# Naturally Occurring Quinones. Part XXIII.[1] Cordiachromes from *Patagonula americana* L.

By **Michael Moir** and **Ronald H. Thomson,*** Department of Chemistry, University of Aberdeen, Old Aberdeen, Scotland

Two optically active (—) pigments, cordiachrome G (4) and leucocordiachrome H (7), have been isolated from the wood of *Patagonula americana*. They have the same benzogeijerene skeleton as cordiachrome C with an additional chiral centre; leucocordiachrome H is a quinol.

In Part XXII [1] we described six cordiachromes, a group of terpenoid benzoquinones found in *Cordia* spp. We now report on two related pigments from *Patagonula*, another genus of the tribe Cordioideae (Boraginaceae). Extraction of the heartwood of *P. americana* afforded three major yellow pigments, two of which belong to the cordiachrome group, the third being a completely unrelated aldehyde.[2]

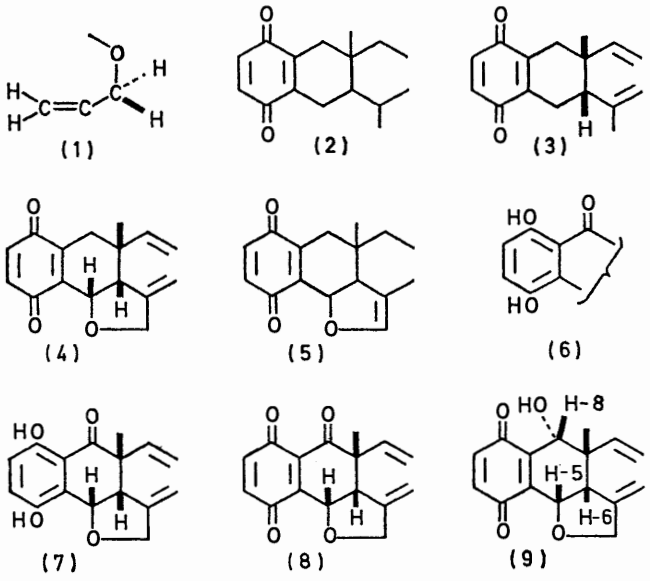
*Cordiachrome G.* This optically active, yellow oil, $C_{16}H_{16}O_3$, was recognised as a 2,3-dialkylbenzoquinone from its spectra ($\lambda_{max.}$ 248 and 326 nm, $\nu_{max.}$ 1660 and 1608 $cm^{-1}$), redox properties, and a positive Craven test. All sixteen protons can be identified in the n.m.r. spectrum. In the olefinic region a singlet (2H) at $\tau$ 3·27 can be assigned to quinonoid protons, and signals from a vinyl group appear at $\tau$ 3·87 (dd, $J$ 11 and 17 Hz), 4·77 (d, $J$ 11 Hz), and 4·86 (d, $J$ 17 Hz). Two broad singlets at $\tau$ 5·26 and 5·29 are attributed to exocyclic methylene protons, one of which is weakly coupled to a geminal AB pair ($J_{gem}$ 13 Hz) at $\tau$ 6·11 suggesting the part structure (1). An AB quartet at $\tau$ 7·40 ($J$ 6 Hz), arising from a methylene group adjacent to the quinone ring, overlaps with a doublet (1H) which is coupled to another doublet (1H) at $\tau$ 5·41 ($J$ *ca.* 1—2 Hz). (All couplings were established by double irradiation experi-

[1] Part XXII, M. Moir and R. H. Thomson, *J.C.S. Perkin I*, 1973, 1352.

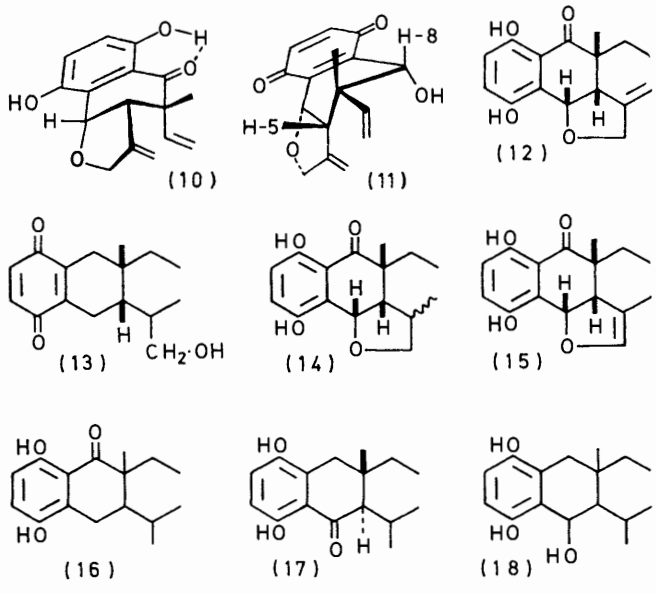
[2] M. Moir and R. H. Thomson, unpublished work.

ments.) A singlet (3H) from a tertiary methyl group at $\tau$ 9·08 completes the spectrum.

