The Hydroquinone Terpenoids of *Cordia alliodora*

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Six new geranyl-hydroquinone-derived compounds have been isolated from the acetone extract of *Cordia alliodora* heartwood and characterized. The structural character of these compounds allows the proposal of a detailed biogenetic pathway to the geranyl-hydroquinone and geranyl-benzoquinone constituents of *Cordia* sp.

Cordia alliodora Ruiz. and Pav. (Boraginaceae) is a native tropical American tree whose wood is recognized for its durability in marine use.[1,2] Recent examinations of the extractive constituents of this wood have established the presence of cordiachromes A—C[3] (1)—(3) and the geranyl aldehyde hydroquinone alliodorin [4] (4). We now report the isolation and characterization of six new compounds from the acetone extract of *C. alliodora* heartwood.

The crude acetone extract yielded a benzene-insoluble fraction shown by t.l.c. to contain several compounds which reduced silver nitrate. Preparative absorption gel chromatography and column chromatography on silica gel afforded six compounds, reported here in decreasing order of elution from the column and t.l.c. R_F value (benzene–ethanol, 9 : 1).

Cordiachromen A (5) was obtained as an oil ($C_{16}H_{20}O_2$), $\lambda_{max.}$ 331 and 363 nm, slowly reducing silver nitrate and forming a phenolic monoacetate (oil). The n.m.r. spectrum of compound (5) showed signals for a single chromen methyl group [δ 1.36(s)], two vinyl methyl groups [δ 1.56 and 1.65 (each s)], four alkyl protons [δ 1.90—2.26 (m)], two vicinal vinyl (chromen) protons [δ 5.56 and 6.22 (d, *J* 10 Hz)], a single aromatic hydroxy-proton [δ 5.96br(s)], a single vinyl proton [δ 5.09 (t, *J* 6 Hz)], and three aromatic protons [δ 6.40—6.64 (m)]. The monoacetate showed δ 2.24 (3 H, s). These data agree with structure (5), which was unequivocally established through synthesis from geranylhydroquinone (6) (obtained by condensation of geraniol and hydroquinone catalysed by aqueous oxalic acid), by oxidation (Ag_2O) and cyclisation in boiling pyridine.[5]

Cordiaquinol C (7) immediately reduces silver nitrate and was obtained by column chromatography as an optically inactive oil ($C_{16}H_{20}O_2$), $\lambda_{max.}$ 290 nm, which forms an aromatic diacetate. The n.m.r. spectrum of compound (7) shows signals for a tertiary methyl group [δ 1.16(s)], a vinylic methyl group [δ 1.78(s)], five alkyl protons [δ 2.00—2.96(m)], and three vinylic protons (δ 4.78—4.90), one of which is associated with the AMX spectral pattern of a terminal vinyl group whose remaining protons resonate at δ 4.93 (dd, *J* 18 and 2 Hz) and 6.07 (dd, *J* 18 and 11 Hz). Two aromatic protons [δ 6.49(s)] and two aromatic hydroxy-protons [δ 7.40(s)] complete the spectrum.

Acetylation confirmed the presence of two aromatic hydroxy groups [δ 2.27 (6 H, s)] and expanded the three-proton multiplet (δ 4.85—5.07) thereby allowing the designation of the three vinyl proton AMX pattern [δ 4.93 (dd, *J* 18 and 2 Hz), 4.97 (dd, *J* 11 and 2 Hz), and 5.46 (dd, *J* 11 and 18 Hz)] of a terminal vinyl group. These data suggest structure (7) for cordiaquinol C and, therefore, that it is the quinol precursor of the previously reported cordiachrome C (3). The structural assignment (7) was confirmed by oxidation with silver oxide to a quinone (3), whose properties were identical with those reported for cordiachrome C.[3]

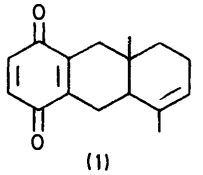
Alliodorol (8), obtained chromatographically in conjunction with alliodorin (4) as a dark oil ($C_{16}H_{22}O_3$), rapidly reduces silver nitrate, shows $\lambda_{max.}$ 293 nm, and forms a triacetate. The n.m.r. spectrum shows signals for two vinylic methyl groups [δ 1.64 (6 H, s)], four alkyl protons (δ 2.06—2.30), a benzylic methylene group [δ 3.27 (d, *J* 7 Hz)], an allyl alcohol methylene group [δ 4.05br (s)], two vinyl protons [δ 5.28 and 5.70 (each br, s)], and three aromatic protons (δ 6.42—6.70). Addition of D_2O showed the presence of three hydroxy-proton signals under the alkyl, vinyl, and aromatic resonances. The n.m.r. spectrum of alliodorol triacetate shows acetate signals at δ 2.28, 2.30, and 2.07, suggesting that alliodorol contains an alcoholic hydroxy-group in addition to two phenolic hydroxy-groups.

