (%) 280(9), 250(7), 249(30), 248(100), 220(25), 171(50), 170(6), 169(27), 139(100), 110(16), 109(32), and 95(60).

(b) *Ozonolysis.* Dihydrocordiachrome B (300 mg) was ozonised in dichloromethane (20 ml) at −60° for 3 h. After removal of solvent *in vacuo* at 25° the oily ozonide was suspended in water (20 ml) with 30% hydrogen peroxide (2 ml) and concentrated sulphuric acid (2 drops), and heated to 100° for 3 h. Extraction with ether and work-up gave a yellowish oil (160 mg) which was treated with an excess of ethereal diazomethane at 0° and left for 2 h at room temperature. The solvent was removed and the residue was passed through a column of alumina in benzene to give the cis-*diester* (9) * as an oil (Found: M^+ − OMe, 225·1487. $C_{13}H_{21}O_3$ requires 225·1490), $\nu_{max.}$ (film) 1745, 1265, and 1165 cm^{-1}, τ 6·35 and 6·37 (each 3H, s, OMe), 8·95 (3H, s, tertiary Me), 9·21 (3H, d, *J* 5·5 Hz, *Me*CH), and CH and CH_2 signals, *m/e* (%) 225(30), 193(13), 184(21), 183(100), 182(45), 151(50), 123(40), 122(20), 109(85), and 108(32). [Ozonolysis of cordiachrome B gave formaldehyde (chromotropic acid test) as the only identified product.]

Dimethyl 1-*Methylcyclohexane*-cis-1,2-*diacetate* (10).—The diacid [7] (100 mg) was methylated with diazomethane and purified as above to give the cis-*diester* (10) (100 mg) (Found: M^+, 211·1334. $C_{12}H_{19}O_3$ requires *M*, 211·1334), $\nu_{max.}$ (film) 1735 cm^{-1}, τ 6·35 and 6·37 (each 3H, s, OMe), 8·95 (3H, s, Me), and CH and CH_2 signals, *m/e* (%) 211(42), 179(26), 170(35), 169(100), 168(73), 137(78), 136(23), 109(86), 108(32), 95(88), 94(50), 74(37), and 67(27).

* A mixture of epimers.

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