After hydrogenation of the pigment over palladium–charcoal, and reoxidation of the quinol with silver oxide, two yellow products were isolated, one of which was identical with tetrahydrocordiachrome C (2) except for




its optical activity ($[\alpha]_D$ +49°). [Tetrahydrocordiachrome C was obtained previously [1] from optically inactive cordiachrome C (3).] The carbon skeleton of




cordiachrome G is thus determined and the structure can now be defined as (4) in accord with the n.m.r. spectrum. Correlation with cordiachrome C (3) implies that the C-6 proton and the C-7 methyl group are *cis*, and the small vicinal coupling constant for H-5 and H-6 ($J_{5,6}$ *ca.* 2 Hz) indicates that these also have a *cis* relationship. This stereochemistry agrees with that deduced for leucocordiachrome H (see later).

In contrast to cordiachromes A—F, cordiachrome G behaves like a normal quinone under electron bombardment, and several ions are formed by consecutive loss of one and two molecules of carbon monoxide (see Scheme 1). The base peak at *m/e* 91 is probably the tropylium ion derived from the molecular ion by fragmentation b (arrows).

The second hydrogenation product obtained from cordiachrome G was a dihydro-derivative, $C_{16}H_{18}O_3$. The n.m.r. spectrum includes singlets from methyl groups at $\tau$ 9·16 (tertiary) and 8·42 (vinylic), a triplet at 9·06 (the methyl part of an ethyl group), and a vinylic multiplet (1H) at $\tau$ 4·16. The dihydro-derivative therefore has structure (5), consistent with the absence of signals from the original vinyl, exocyclic methylene, and oxymethylene groups. Double-bond migration is frequently observed [3] when olefins are hydrogenated over palladium catalysts in acidic solvents.

*Leucocordiachrome H.* The second yellow pigment from *P. americana*, $C_{16}H_{16}O_4$, $[\alpha]_D$ +358°, is not a quinone. It is soluble in aqueous sodium hydroxide and forms a diacetate; the broad absorption at 3280 $cm^{-1}$ then disappears and $\nu_{CO}$ shifts from 1655 to 1696 $cm^{-1}$. The chromophore ($\lambda_{max.}$ 239, 271, and 385 nm) was recognised by comparison with 5,8-dihydroxy-1-tetralone ($\lambda_{max.}$ 236, 266, and 376 nm),[4] and an AB quartet (2H) in the n.m.r. spectrum centred at $\tau$ 2·82 and 3·24 ($J$ 9 Hz) confirms the partial structure (6). The remainder of the n.m.r. spectrum shows a striking resemblance to that of cordiachrome G (4) except that the quartet at $\tau$ 7·40, assigned to the methylene protons adjacent to the quinone ring, is absent. This pigment is therefore the quinol (7). For convenience proton assignments were verified by decoupling experiments with the diacetate; the low value for $J_{5,6}$ (*ca.* 2 Hz) again suggests the *cis* arrangement for H-5 and H-6.

Cordiachrome H (8) was not found in *P. americana* but was obtained from the quinol (7) by oxidation with silver oxide as an unstable orange oil, $\nu_{max.}$ 1720, 1675, and 1630 $cm^{-1}$, $\lambda_{max.}$ 248 and 382 nm (log $\varepsilon$ 3·89 and 3·01). The n.m.r. spectrum of (8) was similar to that of (7) with the aromatic quartet shifted upfield (in cordiachromes A, B, C, and G, the quinonoid protons resonate as a singlet) but no mass spectrum could be obtained at low probe temperatures; the weak spectrum obtained at 240° was that of the quinol (7).

Three unsuccessful attempts were made to convert leucocordiachrome H (7) into cordiachrome G (4) by reduction of the chelated carbonyl group. Treatment of *o*- or *p*-hydroxy-ketones in alkaline solution with sodium borohydride usually gives the corresponding methylene compound, whereas *m*-hydroxy-ketones are reduced only to the *m*-hydroxybenzyl alcohol.[5] Reduction of leucocordiachrome H in this way, followed by

[3] M. Freifelder, 'Practical Catalytic Hydrogenation,' Wiley, London, 1971.

[4] I. A. Kaye, R. S. Matthews, and A. A. Scala, *J. Chem. Soc.*, 1964, 2816.

[5] K. H. Bell, *Austral. J. Chem.*, 1969, **22**, 601.

