Cordiachromes: A New Group of Terpenoid Quinones from *Cordia* spp.

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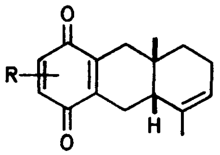
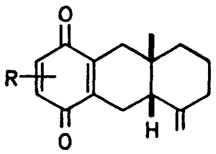
Summary *Cordia millenii* contains six optically inactive benzoquinones, cordiachromes (A)—(F); (C) and (F) have a benzogeijerene skeleton and the others have a tricyclic benzocogeijerene structure; they are probably derived from a benzenoid precursor and geranyl pyrophosphate.

WOODWORKERS handling *Cordia* spp. (Boraginaceae) are prone to contract skin allergies.[1] This led us to examine the constituents of these timbers and a cold chloroform extract of the heartwood of *C. millenii* has been found to contain at least six quinones, cordiachromes (A—F), separable by extensive chromatography on silica gel–silver nitrate plates.

Cordiachromes (A—C), $C_{16}H_{18}O_2$, are isomeric. They give positive Craven tests, form leuco-diacetates, and show λ_{max} (EtOH) 250 and 348 nm (log ϵ 4·1 and 2·9), λ_{max} (EtOH–BH_4^-) 292 nm, ν_{CO} *ca.* 1650 cm^{-1}, and τ ($CDCl_3$) *ca.* 3·30 (2H, s). Thus they are 2,3-dialkylbenzoquinones, the non-quinonoid moieties being $C_{10}H_{16}$. Each quinone contains a tertiary methyl group (τ *ca.* 9·0) but they differ in their olefinic absorption; in (A) (a yellow oil) a broad singlet (3H) at τ 8·27 is coupled to a vinylic multiplet (1H) at 4·69, while (B) (golden needles, m.p. 64—65°) shows two singlets (each 1H) at τ 5·27 and 5·62. Further, (B) absorbs strongly at 913 cm^{-1}, gives formaldehyde on ozonolysis, and on fusion with zinc dust yields an aromatic hydrocarbon [λ_{max} (C_6H_{12}) 238, 260, 332, 350, 367, and 386 nm], probably a dimethylanthracene. As both (A) and (B) gave the same dihydro-derivative after hydrogenation and reoxidation with silver oxide, we formulate them as (I; R = H) and (II; R = H), respectively, (ignoring stereochemistry). The dihydro-derivative (IV) is clearly a pair of epimers, the overlapping methyl signals at τ 9·14 (6H) ($CDCl_3$) separating into two sets of overlapping signals at τ 9·32 and 9·40 in C_6D_6. Oxidation of (IV) with alkaline hydrogen peroxide



(I)



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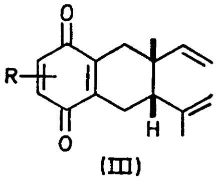

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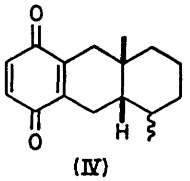

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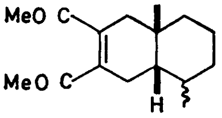

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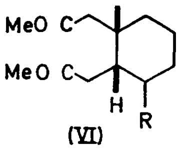

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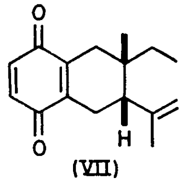

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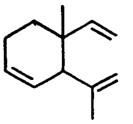
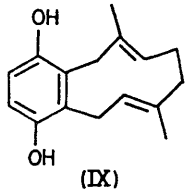
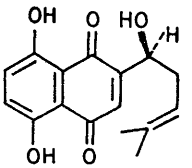


(VIII)



(IX)



(X)

afforded, after methylation, the maleic ester (V), $C_{16}H_{24}O_4$, consistent with all spectroscopic parameters, while ozonolysis of (IV) followed by acidic hydrogen peroxide, and then methylation, gave (VI; R = Me), $C_{14}H_{20}O_4$. The mass spectrum of (VI; R = Me) is virtually identical with that of (VI; R = H) displaced by 14 m.u. The *cis*-geometry of (VI; R = Me), and hence of (I) and (II), follows from the chemical shift of the tertiary methyl at τ 8·95 identical with that in the spectrum of *cis*-(VI; R = H)[2] whereas for the *trans*-isomer[3] of (VI; R = H) the signal appears at τ 9·07.

Cordiachrome C (III), a yellow oil, contains five olefinic protons (besides QH) and shows, *inter alia*, ν 913 and 895 cm^{-1}, τ ($CDCl_3$) 4·08 (1H, dd, J 11 and 17 Hz, $-CH{=}CH_2$), 4·98 (1H, d, J 11 Hz, $-CH{=}CH_2$), 5·10 (1H, d, J 17 Hz, $-CH{=}CH_2$), 5·08 and 5·22 (each 1H, s, $>{=}CH_2$), and 8·23 (3H, s, $CH_3{-}C{=}C$). The tertiary methyl protons resonate at τ 8·89 which suggests that (C) is also *cis*-(III) but this point is not established. Hydrogenation in acetic acid (followed by reoxidation) gave a tetrahydro-derivative, but in ethyl acetate the dihydro-derivative (VII) was obtained [ν 895 cm^{-1}, τ 5·12 and 5·30 (each 1H)].

Cordiachromes (D—F), $C_{17}H_{20}O_3$, are methoxylated analogues of (A—C), *i.e.* (I, II, and III; R = OMe). Corresponding pairs are spectroscopically identical except that (D—F) show methoxy-signals at τ 6·20 and only one quinonoid proton at τ 4·12.

Like geijerene (VIII),[4] the cordiachromes are racemic and probably arise from an optically inactive[5] "benzogermacrane"-type precursor, *e.g.* (IX),[6] derived from geranyl pyrophosphate and an aromatic unit. It is interesting that the only other quinones known in the Boraginaceae are naphthazarins (X and close relatives),[7] and it has been established recently[8] that alkannin (X) is biosynthesised from *p*-hydroxybenzoic acid and mevalonate. It appears that both the cordiachromes and alkannin are formed by attachment of a geranyl side chain to an aromatic precursor, followed by oxidation of an allylic methyl group which then cyclises.

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