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DALBERGIA SPECIES—II.*

ISOLATION OF (S)-DALBERGIONE FROM *DALBERGIA BARONI* BAKER

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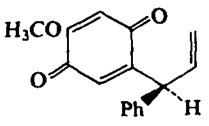
Abstract—The structure of a quinone isolated from the ligroin extract of *Dalbergia baroni* Baker was established as (S)-dalbergione (I).

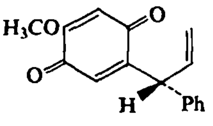
AN INVESTIGATION of the heartwood of *Dalbergia nigra* Fr. Allem.[1,2] and *Dalbergia latifolia* Roxb.[3,4] led to the isolation of a quinone called dalbergione, m.p. 114–116°; $[\alpha]_D^{21.5^\circ} + 13^\circ$ (chloroform). The absolute configuration of this compound has been established by Eyton *et al* [1] as (R)-dalbergione (II).

A quinone (I) has now been isolated from wood shavings of *Dalbergia baroni* Baker (Voamboana, Rosewood of Madagascar), by exhaustive extraction with hot ligroin. The yellow solid, obtained on evaporation of the solvent, was crystallized from ligroin to yield yellow needles, m.p. 118–119°; $[\alpha]_D^{22^\circ} - 13^\circ$ (chloroform). The i.r. spectrum of this compound in potassium bromide exhibited bands at 1629 cm^{-1}, 985 cm^{-1} and 914 cm^{-1} (vinyl group); 1600 cm^{-1}, 758 cm^{-1} and 699 cm^{-1} (mono-substituted aromatic ring). A solution of the compound in chloroform showed, in the i.r. spectrum, a doublet at 1646 cm^{-1} and 1667 cm^{-1} which resembled that described for a 5-alkyl-2-methoxy-*p*-benzoquinone.[5] A comparison of the u.v. curves of quinone (I) with its dihydroquinone derivative, and the quinol diacetate with the dihydroquinol diacetate showed that the vinyl group double bond was unconjugated.

An equimolecular mixture of (R)-dalbergione (II) isolated from *Dalbergia latifolia* and the quinone (I) obtained from *Dalbergia baroni* gave on crystallization from ligroin, a racemate, m.p. 125–126°; $[\alpha]_D^{21^\circ} \pm 0{\cdot}00^\circ$ (chloroform).



(I)



(II)

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* Part I, C. B. DEMPSEY, D. M. X. DONNELLY and R. A. LAIDLAW, *Chem. & Ind.* (*London*) 491 (1963).

[1] W. B. EYTON, W. D. OLLIS, I. O. SUTHERLAND, L. M. JACKMAN, O. R. GOTTLIEB and M. T. MAGALHÃES, *Proc. Chem. Soc.* 301 (1962).

[2] G. B. MARINI-BETTOLO, C. G. CASINOVI, O. GONÇALVES DA LIMA, M. H. DALIA MAIA and I. L. D'ALBUQUERQUE, *Ann. Chim.* (*Italy*) 1190 (1962).

[3] M. M. RAO and T. R. SESHADRI, *Tetrahedron Letters* 211 (1963).

[4] C. B. DEMPSEY, D. M. X. DONNELLY and R. A. LAIDLAW, *Chem. & Ind.* (*London*) 491 (1963).

[5] P. YATES, M. I. ARDAO and L. F. FIESER, *J. Am. Chem. Soc.* **78**, 650 (1956).

Determination of the optical rotatory dispersion curves (Fig. 1) confirmed that quinone (I) is (S)-dalbergione.

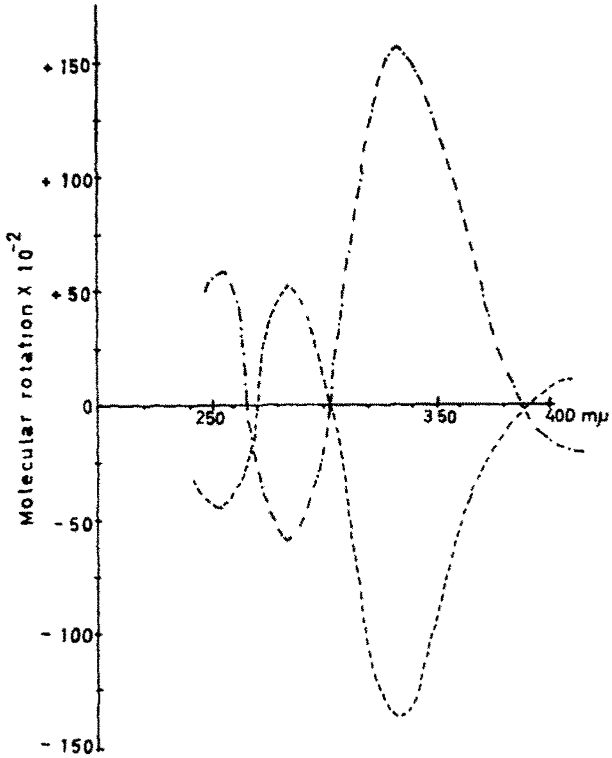

FIG. 1 OPTICAL ROTATORY DISPERSION CURVES IN METHANOL.