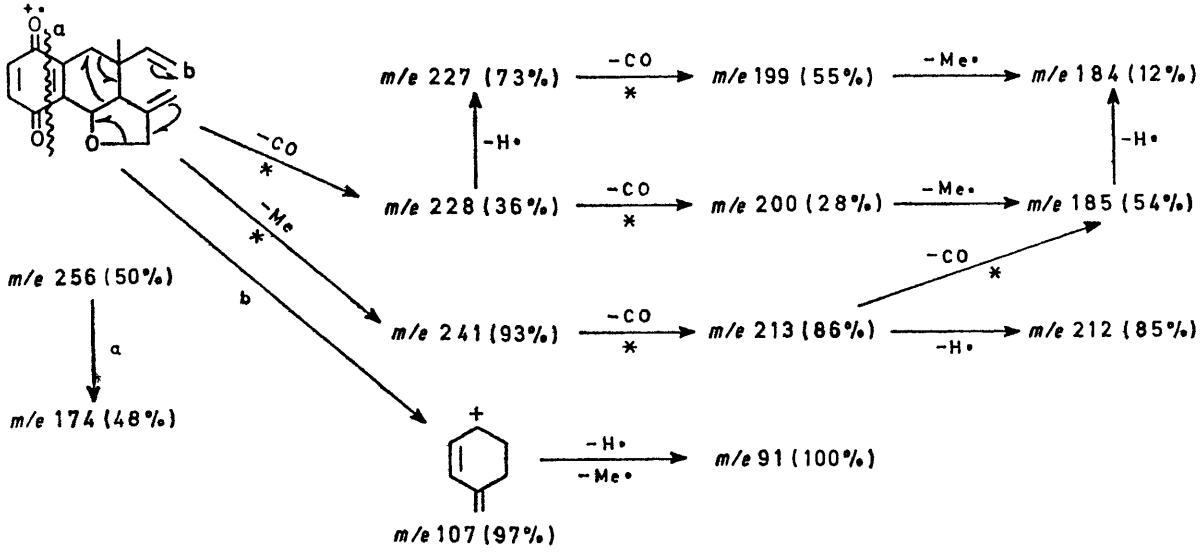
oxidative work-up, gave only the hydroxy-quinone (9); it was unstable and slowly reverted to the isomeric dihydroxy-ketone (7). The stereochemistry shown in formula (9) is suggested by the n.m.r. signal from H-6 ($\tau$ 7·34) which is a double doublet coupled to H-5 at $\tau$ 5·42 ($J$ 2 Hz) and to another proton resonating at $\tau$ 5·13 ($J$ 5 Hz) which can only be H-8. Dreiding models show that the most favourable structure for leucocordiachrome H which would account for the formation of only one epimer on reduction with borohydride is (7), in conformation (10), in which the α-face of the molecule is heavily crowded whereas the β-face is almost flat. The borohydride reduction product is therefore (9), and in the most favourable conformation (11) with the methyl group at C-7 axial, it can be seen that H-6 and H-8 are linked by three carbon atoms in a W-conformation. The resulting long-range coupling [6] explains why the signal from H-6 is a double doublet. An attempt to prepare the tosylate of (9), with a view to producing leucocordiachrome G by subsequent hydrogenolysis, was unsuccessful.

The conversion of aldehydes and ketones into the corresponding methylene compounds by reduction of their tosylhydrazones with sodium borohydride has been reported.[7] Treatment of (7) with an excess of toluene-*p*-sulphonohydrazide in boiling methanol failed to give the desired derivatives, no doubt for steric reasons, and the product, $C_{16}H_{18}O_4$, obtained in 90% yield, was identified as the dihydro-derivative (12). This was evident from its spectroscopic properties, in particular the disappearance from the n.m.r. spectrum of the three vinyl proton signals and the appearance of a quartet (2H) at $\tau$ 8·33 and a triplet (3H) at $\tau$ 9·07, and the presence of a significant peak (31%) at $M - 29$ in the mass spectrum. The reducing agent is obviously diimide generated from toluene-*p*-sulphonohydrazide by thermolysis.[8]

Hydrogenation of leucocordiachrome H over palladium–charcoal in ethanol containing 5% perchloric acid, followed by aerial oxidation, gave four new yellow compounds (CH1—CH4) and a trace of tetrahydrocordiachrome G (2) (identified by t.l.c. and g.l.c. only).

*CH*1. This compound, a yellow oil, $C_{16}H_{22}O_3$, was recognised as a benzoquinone by the usual chemical and spectroscopic criteria. The absence of vinylic (other than quinonoid) proton signals in its n.m.r. spectrum and the presence of a methyl doublet at $\tau$ 8·90 and a methyl triplet at $\tau$ 9·08 established that both acyclic double bonds had been saturated, and a four-proton multiplet at $\tau$ 7·5 arising from methylene protons adjacent to the quinone ring showed that complete reduction of the C-8 carbonyl group and hydrogenolysis of the allylic ether at C-5 had occurred. The presence of a hydroxymethyl group is indicated by a two-proton multiplet at $\tau$ 6·5 and hydroxy-absorption in the i.r. spectrum at 3500 cm$^{-1}$. CH1 is therefore formulated as (13). The mass spectrum is consistent with this structure and an important peak at *m/e* 203 is assigned to the ion *a* (Scheme 2); the position of the hydrogen atom transferred is arbitrary. The $M + 2$ ion, usually attributed to interaction with moisture, is actually more intense than the molecular ion peak. This is very unusual for a 1,4-benzoquinone [9] and may have arisen from a trace of quinol in the sample of CH1.

