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COMPONENTS OF THE HEARTWOOD OF DALBERGIA LATIFOLIA, ROXB.,

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We have earlier reported[1] the isolation of latifolin from the light petroleum extract of the heartwood of Dalbergia latifolia, and discussed the constitution of its dimethyl ether. Latifolin, m.p. 122-123°, a colourless crystalline compound, had the molecular composition $C_{17}H_{18}O_4$, with two methoxyls, two hydroxyls and an ethylenic double bond. It was optically active and its dimethyl ether underwent isomeric change by means of alkali to yield iso latifolin-O-dimethyl ether (II). Oxidation of o-dimethyl latifolin with neutral potassium permanganate yielded ortho-methoxybenzoic acid. Based on its properties and reactions, O-dimethyl latifolin was formulated as in I. This was fully supported by its NMR spectrum and also by a synthesis of iso latifolin-O-dimethyl ether. Results of further work that has been done so far are given here in view of the recent communication by Eyton et. al.[2] on the

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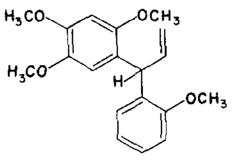
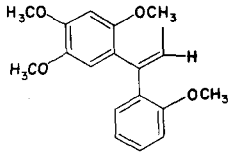
[1] Balakrishna, Rao and Seshadri, Tetrahedron (under publication).

[2] Eyton, Ollis, Sutherland, Jackman, Gottlieb and Magalhaes, Proc. Chem. Soc., 301 (1962).

components of the heartwood of Dalbergia nigra that has just now reached us.

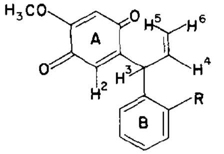


I

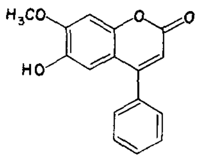


II

Oxidation of O-dimethyl latifolin with chromic acid has yielded an yellow quinone, m.p. 161-162°, having the molecular composition $C_{17}H_{16}O_4$ with two methoxyls, and it has been named latifolinone. A study of its reactions and spectral characteristics agree with the structure (III) which is also supported by its NMR spectrum (see Table I).



III R = OCH_3
IV R = H



V

Since there was a possibility that latifolinone may occur in the heartwood extractives, the light petroleum extract has been further investigated. The red viscous oil left after the separation of latifolin gave a colour reaction (blue colour with alcoholic alkali) similar to that of latifolinone, but no crystalline compound could so far be isolated from this fraction.

The heartwood residue was subsequently extracted with hot acetone and the dark coloured extract fractionated. Hot ethyl acetate extraction of this material left behind a dark purple coloured amorphous substance. It was readily soluble in alcohol producing a purple colour which changed to orange red on the addition of concentrated hydrochloric acid. Its constitution is under investigation. The ethyl acetate solution was chromatographed over deactivated neutral alumina followed by elution with a series of solvents in the increasing order of polarity. Light petroleum eluted a fraction which on crystallisation and rechromatography afforded four crystalline compounds, (1) latifolin, (2) dalbergin, (3) a yellow quinone and (4) a red quinone.

The yellow compound, m.p. 112-113° resembled latifolinone closely in reactions and spectra. But it had the composition $C_{16}H_{14}O_3$ with one methoxyl and yielded benzoic acid on oxidation with alkaline permanganate. It has therefore been given the structure (IV) and the name dalbergenone in view of the fact that it is related to dalbergin (V) and it is an ethylene and a quinone (see Rao[3]). This structure is also confirmed by its NMR spectrum (see Table I). The corresponding quinol has not yet been isolated. Dalbergenone seems to be the same as dalbergione reported by Eyton et. al.[2]

The red coloured quinone has been named dalatinone. It has the molecular composition $C_{23}H_{18}O_5$ with two methoxyls and gives no ferric chloride colour. Its colour, U.V. spectrum (λ_{max} 249, 305 and 428 mμ) and I.R. spectrum (ν_{max} 1667 cm^{-1}) indicated its quinonoid nature. It gave

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[3] M.M. Rao, Ph.D. Thesis, Delhi University, 1962.

TABLE 1

NMR* of latifolinone and dalbergenone

(τ values as PPM)

	H^1	H^2	H^3	H^4	H^5 & H^6
Latifolinone	4.05	3.67	4.83	4.17-3.58	5.13, 4.67.
Dalbergenone	4.09	3.50	4.87	4.13-3.55	5.12, 5.00, 4.80, 4.62.

	Methoxyl	Ring B protons
Latifolinone	6.22, 6.18 (6 protons)	3.25- 2.75 (4 protons)
Dalbergenone	6.17 (3 protons)	2.70 (5 protons)

an orange coloured monoacetate, m.p. 244-245°, (ν_{max} 1761, and 1667 cm^{-1}) showing the presence of a phenolic hydroxyl, and a colourless leucotriacetate (ν_{max} 1770 cm^{-1}) confirming the presence of the quinone unit. All the five oxygens could thus be accounted for. Further investigation is in progress.

The isolation of the above new components from D. latifolia and similar compounds from D. nigra, is of interest for the study of biogenesis. These are closely analogous to dalbergin (V), a 4-phenyl coumarin derivative, and the carbon skeleton and also the oxygenation pattern in ring A of all of them is the same. In an earlier

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*The spectra were recorded on an A-60 Varian spectrometer as solution in $CDCl_3$ with TMS. as an internal standard publication[4], a proposal was made that the biosynthesis of dalbergin and its analogues involves C_9 and C_6 units. But these are linked at the α-carbon atom of the C_9 unit, whereas in the normal flavonoids the linking is with the γ-carbon atom. The structure of the new compounds now discussed supports this view.

Acknowledgement- We wish to express our grateful thanks to Dr. Attilio Malera of Varian A.G. Zurich, for the NMR spectra.

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[4] Seshadri, Curr. Sci. 293 (1957).