These data indicate alliodorol to be a hydroxy-geranylhydroquinone with the alcohol function at either the C-3 or the C-7 methyl group of the geranyl side chain. Since reduction of alliodorin (4) by sodium borohydride yields alliodorol, structure (8) is established for this alcohol.

Allioquinol C (9) forms a triacetate and was isolated as an optically inactive oil ($C_{16}H_{20}O_3$), $\lambda_{max.}$ 290 nm. The n.m.r. spectrum is very similar to that of cordiaquinol

[1] C. R. Southwell and J. D. Bultman, *Biotropica*, 1971, **3**, 81.
[2] R. Nicolait, *National Fisherman*, 1976, **58**, 14-C.
[3] M. Moir and R. H. Thomson, *J.C.S. Perkin I*, 1973, 1352.
[4] K. L. Stevens, L. Jurd, and G. Manners, *Tetrahedron Letters*, 1973, **31**, 2955.
[5] R. H. Thomson, 'Naturally Occuring Quinones,' 2nd edn., Academic Press, New York, 1971, p. 209.

C(7) showing signals for a tertiary methyl group (δ 1.13) and two isolated, geminally coupled, benzylic methylene protons [δ 2.47 and 2.92 (*J* 17 Hz)], and a benzylic methylene [δ 2.90 (dd, *J* 17 and 6 Hz) and 2.53 (dd, *J* 17 and 10.5Hz)] and vicinal methine [δ 2.30 (dd, *J* 10.5 and 6 Hz)] AMX pattern. A broad two-proton singlet at δ 4.14 vinylic proton resonances are directly comparable to those of (7), the terminal methylene protons exhibit a comparative paramagnetic shift indicative of neighbouring functional group deshielding effects. Signals for two aromatic protons and two aromatic hydroxy-groups complete the spectrum. These data suggest the



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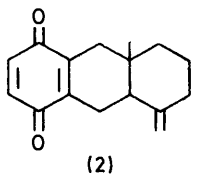

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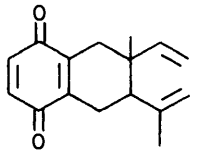

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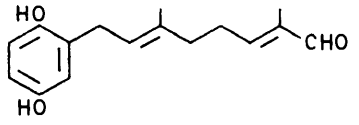

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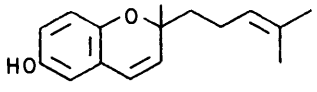

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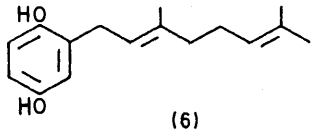

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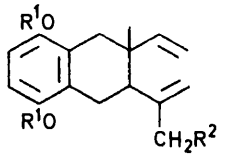
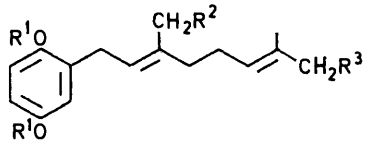
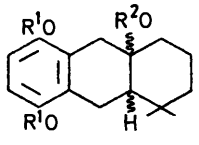


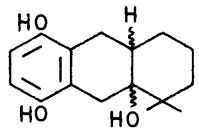
(7) $R^1=R^2=H$
(7a) $R^1=Ac$, $R^2=H$
(9) $R^1=H$, $R^2=OH$
(9a) $R^1=Ac$, $R^2=OAc$



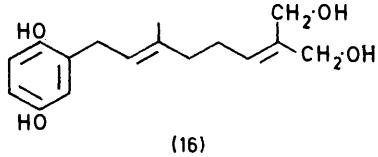
(8) $R^1=R^2=H$, $R^3=OH$
(8a) $R^1=Ac$, $R^2=H$, $R^3=OAc$
(15) $R^1=H$, $R^2=OH$, $R^3=OH$
(15a) $R^1=Ac$, $R^2=OAc$, $R^3=OAc$



(10) $R^1=H$, $R^2=H$
(10a) $R^1=Ac$, $R^2=H$
(10b) $R^1=Ac$, $R^2=Ac$



(11)

