

ALLIODORIN, A PHENOLIC TERPENOID FROM *CORDIA ALLIODORA*

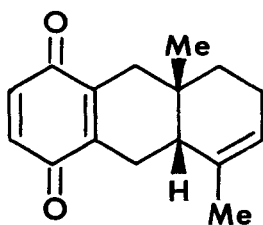
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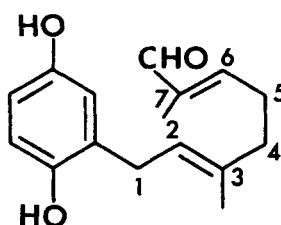
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It was recently suggested (1) that cordiachromes, a novel group of terpenoid quinones, e.g., I, from *Cordia millenii*, probably arise by condensation of a benzenoid precursor with geranylpyrophosphate and subsequent oxidative cyclization of an allylic methyl group. From ether extracts of the heartwood of a related species, *Cordia alliodora*, a new, colorless phenol (m.p. 87°), alliodorin, has now been isolated and structurally identified as II. Alliodorin, therefore, is probably an immediate precursor to the cordiachromes, and its isolation provides significant experimental support for the proposed biosynthetic origin of these substances.

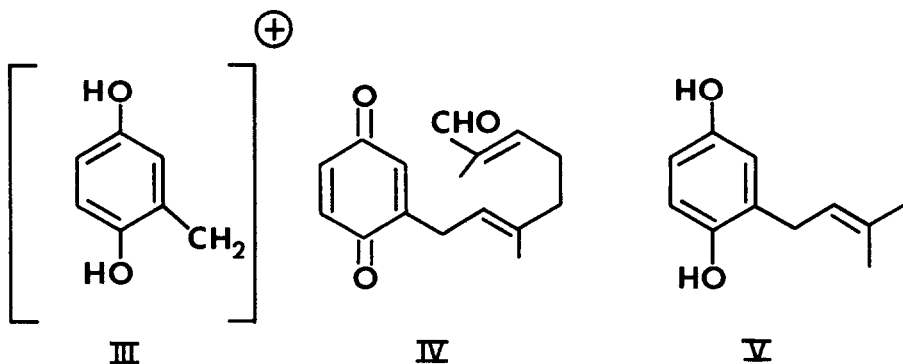


I



II

The mass spectrum of alliodorin established its molecular formula as $C_{16}H_{20}O_3$ with seven units of unsaturation. In accord with structure II a base peak (m/e 123) may be assigned to the benzylic fragment III. Alliodorin forms a dimethyl ether, gives a crystalline monoxime (m.p. 108°), and when oxidized with MnO_2 yields a yellow quinone (oil), subsequently identified as IV. The presence of an α,β -unsaturated aldehyde grouping is indicated both by its IR

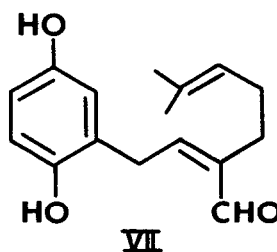
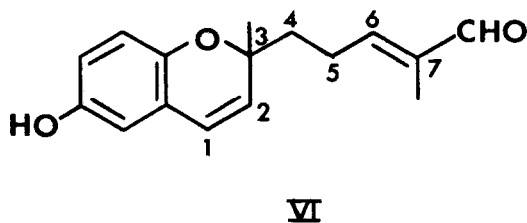


spectrum (ν_{\max}^{null} 1675, 2720, 3025, 1645 cm^{-1}) and by its intense $\lambda_{\max}^{\text{ETOH}}$ at 227 nm (ϵ_{\max} 21300)

(2). It also has a less intense absorption maximum at 294 nm (ϵ_{\max} 4320), which closely coincides with that reported for prenylhydroquinone (ν) $\lambda_{\max}^{\text{ether}}$ 295 nm, (ϵ_{\max} 4100).