*CH*2. This has the molecular formula $C_{16}H_{20}O_4$, the same chromophore ($\lambda_{max.}$ 240, 261, and 382 nm, $\nu_{max.}$ 3250, 1650, and 1598 cm$^{-1}$) as leucocordiachrome H, and shows an aromatic AB quartet in the n.m.r. spectrum




SCHEME 1

[6] L.M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, London, 1969.

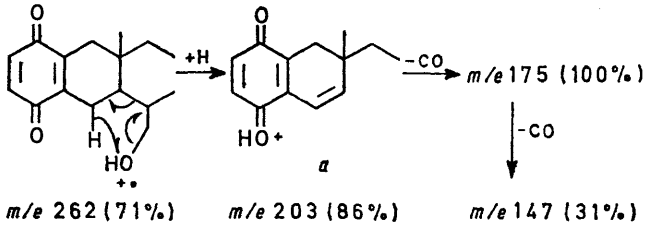
[7] L. Cagliotti and P. Grasselli, *Chem. and Ind.*, 1964, 153.

[8] R. S. Dewey and E. E. van Tamelen, *J. Amer. Chem. Soc.*, 1961, **83**, 3729.

[9] *Cf.* J. Heiss, K.-P. Zeller, and A. Rieker, *Org. Mass. Spectrometry*, 1969, **2**, 1325.

but no vinylic absorption. However in the high field region there is a doublet (3H) at τ 9·02 and a triplet (3H) at τ 9·20 attributable to secondary and primary methyl groups, respectively. These data are consistent with structure (14). In support a broad multiplet (2H) at τ 6·42 can be assigned to the oxymethylene protons, and a narrow doublet at τ 5·26 (*J* 2 Hz) to H-5, while the mass spectrum includes important peaks at $M - H_2O$ (32%), $M - C_2H_5$ (22%), and $M - H_2O - C_2H_5$ (50%).

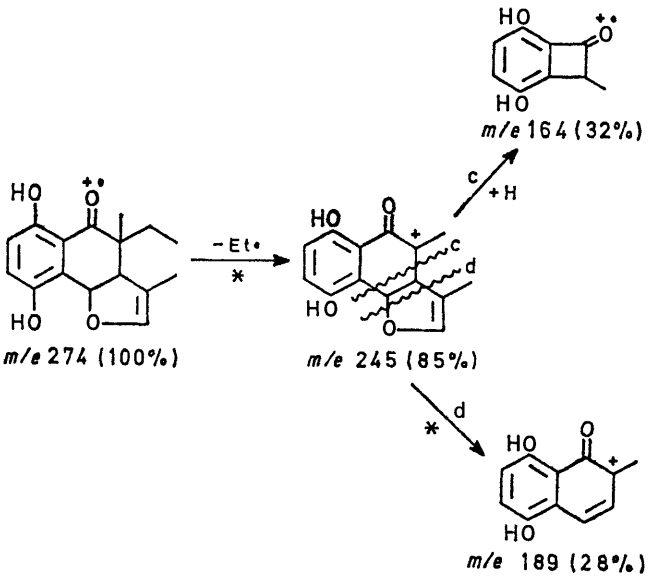
*CH3*. This was the major product (32%) from the hydrogenation of leucocordiachrome H, and the u.v., i.r., and n.m.r. spectra showed that it retained the 2-acyl-1,4-quinol system. The n.m.r. spectrum also established that the vinyl group had been saturated [quartet (2H) at τ 8·45 coupled to a triplet (3H) at τ 9·07], and that the signals of the oxymethylene and exocyclic




SCHEME 2

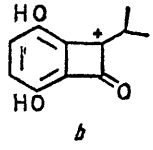
methylene groups had been replaced by a multiplet (1H) at τ 3·95 coupled to a broad singlet (3H) at τ 8·39. CH3 thus has structure (15), and its formation is another example of double-bond migration [*cf.* (5)]. The signals from H-5 and H-6 are doublets (*J* 2 Hz) at τ 4·86 and 7·38, respectively, providing further evidence for the *cis*-stereochemistry of leucocordiachrome H at these centres. In the mass spectrum of CH3 the molecular ion forms the base peak, the next most intense ion being $M$ — Et, which fragments as indicated (Scheme 3) to give peaks at *m/e* 164 and 189. The $M$ — Me ion is much less intense but fragments in the same way to give peaks at *m/e* 178 and 203.