(R)-Dalbergione (–·–·–·), c 0·0086, 400–286; c 0·0017, 266–248 mμ
(S)-Dalbergione (– – – – –), c 0·0092, 400–284; c 0·0018, 271–248 mμ.

A comparative study of dalbergione derivatives is summarized in Table 1.

TABLE 1

	D. baroni		*D. latifolia*	
	m.p	$[\alpha]_D$*	m.p	$[\alpha]_D$*
Dalbergione	118–119	−13 ($CHCl_3$)	114–116	−13 ($CHCl_3$)
Dihydroquinone	142–143	−70·6	143	+67·4
Quinol diacetate	65	−20·9	98–99	+21·1
Dihydroquinol diacetate	90–92	−40·9	92–93	+37
2.4-DNP product	237 (dec.)	–	248 (dec.)	

* Rotations were measured in acetone solution unless otherwise stated.

The occurrence of antipodes in the same plant is rare. Some evidence[6] exists for the presence in various proportions of (+)- and (−)-sesamin in *Fagara xanthoxyloides*; in the

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[6] B. CARNMALM, H. ERDTMAN and Z. PELCHOWICZ, *Acta Chem. Scand.* 9, 1111 (1955).

case of prolichesterinic acid which occurs in *Cetraria islandica* Ach., the *dextro*-rotatory form appears in the European specimens of the lichen and the *laevo*-rotatory in the Japanese variety.[7, 8] The appearance of antipodes in the same genera but different species has been more widely observed, for example, the epicatechins in *Eucalyptus* species;[9] usnic acid in *Cladonia* species and α-pinene in the *Pinus* species.[10]

EXPERIMENTAL*

Isolation of Dalbergiones

Wood shavings (3 kg) of *Dalbergia baroni* Baker were extracted in a soxhlet with hot ligroin (7·5 l.). Evaporation of the solvent gave a yellow solid (25·7 g) which on repeated crystallization from ligroin afforded dalbergione (I) in yellow needles, m.p. 118–119°; $[\alpha]_D^{22°}$ − 13° (CHl_3); +99·8° (C_6H_6); λ_{max}^{EtOH} 207 mμ (log ε 4·13), 262 mμ (log ε 4·09); ν_{max}^{KBr} 1629 cm^{-1}, 985 cm^{-1}, 914 cm^{-1} (vinyl); 2841 cm^{-1} (methoxyl); 1605 cm^{-1}, 1488 cm^{-1}, 788 cm^{-1}, 699 cm^{-1} (mono-substituted phenyl). The i.r. spectrum (chloroform) in the carbonyl region shows a doublet at 1646 cm^{-1} and 1667 cm^{-1}. (Found: C, 76·1; H, 5·7; OMe, 12·2. $C_{16}H_{14}O_3$ calc. for dalbergione: C, 75·6; H, 5·6; OMe, 12·2%.) The product from reaction with 2,4-dinitrophenylhydrazine gave bronze needles, m.p. 237–239° (dec.). (Found: C, 60·2; H, 4·2; N, 12·7. Calc. for $C_{22}H_{18}N_4O_6$: C, 60·8; H, 4·2; N, 12·9%.)

Wood shavings of *Dalbergia latifolia* were extracted in a soxhlet with hot petroleum ether (b.p. 60–80°). Crystals of latifolin[4] were obtained on evaporation of the solvent. The residual oil was diluted with methanol to yield a yellow solid (R)-dalbergione (II) which was collected and crystallized from di-isopropyl ether, m.p. 114–116°; $[\alpha]_D^{22°}$ + 13° ($CHCl_3$). (Found: C, 75·7; H, 5·9; OMe, 12·2.) (R)-Dalbergione on treatment with 2,4-dinitrophenylhydrazine gave bronze needles, m.p. 243° (dec.) (Found: C, 60·85; H, 4·2; N, 13·0; OMe, 7·4. Calc. for $C_{22}H_{18}N_4O_6$: OMe, 7·4%.)

An equimolecular mixture of the dalbergiones (I) and (II) gave on crystallization from ligroin, a racemate m.p. 125–126°; $[\alpha]_D^{22°}$ ± 0·00°.