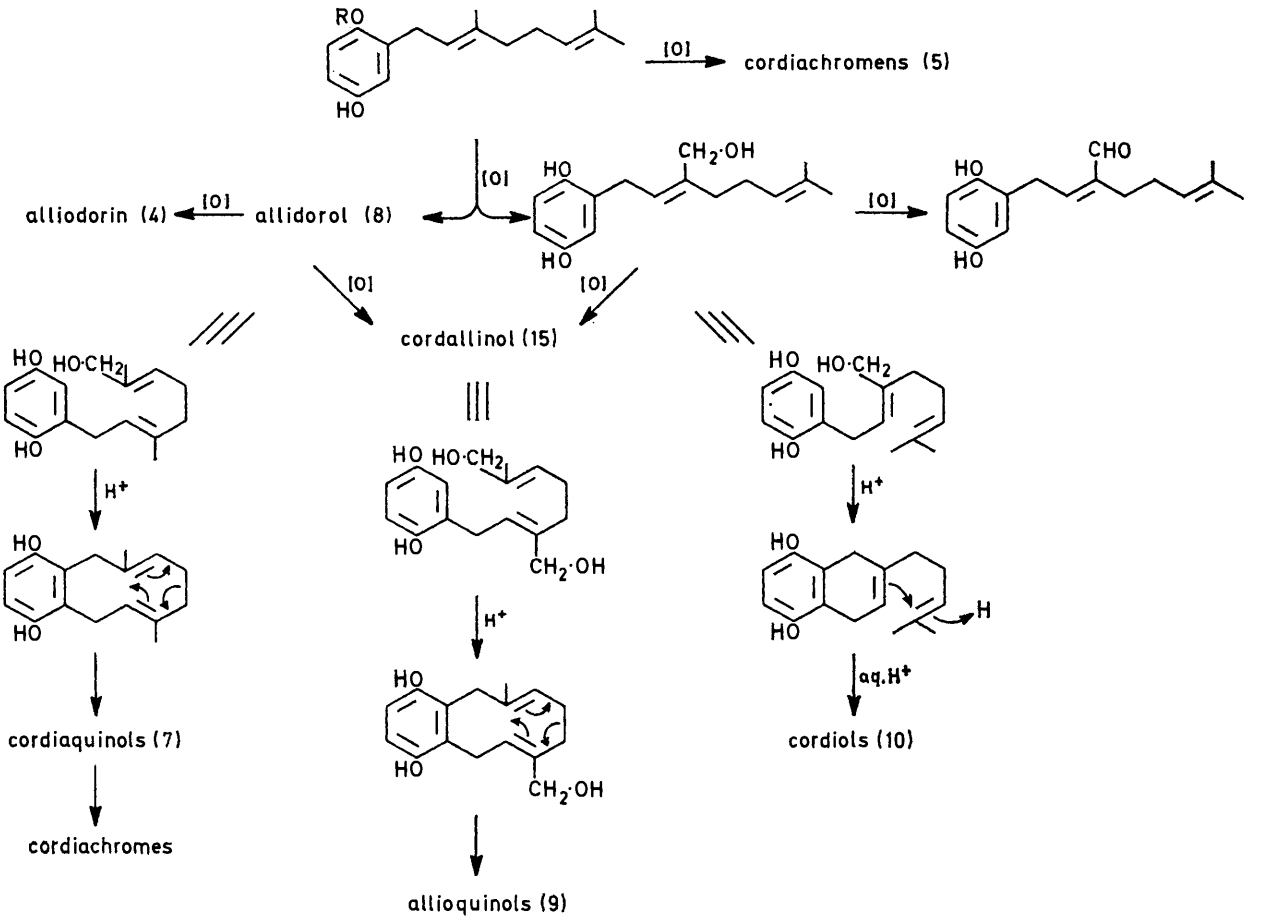


(16)

changing to a broad one-proton singlet upon addition of D_2O is consistent with the allylic methylene/alcoholic hydroxy group co-resonance, as observed for alliodorol (8). A three-proton (δ 4.92, 4.95, and 6.03) ABX pattern and two coupled broad single resonances (δ 5.01 and 5.26) indicate monosubstituted vinyl and terminal methylene groups, respectively. Whereas the terminal (tentative) structure (9) for allioquinol, an allyl alcohol derivative of cordiaquinol C. The n.m.r. spectrum of allioquinol C triacetate confirms the presence of an allyl alcohol function [δ 2.09, 2.30, and 2.31 (each 3 H, s)] in allioquinol C, and is in full accord with structure (9).

Cordiol A (10) crystallized (after chromatography) as optically inactive needles, $C_{16}H_{22}O_3$, $\lambda_{max.}$ 289 nm. The

n.m.r. spectrum shows signals for two tertiary methyl groups (δ 0.91 and 1.00), seven alkyl protons [δ 1.40—1.75 (m)], and two isolated geminally coupled benzylic methylene protons [δ 2.28 (d, J 18 Hz) and 2.69 (d, J 18 Hz)]. Two other benzylic methylene protons resonate as part of an AMX system [δ 3.26 (dd, J 18 and 2 Hz) and 2.58 (dd, J 18 and 8 Hz)]. The signal for the third proton of this system was located by double resonance at δ 1.62 (J 8 and 2 Hz).



SCHEME Proposed biogenesis of *Cordia alliodora* constituents

Acetylation of the phenolic hydroxy-groups of cordiol A with acetic anhydride–pyridine at room temperature produced a crystalline phenolic diacetate. Acetylation of cordiol A with isopropenyl acetate at room temperature yielded a crystalline triacetate. The n.m.r. spectrum of the triacetate shows signals for two tertiary methyl groups (δ 1.02 and 1.25), six alkyl protons (δ 1.40—1.78), five other alkyl protons (δ 2.02—2.79), two aromatic acetate groups (δ 2.30 and 2.32), a tertiary alkyl acetate group (δ 1.98), and two aromatic protons [δ 6.88 (s)].