*CH4*. This was a yellow oil, $C_{16}H_{22}O_3$, and is clearly another 2-acyl-1,4-quinol on the basis of spectroscopic evidence. In addition to the aromatic AB quartet the n.m.r. spectrum (in $C_6H_6$) revealed the presence of two benzylic protons (singlet at τ 7·43), a tertiary methyl singlet (τ 9·26), and signals from an ethyl group (2H quartet at τ 8·79 coupled to a methyl triplet at τ 9·36) and an isopropyl group (1H multiplet at τ 8·14 coupled to methyl doublets at τ 8·96 and 9·37). The remaining resonance in the spectrum is a one-proton doublet at τ 7·84 which is coupled to the isopropyl methine multiplet (all couplings were confirmed by appropriate double resonance experiments). At first sight these data suggest that CH4 is the dihydroxytetralone (16), formed by hydrogenolysis of CH3 (15), but the chemical shift of H-6 (τ 7·84) is in much better accord with the isomeric structure (17) and this also explains why H-6 is coupled only to the isopropyl methine proton. The mass spectrum is broadly similar to those of CH2 and CH3 but the $M$ — Et peak is weak (9%) and the $M$ — $Pr^i$ peak is relatively strong (46%). The most intense peak (apart from the molecular ion) at *m/e* 191 corresponds to




SCHEME 3

ion *b*. A negative optical rotation for CH4 ($[\alpha]_D$ −18°) suggests that epimerisation may have occurred at C-6 under acidic conditions, and as the specific rotation was

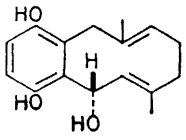


*b*

scarcely affected by heating for 1 h in ethanolic hydrochloric acid, structure (17) is preferred, with a *trans*-arrangement of the ethyl and isopropyl groups. A total non-equivalence [7] of 0·41 p.p.m. between the isopropyl methyl groups can be attributed to the adjacent asymmetric centres, and to some restricted rotation of the isopropyl group with associated long-range deshielding by the adjacent carbonyl group. The formation of (17) can be seen as a series of hydrogenations and hydrogenolyses of leucocordiachrome—leading to (18), followed by oxidation of the benzylic alcohol function during work-up either by air or by another quinone.

*Biogenesis*. A significant difference between the cordiachromes of *C. millenii* [1] and those now reported from *P. americana* is that the latter are optically active. They possess an additional chiral centre but the conversion of cordiachrome G (4) into optically active (—) tetrahydrocordiachrome C (3) shows that the activity does not reside entirely at C-5. We suggested [1] that cordiachrome C was derived from an optically inactive benzocyclodecatriene derivative, and the optically-active pigments of *P. americana* are presumably formed by a similar pathway modified by stereospecific allylic oxidation at some stage, *e.g.* (19), prior to formation of the tetrahydrofuran ring and the *o*-isopropenylvinyl system.

*Ehretia* and *Tournefortia* are two other woody genera of the Boraginaceae. Small samples of *E. tournefolia*



(19)

and *T. astrotricha* were examined but no cordiachromes were detected.

EXPERIMENTAL

Spectra were measured for solutions in EtOH (u.v.), for KBr discs (i.r.), and for solutions in $CDCl_3$ (n.m.r.) unless otherwise stated. T.l.c. was carried out on silica gel plates; petroleum had b.p. 60—80°.

*Extraction of* Patagonula americana.—Finely ground heartwood (750 g) was extracted (Soxhlet) successively with petroleum (8 l) and chloroform (8 l). The petroleum extract, an orange oil (5·5 g), was transferred to a column of silica gel and eluted with benzene. Further elution with increasing proportions of chloroform displaced an orange band as red (750 mg) and yellow (2·68 g) fractions. Evaporation of the chloroform extract gave a heavy brown tar (55 g) which was chromatographed in chloroform. An orange band was collected, and separated by p.l.c. in hexane–butanone (85 : 15) into red (150 mg) and yellow (5·96 g) fractions. The red fractions contained very little pigment and were not examined. The yellow fractions were combined and separated by p.l.c. in hexane–butanone (10 : 3) to give three major yellow bands containing, in decreasing $R_F$ order, cordiachrome G, leucocordiachrome H, and an aldehyde.[2]

*Band* (i). This material was purified by further chromatography on a column of silica gel in benzene to give *cordiachrome G* (4) (100 mg) as a yellow oil (Found: C, 74·9; H, 6·3%; $M^+$, 256. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·2%; $M$, 256), $[\alpha]_D^{26}$ +18° (*c* 3·0 in $CHCl_3$), $\lambda_{max.}$ 248 and 326 nm (log ε 4·10 and 2·76), $\nu_{max.}$ (film) 1660, 1608, 1302, 1065, 900, and 850 cm$^{-1}$, τ ($CCl_4$) 3·27 (2H, s, quinone-H), 3·87 (1H, dd, *J* 11 and 17 Hz, $-CH{=}CH_2$), 4·77 (1H, d, *J* 11 Hz, $-CH{=}CH_2$ *cis*), 4·86 (1H, d, *J* 17 Hz, $-CH{=}CH_2$ *trans*), 5·26 and 5·29 (each 1H, s, $C{=}CH_2$), 5·41 (1H, d, *J ca.* 1·5 Hz, quinone–CH–O), 6·11 (2H, q, *J* 13 Hz, $O{-}CH_2{-}C{=}$), 7·40 (2H, q, *J* 6 Hz, quinone-$CH_2$), 7·42 (1H, d, *J ca.* 1·5 Hz, $-CH{-}C{=}$), and 9·08 (3H, s, tertiary Me), *m/e* (%) 256(50), 241(93), 228(36), 227(73), 213(86), 212(85), 199(55), 185(53), 174(48), 173(89), 150(36), 149(12), 115(39), 107(97), and 91(100).