Dihydrodalbergiones

A mixture of (S)-dalbergione (I) (0·2 g), acetic acid (15 ml) and Adam's catalyst (0·12 g) was hydrogenated (2 moles absorbed). The filtrate was diluted with water and extracted with ether. The dried ethereal solution was treated with silver oxide (0·63 g) and anyhdrous sodium sulphate (0·65 g) and stirred in an atmosphere of nitrogen for 2 hr. The dihydrodalbergione (150 mg) which separated from the filtrate was collected and crystallized from di-isopropyl ether to give yellow needles, m.p. 142–143°; $[\alpha]_D^{22°}$ − 70·6°; λ_{max}^{EtOH} 207 mμ (log ε 4·09), 262 mμ (log ε 4·13); $\nu_{max}^{CHCl_3}$ 1672 cm^{-1}, 1653 cm^{-1} (carbonyl). (Found: C, 75·2; H, 6·6; OMe, 12·2. Calc. for $C_{16}H_{16}O_3$: C, 75·0; H, 6·3; OMe, 12·1%.)

The dihydro derivative, prepared from (R)-dalbergione (II), separated from methanol in yellow needles, m.p. 143°; $[\alpha]_D^{22°}$ + 67·4°. (Found: C, 75·1; H, 6·4; OMe, 12·2; C—CH_3, 6·43. Calc. for $C_{16}H_{16}O_3$: C, 75·0; H, 6·3; OMe, 12·1%; C—CH_3, 5·8%.)

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* Optical rotations were determined in acetone unless otherwise stated. Ultra-violet spectra were measured in absolute ethanol in a Bausch and Lomb Spectronic 505 and infra-red spectra were measured in a Beckman I.R.-5 Spectrophotometer.

[7] F. M. Dean, *Naturally Occurring Ring Compounds*, p. 59, Butterworths, London (1963).

[8] Y. Asahina and M. Yasue, *Ber.* **70**, 1053 (1937).

[9] R. P. Biggs, W. L. Cooper, E. O. Hazleton, M. Nierenstein and P. H. Price, *J. Am. Chem. Soc.* **53**, 1500 (1931).

[10] M. Berthelot, *Ann.* **88**, 342 (1853).

An equimolecular mixture of the dihydro derivatives from (I) and (II) gave on crystallization from di-isopropyl ether, a racemate, m.p. 157–158°; $[\alpha]_D^{22}$ (±) 0·00°.

Quinol Diacetates

A mixture of (S)-dalbergione (I) (1 g), sodium acetate (0·208 g), zinc dust (5·6 g) and acetic anhydride (60 ml) was refluxed for 2 hr. The filtered solution was diluted with ice-water to give a precipitate of quinol diacetate (1 g). The white solid was collected and crystallized from 95% ethanol to yield needles, m.p. 65–66°; $[\alpha]_D^{22}$ −20·9°; $\nu_{max}^{CHCl_3}$ 1757 cm^{-1} (phenolic ester). (Found: C, 70·6; H, 6·2. Calc. for $C_{20}H_{20}O_5$: C, 70·5; H, 5·9%.)

The quinol diacetate prepared from (R)-dalbergione (II) formed plates when crystallized from 95% ethanol, m.p. 98–99°; $[\alpha]_D^{22}$ +21·1°; λ_{max}^{EtOH} 230 mμ (shoulder) (log ε 4·14), 278 mμ (log ε 3·49). (Found: C, 70·6; H, 6·3.)

An equimolecular mixture of the quinol diacetates from (I) and (II) gave on crystallization from 95% ethanol, a racemate, m.p. 105–106°; $[\alpha]_D^{21}$ (±) 0·00°.

Dihydroquinol Diacetates

A mixture of the dihydrodalbergione (100 mg), obtained from (S)-dalbergione (I), sodium acetate (20·8 mg), zinc dust (500 mg) and acetic anhydride (6 ml) was refluxed for 1 hr. The filtrate was poured into ice-water. The precipitated dihydroquinol diacetate (90 mg) was collected and crystallized from 95% ethanol to form needles, m.p. 90–92°; $[\alpha]_D^{22}$ −40·9°; $\nu_{max}^{CHCl_3}$ 1575 cm^{-1} (carbonyl). (Found: C, 70·6; H, 6·3. Calc for $C_{20}H_{22}O_5$: C, 70·2; H, 6·4%.) This dihydroquinol diacetate was identical with the hydrogenation product of quinol diacetate from (S)-dalbergione.

The dihydroquinol diacetate prepared from (R)-dalbergione (II) was crystallized from 95% ethanol to yield needles, m.p. 92–93°; $[\alpha]_D^{22}$ +37°. (Found: C, 70·6; H, 6·3; OMe, 9·1. Calc. for $C_{20}H_{22}O_5$: C, 70·2; H, 6·4; OMe, 9·07%.)

Note added in proof: (S)-Dalbergione has been isolated from *Dalbergia violacea* by Dr. O. R. Gottlieb, private communication.

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