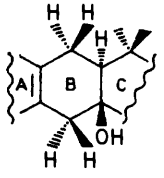
These data are consistent with structure (10) or (11) for cordiol A. Of these, (10) would be favoured if cordiol A is biogenetically derived from an alcoholic geranylhydroquinone (see Scheme).

Verification of the biogenetic formulation and designation of structure (10) for cordiol A was obtained from an INDOR [6] experiment. The n.m.r. spectrum of cordiol A in [$^2H_5$]pyridine shows signals for the tertiary methyl groups (δ 1.11 and 1.23), six alkyl protons [δ 1.22—1.90 (m)], one alkyl proton (a partially obscured double doublet, δ 1.99), three benzylic protons (δ 2.62—3.30), a single low field benzylic proton [δ 3.98 (dd, J 18 and 2 Hz)], a hydroxy-group (δ 5.30br), and two aromatic protons [δ 6.89(s)]. INDOR observation of the low-field signals at δ 3.98 amd 3.12 allowed specific designation of the four benzylic proton resonances [δ 2.76 (d, J 18 Hz), 3.12 (dd, J 18 and 2 Hz), 3.14 (dd, J 18 and 1 Hz), and 3.98 (dd, J 18 and 2 Hz)]. These INDOR observations also enabled assignment of the proton resonance at δ 1.99 to the methine proton of an AMX system, coupled (J 8 and 2 Hz) to the δ 3.12 and 3.98 benzylic protons. A final INDOR experiment involving the δ 1.99 methine resonance confirmed the AMX system and showed no couplings in the δ 1.20—1.90 alkyl methylene range. The methine proton is therefore coupled only to the benzylic protons resonating at δ 3.12 and 3.98 in an isolated AMX system, thus substantiating structure (10) for cordiol A.

The establishment of structure (10) for cordiol A

[6] E. B. Baker, *J. Chem. Phys.*, 1962, **37**, 911.

allows only three configurations of rings B and C [partial structures (12)—(14)]. Although the absolute stereochemistry of cordiol A has not been determined, various n.m.r. characteristics of the compound and its derivatives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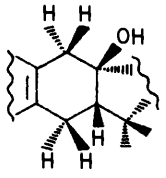
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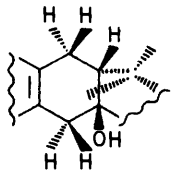
(14)

suggest that configuration (12) is the most likely. The unusual low-field position of one of the benzylic methylene resonances (δ 3.26) of the AMX system, the significant shift of the tertiary methyl signals in cordiol A triacetate (δ 0.91 and 1.00 to δ 1.25 and 1.02), and the absence of any chemical shift changes for the tertiary methyl groups in cordiol A diacetate indicate that cordiol A must have a tertiary hydroxy-group which is close to both the benzylic methylene proton and a tertiary methyl group.[7] If we assume a pseudo-chair conformation for the cyclohexene ring, structure (12) is the only stereoisomer with the appropriate 1,3-diaxial, 1,3-diequatorial stereochemical relationship of the hydroxy and benzylic and the hydroxy and methyl protons, respectively. In addition, the observed vicinal coupling constants (J 8 and 2 Hz.) of the methine and benzylic methylene protons agree with expected values[8] of the diaxial and axial-equatorial orientations represented in stereoisomer (12). These data therefore suggest that cordiol A exists with a *trans*-diequatorial cyclohexane ring junction.

Cordallinol (15), the last silver-nitrate-reducing compound to be isolated chromatographically, was obtained as an oil, $C_{16}H_{22}O_4$, $\lambda_{max.}$ 294 nm, forming a tetra-acetate. The n.m.r. spectrum of cordallinol shows signals for a single vinylic methyl group (δ 1.62), four alkyl protons [δ 2.12—2.34 (m)], a benzylic methylene group [δ 3.37 (d, J 7 Hz)], two allyl alcohol methylene groups (δ 3.96 and 4.23), two hydroxy-protons (δ 3.85 and 3.90), two vinylic protons [δ 5.40 (t, J 7 Hz) and 5.43 (m)], three aromatic protons (δ 6.40—6.75), and two aromatic hydroxy-protons (δ 7.69).

The tetra-acetate was an oil whose n.m.r. spectrum has signals for a single vinylic methyl group (δ 1.64), two aliphatic acetate systems [δ 2.05 (6 H)], four alkyl protons (δ 2.10—2.16), two aromatic acetate groups (δ 2.27 and 2.30), a benzylic methylene group [δ 3.35 (d, J 7 Hz)], two allylic acetate methylene groups (δ 4.67 and 5.50), two vinyl protons [δ 4.43 (m) and 5.30 (t, J 7 Hz)], and three aromatic protons (δ 6.86—7.04).