*Band* (ii). The brown solid from this zone crystallised from petroleum–dichloromethane to give *leucocordiachrome H* (7) (1·16 g) as yellow needles, m.p. 175—176°, $[\alpha]_D^{25}$ +358° (*c* 0·71 in $CHCl_3$) (Found: C, 70·9; H, 6·1%; $M^+$, 272. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%; $M$, 272), $\lambda_{max.}$ 241sh, 271, and 385 nm (log ε 3·97, 3·69, and 3·64), $\nu_{max.}$ 3280br, 1655, 1620, 1590, 1040, 915, and 876 cm$^{-1}$, τ [$CCl_4$–$(CD_3)_2CO$ (9 : 1)] 2·82 and 3·24 (each 1H, d, *J* 9 Hz, ArH), 3·79 (1H, dd, *J* 11 and 17 Hz, $-CH{=}CH_2$), 4·80 (2H, m, $-CH{=}CH_2$), 5·03 (3H, m, $C{=}CH_2$ and ArCH–O), 6·08 (2H, q, $O{-}CH_2{-}C{=}$), 6·84 (1H, d, *J* 2 Hz, $-CH{-}C{=}$), and 8·98 (3H, s, tertiary Me), *m/e* (%) 272(100), 257(7), 254(9), 239(26), 211(9), 176(63), 165(47), 115(11), and 91(18). The *diacetate* separated from petroleum–dichloromethane in needles, m.p. 154—155° (Found: C, 67·7; H, 5·9. $C_{20}H_{20}O_6$ requires C, 67·5; H, 5·6%), $\lambda_{max.}$ 248 and 303 nm (log ε 3·93 and 3·44), $\nu_{max.}$ 1772, 1696, 1650, 1612, 1190, 1064, and 918 cm$^{-1}$, τ ($CCl_4$) 2·65 and 2·93 (each 1H, d, *J* 9 Hz, ArH), 3·79 (1H, dd, *J* 11 and 17 Hz, $-CH{=}CH_2$), 4·82 (1H, d, *J* 11 Hz, $-CH{=}CH_2$ *cis*), 4·84 (1H, *J* 17 Hz, $-CH{=}CH_2$ *trans*), 5·07br (2H, s, $C{=}CH_2$), 5·30 (1H, d, *J* 2 Hz, ArCH–O), 6·13 (2H, q, *J* 14 Hz, $=C{-}CH_2{-}O$), 6·90 (1H, d, *J* 2 Hz, $-CH{-}C{=}$), 7·69 (6H, s, OAc), and 8·97 (3H, s, tertiary Me).

*Cordiachrome H* (8).—Leucocordiachrome H (30 mg) was shaken with silver oxide (500 mg) and anhydrous magnesium sulphate (200 mg) for 30 min; the mixture was filtered and evaporated, and the residue was purified by t.l.c. in hexane–butanone (7 : 3). The major red band yielded cordiachrome G (30 mg) as an unstable orange oil, $\lambda_{max.}$ 248 and 382 nm (log ε 3·89 and 3·01), $\nu_{max.}$ (film) 1720, 1675, and 1630 cm$^{-1}$, τ ($CCl_4$) 3·10 and 3·32 (each 1H, d, *J* 10 Hz, quinone-H), 3·90 (1H, dd, *J* 10 and 18 Hz, $-CH{=}CH_2$), 4·60—5·10 (4H, m, $-CH{=}CH_2$ and $C{=}CH_2$), 5·20 (1H, d, *J* 2·5 Hz, quinone-CH–O), 5·88 (2H, m, $O{-}CH_2{-}C{=}$), 6·90 (1H, d, *J* 2·5 Hz, $-CH{-}C{=}$), and 8·92 (3H, s, tertiary Me), *m/e* 272·1041; the fragmentation pattern was the same as that of leucocordiachrome H.