The 100 MHz NMR spectrum of alliodorin in $CDCl_3$ showed the presence of two vinylic methyl groups (at C_3 , C_7 in structure II) as a 6 H singlet at δ 1.73, two methylene groups (at C_4 , C_5) as multiplets at δ 2.22 and δ 2.49, a benzylic methylene group (at C_1) as a doublet at δ 3.29 ($J = 7.0$ Hz), a vinylic proton (at C_2) as a triplet ($J = 7.0$ Hz) at δ 5.34, and a vinylic proton (at C_6), β - to the aldehyde group, as a triplet ($J = 7.0$ Hz) at δ 6.50. The aldehydic proton occurs as a sharp singlet at δ 9.34, while the three aromatic protons show a typical ABC pattern (1,2,4-

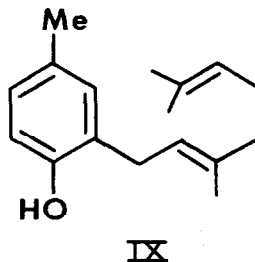
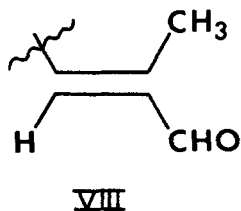
substituted aromatic) between $\delta 6.50 - \delta 6.73$, the spectrum in this region being identical with that of prenylhydroquinone (V) (4). When the quinone (IV) from alliodorin was heated in pyridine it cyclized to a Δ^3 -chromene (5), identified as VI by its mass and NMR spectra. In CDCl_3 the chromene protons at C_1, C_2 appeared as doublets ($J = 10.0$ Hz) at $\delta 6.31$ and $\delta 5.55$,



the methyl group at C_3 as a 3 H singlet at $\delta 1.38$, the methyl group at C_7 as a 3 H singlet at $\delta 1.68$, and the vinylic proton at C_6 , β - to the aldehyde group, as a triplet at $\delta 6.57$ ($J = 7.0$ Hz). The observation that the vinylic proton β - to the aldehyde group is retained when alliodorin is converted to the Δ^3 -chromene locates the aldehyde group at the end of the geranyl chain and eliminates the possible alternate structure VII in which the aldehyde group is located at C_3 . This was confirmed by treating alliodorin with alkali. A reverse aldol condensation gave propionaldehyde (isolated as its 2,4-DNP) and 2-methyl-2-pentenal, the latter presumably being formed by self-condensation of the liberated propionaldehyde.

The stereochemistry of the two ethylenic double bonds can be established with some certainty by comparison of the NMR spectra of alliodorin derivatives with those of several compounds of known configuration. Thus, a trans configuration for the C_6, C_7 double bond is indicated by (a) the chemical shift of the aldehydic proton in alliodorin at $\delta 9.34$; in 2-methyl-trans-2-enals of type VIII the chemical shift of the aldehydic proton is about $\delta 9.3$ (6), and in isomeric cis-2-enals about $\delta 10.0$ (6), (b) the chemical shift of the C_6 vinylic proton of alliodorin and the chromene VI is $\delta 6.47$ and $\delta 6.40$, respectively, in CCl_4 ; in CCl_4 the chemical shift of the vinylic proton in trans-2-enals VIII is reported to be $\delta 6.40$ (7), and in isomeric cis-2-enals to be $\delta 6.67$ (7), and (c) in alliodorin the proton resonance of the methyl group at C_7 occurs at $\delta 1.73$, in close agreement with reported values for the methyl group of compounds of

type VIII (8). A trans configuration for the C_2, C_3 ethylenic bond is indicated by comparison of the spectrum of alliodorin (II) with that of (IX) in which the methyl at C_3 (trans to the



vinyllic proton at C_2), the vinyllic proton at C_2 , and the benzylic methylene at C_1 give signals at δ 1.73, δ 5.30 and δ 3.28, respectively. In alliodorin the signals of the corresponding protons occur at δ 1.72, δ 5.34, and δ 3.29.

Since alliodorin (II) has the same oxidation level as the cordiachromes, one may envisage a transformation sequence leading to these substances via unexceptional acid catalyzed reactions. Such reactions are currently being investigated.

REFERENCES

1. M. Moir, R. H. Thomson, B. M. Hausen, and M. H. Simatupang, Chem. Comm., 363 (1972).
2. K. L. Stevens, R. E. Lundin, and R. Teranishi, J. Org. Chem., 30, 1690 (1965).
3. F. Bohlmann and Käthe-Marie Kleine, Chem. Ber., 99, 885 (1966).
4. L. Jurd, K. Stevens, and G. Manners, Tetrahedron Letters, 2275 (1971).
5. D. McHale and J. Green, Chem. and Ind., 1867 (1962).
6. A. F. Thomas and M. Ozainne, Chem. Comm, 46, (1969).
7. C. Pascual, J. Meier, and W. Simon, Helv. Chim. Acta, 49, 164 (1966).
8. G. Büchi and H. Wüest, Helv. Chim. Acta, 50, 2440 (1967).