These data distinguish cordallinol as a diol derivative of geranylhydroquinone with structure (15) or (16). A comparison of the n.m.r. spectrum [in $(CD_3)_2CO$] of cordallinol with those of geranylhydroquinone (6), cordiachromen A (5), and alliodoral (8) results in assignment of structure (15) to cordallinol.

The n.m.r. spectrum of geranylhydroquinone has vinylic methyl resonances at δ 1.59, 1.65, and 1.70 and a benzylic methylene signal at 3.28. Cordiachromen A shows vinylic methyl signals at δ 1.56 and 1.64. Therefore, the free vinylic methyl group at C-3 is responsible for the resonance at δ 1.70 and the chemical shift of the benzylic methylene is, as expected, δ 3.28. The single vinylic methyl resonance at δ 1.63 and the benzylic methylene resonance at δ 3.37 establish the C-3 methyl group of cordallinol as substituted. A comparison of vinylic methyl chemical shifts of alliodorol (8), δ 1.64 and 1.70, with those of cordiachromen A (5) establishes the C-7 vinylic methyl resonance of alliodorol, and correspondingly of cordallinol, as that at δ 1.64. The direct chemical conversion of alliodorin into alliodorol further establishes a *trans*-orientation of the vinylic methyl group of cordallinol [structure (15)], as established for alliodorin.[4]

Moir and Thomson[3] have suggested a biogenetic derivation of the cordiachromes from a geranylphenol precursor which undergoes oxidation of a terminal allylic methyl group; intramolecular cyclisation then takes place to form an octadecatriene capable of further acid-catalysed cyclisations and 'biogenetic rearrangements' to yield the cordiachromes. The characterization of cordiachromen A in this investigation verifies the existence of a geranylphenol precursor in *Cordia alliodora*, and the presence of the other new compounds supports the Moir and Thomson proposal and allows a detailed Scheme (illustrated) for the biogenesis of *Cordia* constituents to be postulated. The basic premise of this scheme is that intramolecular geranyl side-chain cyclization proceeds as a simple acid-catalysed reaction of the phenolic nucleus with the geranyl C-3 or C-7 allylic hydroxy-group (*e.g.* alliodorol or cordallinol) followed by further acid-catalysed cyclisations and rearrangements to yield cordiaquinols, allioquinols, and cordiols. These compounds can subsequently be oxidized to the cordiachromes and related compounds.

Attempts to isolate other quinols from this wood and a study of intramolecular allylic alcohol–phenol condensations are under way in an effort to supply further evidence for this biogenetic proposal.

EXPERIMENTAL

Spectra were measured for solutions in ethanol (u.v.), KBr discs (i.r.), and solutions in $CDCl_3$, $(CD_3)_2CO$, or C_5D_5N, as noted (n.m.r.). T.l.c. was run on silica gel plates.

Extraction of Cordia alliodora.—Hammer-milled *C. alliodora* heartwood (8.13 kg) was successively extracted with hot petroleum (b.p. 30—60 °C), ether, acetone, and methanol. Only the acetone extract (542 g) will be considered here.

A portion of the acetone extract (237 g) was boiled with ether (2 × 3.0 l) and the mixture filtered. The ether-soluble fraction (125 g) was concentrated and extracted with saturated aqueous borax (3 × 300 ml). The borax-

[7] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, London, 1969, p. 237.

[8] Ref. 7, p. 281.

insoluble, ether-soluble portion was concentrated on a steam bath (under N_2) during addition of benzene (1 l). The resulting tarry benzene-insoluble portion was dissolved in acetone and the solution evaporated onto Celite. The extract on Celite was heated with water (1 l), the solution was filtered, and the filtrate was cooled and extracted with ether; the extract was dried ($MgSO_4$) and evaporated to dryness to yield ether-soluble material (12 g).

The ether-soluble material was separated on a preparative LH 20 (10 × 45 cm) column ($CHCl_3$–MeOH, 9:1) into twelve 1 l fractions. T.l.c. of fractions 2—12 (PhH–EtOH, 9 : 1) showed the presence of several compounds which reduced silver nitrate. Each fraction was extensively rechromatographed on preparative LH 20 and silica gel columns [$CHCl_3$–MeOH (9 : 1) and PhH–EtOH (20 : 1 to 9 : 1)] to obtain the compounds herein described in yields of less than 0.5% (based on dry weight of wood).