*Hydrogenation of Cordiachrome G.*—The quinone (30 mg) was hydrogenated over 10% palladium–charcoal in ethanol containing 5% acetic acid at room temperature for 3 h. After removal of the catalyst, and evaporation, the residual oil in ether (20 ml) was stirred with silver oxide (0·58 g) and anhydrous magnesium sulphate (0·5 g) for 30 min. After work-up the product was separated by t.l.c. in chloroform into two major bands. One yielded tetrahydrocordiachrome C (2) (6 mg), $[\alpha]_D^{23}$ +49 ± 2° (*c* 0·60 in $CHCl_3$), identical (t.l.c., g.l.c., and u.v., i.r., and n.m.r. spectra) with a sample prepared by hydrogenation of cordiachrome C. The other band yielded the *quinone* (5) (6 mg) as a yellow oil (Found: $M^+$, 258·1267. $C_{16}H_{18}O_3$ requires $M$, 258·1256), $\nu_{max.}$ (film) 1664, 1630, 1609, and 1120 cm$^{-1}$, τ ($CCl_4$) 3·32 (2H, s, quinone-H), 4·16 (1H, s, O–CH=C), 5·30 (1H, m, quinone-CH–O), 7·45 (3H, m, quinone-$CH_2$ and $CH{-}C{=}$), 8·42 (3H, s, MeC=), 9·06 (3H, t, *J* 7 Hz, $MeCH_2$), and 9·16 (3H, s, tertiary Me).

*Reduction of Leucocordiachrome H.*—(a) *With sodium borohydride.* Leucocordiachrome H (100 mg, 0·378 mmol) in 0·75M-sodium hydroxide (1 ml, 0·75 mmol) was treated with sodium borohydride (30 mg, 0·80 mmol) and water (4 ml). The mixture was cautiously warmed on a steam-bath for 1 h, cooled, acidified with 5M-hydrochloric acid, and extracted with chloroform (15 ml). The washed and dried ($MgSO_4$) extract was shaken with silver oxide (0·5 g) for 15 min, filtered, and evaporated; the residue was purified by t.l.c. in hexane–butanone (7 : 3) to yield the *quinone* (9) (52 mg, 51%) as an unstable, yellow, oily solid (Found: $M^+$, 272·1052. $C_{16}H_{16}O_4$ requires $M$, 272·1048), $\lambda_{max.}$ 249 and 315 nm, $\nu_{max.}$ (film) 3500, 1664, and 1609 cm$^{-1}$, τ ($CCl_4$) 3·22 (2H, s, quinone-H), 3·90 (1H, dd, *J* 11 and 17 Hz, $-CH{=}CH_2$), 4·86 (1H, d, *J* 17 Hz, $-CH{=}CH_2$ *trans*), 4·87 (1H, d, *J* 11 Hz, $-CH{=}CH_2$ *cis*), 5·07 and 5·23 (each 1H, s, $C{=}CH_2$), 5·13 (1H, d, *J* 5 Hz, ArCH–OH), 5·42 (1H, d, *J* 2 Hz, ArCH–O), 6·08 (2H, q, $-O{-}CH_2{-}C{=}$), 6·50br (1H, s, OH), 7·34 (1H, dd, *J* 2 and 5 Hz, $-CH{-}C{=}$), and 9·05 (3H, s, tertiary Me). When the reduction was carried out with a ten-fold excess of borohydride the quinone (9) was isolated in 80% yield. It slowly reverted to leucocordiachrome H.

(b) *With di-imide.* Leucocordiachrome H (20 mg) was heated with toluene-*p*-sulphonohydrazide (50 mg) in

methanol (4 ml) under reflux for 18 h. The solvent was removed and the residue was purified by t.l.c. in chloroform–methanol (19 : 1) and crystallised from benzene to give the *quinone* (12) as pale yellow needles, m.p. 182—184° (18 mg) (Found: $M^+$, 274·1175. $C_{16}H_{18}O_4$ requires $M$, 274·1205), $\tau$ [$CCl_4$–$(CD_3)_2CO$] 2·84 and 3·25 (each 1H, d, $J$ 9 Hz, ArH), 5·10 (3H, m, ArC*H*–O and C=$CH_2$), 6·11 (2H, m, O–$CH_2$–C=), 6·95 (1H, d, $J$ 2·5 Hz, –CH–C=), 8·33 (2H, q, $J$ 7 Hz, C*H*$_2$Me), 9·07 (3H, t, $J$ 7 Hz, $CH_2$*Me*), and 9·15 (3H, s, tertiary Me), *m/e* (%) 274(100), 256(15), 245(31), 241(16), 227(48), 178(18), and 164(48).

(c) *Hydrogenation*. Leucocordiachrome H (55 mg) was shaken with hydrogen and 10% palladium–charcoal in ethanol (containing 5% perchloric acid) (20 ml) at atmospheric pressure for 3 h. The solution was filtered, poured into water, and extracted with ether. The extract was washed, dried ($MgSO_4$), and evaporated leaving a yellow oil which was separated by t.l.c. in chloroform into five major components, listed in increasing $R_F$ order.

