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THE ABSOLUTE CONFIGURATION OF LATIFOLIN

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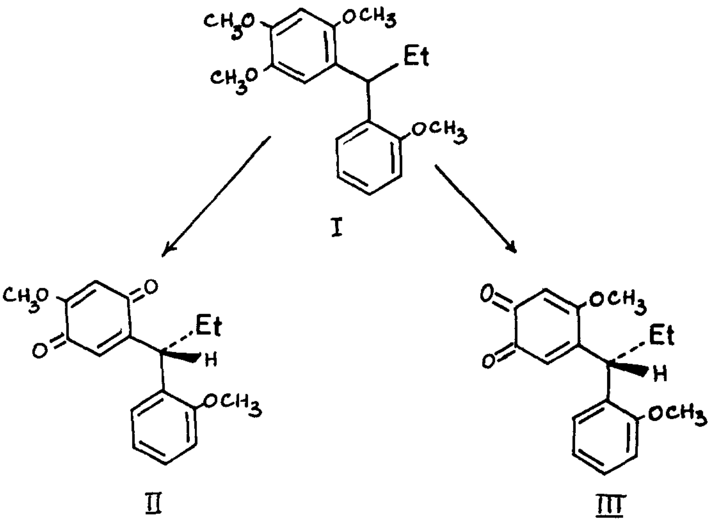
Latifolin (IV), an optically active component of the heartwood Dalbergia latifolia has been under investigation in these laboratories. Its constitution[1] and synthesis[2] have been described in previous publications; in this publication we report its absolute stereochemistry.

Donnelly et al.,[3] made an attempt in this direction by studying the O.R.D. curve of latifolin. They reported a negative plain dispersion curve from which they were unable to obtain any stereochemical information. Since the introduction of a chromophoric group in the immediate environment of the asymmetric centre, causes the Cotton effect to be enhanced in the O.R.D. curve and since the stereochemistry of dalbergenones, quinonoid compounds of related structure, is very well established, it seemed to us that a quinonoid derivative of latifolin would give us the best possible answer to this problem.

Oxidation of latifolin itself did not proceed satisfactorily. Dihydrolatifolin dimethyl ether (I) gave, on treatment with chromic acid in acetic acid solution, two quinones, yellow and red, separable by column chromatography on neutral alumina. Oxidation at ice temperature with 1 mol of the reagent gave the red quinone as major product whereas at 35° and with larger amount of the oxidant gave the yellow quinone with only traces of the red one.

The yellow quinone formed plates from petroleum ether, m.p. 140-41° (Found: C, 71.2; H, 6.4. $C_{17}H_{18}O_4$ requires, C, 71.3; H, 6.2%); λ_{max}^{EtOH} 268 mμ (log ε 4.32); ν_{max}^{nujol} 1685, 1655 cm^{-1} (quinone >C=O); it gave a colourless acetate with acetic anhydride and zinc dust. The acetate formed needles from methanol, m.p. 103-4° (Found: C, 68.0; H, 6.8. $C_{21}H_{24}O_6$ requires C, 67.7; H, 6.5%); λ_{max}^{EtOH} 273 mμ (log ε 3.72) and 279 mμ (log ε 3.73); $[\alpha]_D^{23}$ -58.1° (in $CHCl_3$); it yielded dihydrolatifolin dimethyl ether (I) on methylation with dimethyl sulphate and sodium hydroxide.

The red quinone formed plates from ethyl acetate - light petroleum, m.p. 136-7° (Found: C, 71.0; H, 6.4. $C_{17}H_{18}O_4$ requires C, 71.3; H, 6.2%); λ_{max}^{EtOH} 274 mμ (log ε 4.01); ν_{max}^{nujol} 1685, 1650 cm^{-1} (quinone >C=O), 1170 cm^{-1} (4:5 disubstituted o-quinone)[4]. It gave a colourless acetate with acetic anhydride and zinc dust. This acetate formed needles from methanol, m.p. 63-4° (Found: C, 68.0; H, 6.8. $C_{21}H_{24}O_6$ requires C, 67.7; H, 6.5%), λ_{max}^{EtOH} 273 and 279 mμ (log ε 3.75 and 3.77 respectively), $[\alpha]_D^{23°}$-49.3° (in chloroform); it also gave dihydrolatifolin dimethyl ether (I) on methylation. In addition the red quinone gave a phenazine derivative with o-phenylene diamine which crystallised from methanol as yellow rhombs m.p. 124-25° (Found: C, 76.9; H, 6.0. Calculated for $C_{23}H_{22}O_2N_2$ C, 77.0; H, 6.1%).



The two quinones are therefore isomeric. The red quinone should be the ortho isomer (III) as evident from its colour, I.R. spectrum and the formation of a phenazine derivative. The yellow quinone, therefore, should be the p-isomer (II). The formation of an o-quinone in good yield is worth mentioning. Although examples of p-quinone formation by oxidative demethylation are known, this is probably the first example of o-quinone being produced by this method. The N.M.R. spectra of these two quinones differ only in the ring A protons and the data is given in the table I.

TABLE 1

N.M.R* of Yellow and Red quinone.

Compound	Ring B protons	Ring A protons
Yellow quinone.	2.8 - 3.2(4) m	3.6 (1) d (J = 1.0) 4.1 (1) s
Red quinone .	2.8 - 3.2 (4) m	3.85 (1) d (J = 1.0) 4.3 (1) s
	Methoxyl groups	C_3H_6 residue
Yellow quinone.	6.22 (6) s	9.10 (3) t (J = 7.0) 8.0 (2) q (J = 7.0) 5.56 (1) t ($J \simeq 7.0$)
Red quinone	6.22 (6) s	9.10 (3) t ($J \simeq 7.0$) 8.0 (2) q ($J \simeq 7.0$) 5.64 (1) t ($J \simeq 7.0$)

The O.R.D. curves of these quinones are presented in Fig.1. Both the quinones show enhanced negative Cotton effect in their O.R.D curves. Since negative Cotton effect has been correlated with R-configuration of 4-methoxy dalbergenone[5] having similar structure and since their O.R.D curve shapes are also very similar, the above two quinones must have R- configuration.

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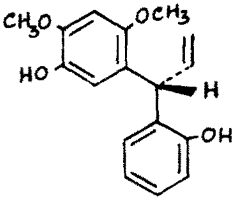
* Chemical shifts are given on the τ scale and proton integrals in brackets; s = singlet; d= doublet; t= triplet, q= quartlet; m = multiplet. The spectra were recorded on an A 60 varian spectrometer as solution in $CDCl_3$ with TMS as an internal standard.

Since these quinones are formed from latifolin by reactions which do not involve the asymmetric centre, latifolin should also possess the same R-configuration (IV).



IV

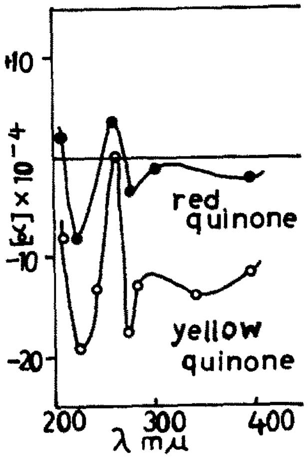


Fig. 1

Our thanks are due to Prof. W. Klyne, for the O.R.D. curves.

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