Cordiachromen A [2-*methyl*-2-(4-*methylpent*-3-*enyl*)-2H-*chromen*-6-*ol*] (5). Elution with benzene–ethanol (20 : 1) of the clarified acetone extract (benzene-insoluble portion) on a silica gel column first yielded a light yellow *oil* (5) (t.l.c. R_F 0.51) (Found: M^+, 244.145 9. $C_{16}H_{20}O_2$ requires M, 244.146 3), $\lambda_{max.}$ 331 (log ε 3.78), *ca.* 300 (3.66), and 263 nm (3.90), $\nu_{max.}$ 3 400, 1 620, 1 585, 1 595, 1 460, 1 210, 1 080, 920, and 815 cm^{-1}, δ($CDCl_3$) 1.36 (3 H, s), 1.56 (3 H, s), 1.65 (3 H, s), 1.90—2.26 (4 H, m), 5.09 (1 H, t, *J* 6 Hz), 5.65 (1 H, d, *J* 10 Hz), 5.96br (1 H, s), and 6.40—6.64 (3 H, m), *m/e* 244(9%), 229(3), and 161(100); *acetate* (5a), light yellow oil (Found: M^+, 286.156 7. $C_{18}H_{22}O_3$ requires M, 286.156 9), δ($CDCl_3$) 1.38 (3 H, s), 1.57 (3 H, s), 1.66 (3 H, s), 1.92—2.26 (4 H, m), 2.24 (3 H, s), 5.10 (1 H, t, *J* 6 Hz), 5.56 (1 H, d, *J* 10 Hz), 6.28 (1 H, d, *J* 10 Hz), and 6.63—6.80 (3 H, m), *m/e* 286(10%), 271(3), 203(100), 161(67), 132(4), 69(14), 43(20), and 41(21).

Hydroquinone (24 g) in warm aqueous 2% oxalic acid (600 ml) was treated dropwise with geraniol (30.8 g) during 15 min with stirring. After 2 h the mixture was diluted with water and extracted with ether, and the product was preparatively chromatographed (LH 20; $CHCl_3$–MeOH, 9 : 1) to yield geranylhydroquinone [9] (6) (4.3 g, 8.9%). This product was then oxidized with silver oxide in acetone to yield geranylbenzoquinone (oil). The crude geranylbenzoquinone was cyclized by heating to boiling in pyridine [5] for 20 min. After cyclization the product was extracted with ether and preparatively chromatographed (silica gel; benzene) to yield compound (5) (11%), identical with the natural product.

Cordiaquinol C (5,6,7,8-*tetrahydro*-7-*isopropenyl*-6-*methyl*-6-*vinylnaphthalene*-1,4-*diol*) (7). Further silica gel column chromatography (PhH–EtOH, 10 : 1) of the clarified extract yielded a dark *oil* (7) (t.l.c. R_F 0.32) (Found: M^+, 244.146 4. $C_{16}H_{20}O_2$ requires M, 244.146 3), $\lambda_{max.}$ 290 nm (log ε 3.62), $\nu_{max.}$ (film) 3 260, 1 620, 1 400, 1 240, 1 150, 1 035, 1 005, 960, 915, 890, 810, and 740 cm^{-1}, δ[$(CD_3)_2CO$] 1.16 (3 H, s), 1.78 (3 H, s), 2.00—2.96 (5 H, m), 4.78—4.90 (3 H, m), 4.93 (1 H, dd, *J* 18 Hz), 6.07 (1 H, dd, *J* 18 and 11 Hz), 6.49 (2 H, s), and 7.40 (2 H, s), *m/e* 244(100%), 229(35), 215(10), 201(11), 189(19), 175(29), 162(11), 161(19), 149(13), 136(42), 107(12), 81(13), and 69(17); *diacetate* (7a), a light yellow oil (Found: M^+, 328.166 7. $C_{20}H_{24}O_4$ requires M, 328.167 5), δ($CDCl_3$) 1.14 (3 H, s), 1.77 (3 H, s), 2.27 (6 H, s), 2.30—2.90 (5 H, m), 4.75—5.07 (4 H, m), 5.96 (1 H, dd, *J* 17 and 11 Hz), and 6.89 (2 H, s), *m/e* 328(7%), 286(22), 244(100), 229(14), 175(15), 136(15) 55(10), 43(90).

Cordiaquinol C (7) (20 mg) was oxidized with silver oxide in acetone to yield a yellow oil (16 mg), with chromatographic and spectral properties in complete accord with recorded values for cordiachrome C (3).