*Band* (i). This gave the *quinone CH*1 (13) (13 mg) as a yellow oil (Found: $M^+$, 262·1561. $C_{16}H_{22}O_3$ requires $M$, 262·1569), $\lambda_{max.}$ 250 and 348 nm, $\nu_{max.}$ (film) 3500, 1655, and 1605 $cm^{-1}$, $\tau$ 3·31 (2H, s, quinone-H), 6·50 (2H, m, C*H*$_2$·OH), 7·50 (4H, m, quinone-$CH_2$), 8·50 (2H, m, C*H*$_2$Me), 8·90 (3H, d, $J$ 7 Hz, CH*Me*), 9·00 (3H, s, tertiary Me), and 9·08 (3H, t, $J$ 7 Hz, $CH_2$*Me*), *m/e* (%) 264(80), 262(71), 246(13), 244(8), 231(25), 229(23), 217(18), 215(31), 203(86), 187(40), 175(100), 174(53), 173(43), 161(46), 147(31), and 136(74).

*Band* (ii) yielded a brown solid which crystallised from benzene to give the *quinol CH*2 (14) as pale yellow needles, m.p. 205—207° (decomp.) (5 mg) (Found: $M^+$, 276·1341. $C_{16}H_{20}O_4$ requires $M$, 276·1361), $\lambda_{max.}$ 240, 261sh, and 382 nm (log $\varepsilon$ 3·95, 3·69, and 3·53), $\nu_{max.}$ 3250, 1650, 1630, and 1598 $cm^{-1}$, $\tau$ 2·85 and 3·12 (each 1H, d, $J$ 9 Hz, ArH), 5·26 (1H, d, $J$ 2 Hz, ArCH–O), 6·42 (2H, m, O–$CH_2$), 9·02 (3H, d, $J$ 7 Hz, CH*Me*), 9·15 (3H, s, tertiary Me), 9·20 (3H, t, $J$ 7 Hz, $CH_2$*Me*), and CH and $CH_2$ signals, *m/e* (%) 276(100), 258(32), 247(22), 229(50), 217(20), 203(19), 189(31), and 164(28).

*Band* (iii). The solid obtained crystallised from benzene to give the *quinol CH*3 (15) as pale yellow needles, m.p. 160—161° (18 mg) (Found: $M^+$, 274·1189. $C_{16}H_{18}O_4$ requires $M$, 274·1205), $\lambda_{max.}$ 242, 260sh, and 383 nm (log $\varepsilon$ 4·02, 3·59, and 3·68), $\nu_{max.}$ 3380, 1670, 1656, 1630, and 1598 $cm^{-1}$, $\tau$ 2·93 and 3·17 (each 1H, d, $J$ 9 Hz, ArH), 3·95 (1H, m, O–C*H*=CMe), 4·86 (1H, d, $J$ 2 Hz, ArCH–O), 7·38 (1H, d, $J$ 2 Hz, –CH–C=), 8·39 (3H, s, =CMe), 8·45 (2H, q, $J$ 7 Hz, C*H*$_2$Me), 9·07 (3H, t, $J$ 7 Hz, $CH_2$*Me*), and 9·12 (3H, s, tertiary Me), *m/e* (%) 275(42), 274(100), 259(20), 246(27), 245(85), 229(50), 227(27), 217(31), 203(26), 189(28), 178(22), and 164(78).

*Band* (iv). This gave the *quinol CH*4 (17) as a yellow oil (15 mg), $[\alpha]_D$ −18° (*c* 1·5 in $CHCl_3$) (Found: $M^+$, 262·1564. $C_{16}H_{22}O_3$ requires $M$, 262·1569), $\lambda_{max.}$ 238, 268, and 380 nm, $\nu_{max.}$ (film) 3400, 1648, and 1595 $cm^{-1}$, $\tau$ ($C_6D_6$) 3·23 and 3·56 (each 1H, d, $J$ 9 Hz, ArH), 7·43 (2H, s, $ArCH_2$), 7·84 [1H, d, 2·5 Hz, –C(=O)C*H*–CH–], 8·14 (1H, double septet, $J$ 2 and 7 Hz, CH·C*H*$Me_2$), 8·79 (2H, q, $J$ 7 Hz, C*H*$_2$Me), 8·96 and 9·37 (each 3H, d, $J$ 7 Hz, CH$Me_2$), 9·26 (3H, s, tertiary Me), and 9·36 (3H, t, $J$ 7 Hz, $CH_2$*Me*), *m/e* (%) 262(100), 247(7), 245(7), 233(9), 229(46), 205(24), 191(93), 178(23), 177(23), and 163(10).

One of us (M. M.) thanks the Chemical Society for a Briggs Scholarship. We also thank the Instituto De Pesquisas Technológicas and the Instituto Florestal, São Paulo, Brazil, for samples of *P. americana*, Dr. C. D. Adams for *Ehretia* and *Tournefortia* material, and P.C.M.U., Aldermaston, for the mass spectra.

[3/129 *Received*, 19*th January*, 1973]