Alliodorol [2-(8-*hydroxy*-3,7-*dimethylocta*-2,6-*dienyl*)-*hydroquinone*] (8) *and Alliodorin* [8-(2,5-*Dihydroxyphenyl*)-2,6-*dimethylocta*-2,6-*dienal*] (4). Continued silica gel column chromatography of the clarified extract (PhH–EtOH, 9 : 1) yielded alliodorin (4), needles (from methanol), m.p. 87°, identical with an authentic specimen. Rechromatography of the crystallization filtrate on silica gel yielded a light brown *oil* (8) (t.l.c. R_F 0.23) (Found: M^+, 262.154 3. $C_{16}H_{22}O_3$ requires M, 262.156 9), $\lambda_{max.}$ 293 nm (log ε 3.98), $\nu_{max.}$ (film) 3 350, 1 610, 1 505, 1 410, 1 200, 999, 860, and 810 cm^{-1}, δ($CDCl_3$) 1.64 (6 H, s), 2.06—2.30 (5 H m), 3.27 (2 H, d, *J* 7 Hz), 4.05br (2 H, s), 5.28 (1 H, t, *J* 7 Hz), 5.36 (1 H, m), 5.70br (1 H, s), and 6.42—6.70 (4 H, m), δ[$(CD_3)_2CO$] 1.64 (3 H, s), 1.70 (3 H, s), 2.10—2.40 (4 H, m), 3.29 (2 H, d, *J* 7 Hz), 4.01br (2 H, s), 5.25 (1 H, t, *J* 7 Hz), 5.44 (1 H, m), 6.40—6.73 (3 H, m), 7.29 (1 H, s), and 7.51 (1 H, s), *m/e* 262(10%), 244(10), 229(8), 201(59), 176(14), 161(100), 149(10), 147(16), 135(15), 124(18), 123(92), 121(74), 107(30), 93(19), 81(15), 69(13), 67(18) 55(37), and 43(59); *triacetate* (8a), dark yellow oil (Found: M^+, 388.188 3. $C_{22}H_{28}O_6$ requires M, 388.188 7), δ($CDCl_3$) 1.66br (6 H, s), 2.07 (3 H, s), 2.00—2.21 (4 H, m), 2.28 (3 H, s), 2.30 (3 H, s), 3.24 (2 H, d, *J* 7 Hz, 5.36—5.54 (1 H, m), and 6.84—7.02 (3 H, m), *m/e* 388(0.1%), 360(0.1), 346(1), 328(6), 304(2), 286(5), 260(27), 244(25), 218(19), 201(23), 176(31), 161(32), 121(42), 107(10), 55(10), and 43(100).

Alliodorin (4) (100 mg) was treated with sodium borohydride in methanol to yield alliodorol (8) (96 mg), identical with natural alliodorol.

Allioquinol C [5,6,7,8-*tetrahydro*-7-(1-*hydroxymethyl*-*vinyl*)-6-*methyl*-6-*vinylnaphthalene*-1,4-*diol*] (9). Continued column chromatography (silica gel; PhH–EtOH, 9 : 1) next yielded a dark *oil* (9) (t.l.c. R_F 0.21) (Found: M^+, 260.141 0. $C_{16}H_{20}O_3$ requires M, 260.141 3), $\lambda_{max.}$ 290 nm (log ε 3.85), $\nu_{max.}$ (film) 3 450, 1 702, 1 645, 1 465, 1 380, 1 150, 1 035, 1 015, 920, 905, and 805 cm^{-1}, δ[$(CD_3)_2CO$] 1.13 (3 H, s), 2.30 (1 H, dd, *J* 10.5 and 6 Hz), 2.47 (1 H, d, *J* 17 Hz), 2.53 (1 H, dd, *J* 17 and 10.5 Hz), 2.90 (1 H, dd, *J* 17 and 6 Hz), 2.92 (1 H, dd, *J* 17 Hz), 4.14br (2 H, s), 4.92 (1 H, dd, *J* 17 and 1 Hz), 4.95 (1 H, dd, *J* 10 and 1 Hz), 5.01br (1 H, s), 5.26br (1 H, s), 6.03 (1 H, dd, *J* 10 and 17 Hz), 6.54 (2 H, s), and 7.51br (2 H, s), *m/e* 260(96%), 242(15), 229(29), 227(40), 213(17), 200(11), 199(11), 187(35), 175(51), 173(30), 161(46), 160(33), 147(27), 136(100), 131(21), 115(29), 107(27), 91(38), 79(24), 77(37), 65(20), 55(54), 43(28), and 39(29); *triacetate* (9a), light yellow oil (Found: M^+, 386.172 1. $C_{22}H_{26}O_6$ requires M, 386.173 0), δ($CDCl_3$) 1.15 (3 H, s), 2.09 (3 H, s), 2.30 (3 H, s), 2.31 (3 H, s), 2.26—2.84 (5 H, m), 4.56br (2 H, s), 4.92 (1 H, dd, *J* 17 and 1 Hz), 5.03 (1 H, dd, *J* 11 and 1 Hz), 5.08br (1 H, s), 5.22br (1 H, s), 5.92 (1 H, dd, *J* 11 and 17 Hz), and 5.90 (2 H, s), *m/e* 386(4%), 344(9), 326(7), 302(43), 284(21), 243(13), 242(64), 227(16), 187(11), 174(13), 136(13), and 43(100).

Cordiol A (5,6,7,8,8a,9,10,10a-*octahydro*-5,5-*dimethyl*-*anthracene*-1,4,8a-*triol*) (10). Silica gel column chromatography (PhH–EtOH, 9 : 1) yielded an oil which crystallized and was recrystallized (4 : 1 H_2O–EtOH) to yield *needles*

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(10) (<30 mg), m.p. 236—237° (t.l.c. R_F 0.19) (Found: M^+, 262.156 5. $C_{16}H_{22}O_3$ requires M, 262.156 8), $\lambda_{max.}$ 289 nm (log ε 3.51), $\nu_{max.}$ (Nujol) 3 460, 1 618, 1 480, 1 375, 1 280, 1 256, 1 200, 1 015, 955, 812, and 803 cm^{-1}, δ[$(CD_3)_2$-CO] 0.91 (3 H, s), 1.00 (3 H, s), 1.40—1.75 (7 H, m), 2.28 (1 H, d, J 18 Hz), 2.58 (1 H, dd, J 18 and 8 Hz), 2.69 (1 H, d, J 18 Hz), 3.26 (1 H, dd, J 18 and 1 Hz), 3.15br (1 H, s), 6.48 (2 H, s), 7.28br (2 H, s), δ(C_5D_5N) 1.11 (3 H, s), 1.23 (3 H, s), 1.22—1.90 (6 H, m), 1.99 (dd, J 8 and 2 Hz), 2.76 (d, J 18 Hz), 3.12 (dd, J 18 and 2 Hz), 3.14 (dd, J 18 and 1 Hz), and 3.98 (dd, J 18 and 2 Hz), *m/e* 262(62%), 244(72), 229(75), 215(15), 201(11), 187(24), 175(53), 173(34), 162(32), 161(31), 148(24), 137(26), 136(100), 131(14), 115(14), 109(16), 108(16), 107(15), 91(17), 77(15), 71(15), 55(23), and 43(46); *1,4-diacetate* (10a), needles (from methanol), m.p. 101—102° (Found: M^+, 346.178 9. $C_{20}H_{26}O_5$ requires M, 346.178 2), δ($CDCl_3$) 0.91 (3 H, s), 0.98 (3 H, s), 1.26—1.80 (7 H, m), 2.08 (1 H, d, J 18 Hz), 2.31 (3 H, s), 2.32 (3 H, s), 2.30—2.80 (2 H, m), 3.01 (1 H, d, J 18 Hz), and 6.88 (2 H, s), *m/e* 346(4.1%), 328(3.1), 304(25), 286(5.6), 262(100), 244(38), 229(20), 175(16), 161(13), and 136(23); *triacetate* (10b), needles (from methanol), m.p. 165—166° (Found: M^+, 388.187 1. $C_{22}H_{28}O_6$ requires M, 388.188 7), δ($CDCl_3$) 1.02 (3 H, s), 1.25 (3 H, s), 1.40—1.78 (6 H, m), 1.98 (3 H, s), 2.00—2.80 (5 H, m), 2.31 (3 H, s), 2.33 (3 H, s), and 6.88 (2 H, s), *m/e* 328(28%), 286(39), 244(100), 229(27), 148(6), 136(5), 109(3), and 43(3).

Cordallinol [2-(8-*hydroxy*-3-*hydroxymethyl*-7-*methylocta*-2,6-*dienyl*)*hydroquinone*] (15). Silica gel column chromatography yielded an *oil* (15) (t.l.c. R_F 0.09) (Found: M^+, 278.152 3. $C_{16}H_{22}O_4$ requires M, 278.151 9), $\lambda_{max.}$ 294 nm (log ε 3.96), $\nu_{max.}$ (film) 3 430, 1 705, 1 620, 1 505, 1 460, 1 370, 1 205, 1 000, 870, and 815 cm^{-1}, [$(CD_3)_2CO$] 1.62br (3 H, s), 2.12—2.34 (4 H, m), 3.37 (2 H, d, J 7 Hz), 3.85br (1 H, s), 3.90br (1 H, s), 3.96br (2 H, s), 4.23br (2 H, s), 5.40 (1 H, t, J 7 Hz), 5.35—5.48 (1 H, m), 6.40—6.75 (3 H, m), and 7.69br (2 H, s), *m/e* 278 (5%), 260(9.5), 174(28), 161(72), 147(23), 137(33), 124(100), 119(32), 107(27), 91(27), 79(30), 67(30), 55(51), 43(81), and 28(76); *tetra-acetate* (15a), a dark oil (Found: M^+, 446.194 5. $C_{24}H_{30}O_8$ requires M, 446.194 3), δ($CDCl_3$) 1.64br (3 H, s), 2.05 (6 H, s), 2.10—2.16 (4 H, m), 2.27 (3 H, s), 2.30 (3 H, s), 3.35 (2 H, d, J 7 Hz), 4.44br (2 H, s), 4.67br (2 H, s), 5.43 (1 H, m), 5.50 (1 H, t, J 7 Hz), 5.35—5.42 (1 H, m), and 6.86—7.04 (3 H, m), *m/e* 446(0.5%). 404(0.6), 386(1), 362(0.9), 343(2.7), 326(13), 302(10), 284(9), 242(38), 174(26), 161(26), 123(26), 119(37), and 43(100).

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