

QUINONOID CONSTITUENTS OF *DALBERGIA RETUSA* HEARTWOOD

L. JURD, K. STEVENS and G. MANNERS

Western Regional Research Laboratory, Agricultural Research Service U.S. Department of Agriculture, Berkeley, CA 94710, U.S.A.

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Key Word Index—*Dalbergia retusa*; Leguminosae; quinonoids; obtusaquinone; quinhedrone of 4-methoxy-dalbergione.

Abstract—Light petrol. extracts of *Dalbergia retusa* heartwood yield major quantities of obtusaquinone and minor amounts of the blue-black quinhedrone of racemic 4-methoxy-dalbergione.

INTRODUCTION

RECENT studies on *Dalbergia* have shown that the timbers of this genus contain a number of unusual types of natural phenols and phenol-derived quinone pigments.¹ Except for an early report of the presence of an unidentified yellow quinone, mp. 125–126°, the constituents of the Panamanian tree, *Dalbergia retusa* (cocobolo),* have not yet been described.² However, in addition to its phytochemical interest as a member of the *Dalbergia* genus, the wood of this particular tree is significant because of its outstanding resistance to attack by teredos, limnoria, and other marine boring organisms. In this connection Southwell and Bultman of the Naval Research Laboratory recently concluded³ a long-term examination of the durability of woods from 115 different species, all reputed to possess high natural resistance to decay. After immersion in tropical waters for 90 months, only the wood of *Dalbergia retusa* proved to be resistant to attack by all marine borers. At the invitation of Dr. Bultman, a detailed chemical examination of the extractives of this wood is now being undertaken to isolate and identify the larvicidal constituent(s). An indication that the active component may well be a 1,3- or 3,3-diarylpropene derivative of a type previously encountered in other *Dalbergia* species is provided by the recent recognition that obtusa-styrene and similar cinnamyl-phenols possess pronounced microbiocidal properties.⁴

* The Panamanian cocobolo wood used in this investigation was identified by Dr. Bultman as *Dalbergia retusa* Hemsley and this identification has kindly been confirmed by Dr. B. F. Kukachka, Wood Identification Research, Forest Products Laboratory, Madison, Wisconsin. This species is *not* identical with *Dalbergia obtusa*, although some confusion may arise from the fact that the latter species, which was first found in Madagascar and is described as having a violet, almost black wood, was originally called *Dalbergia retusa*, e.g. *Chem. Commun.* 1394 (1968) refers to *D. obtusa* Lecomte (Syn. *D. retusa*)¹. Lecomte (*Bull. Mus. Nation. Hist. Nat. (Paris)* 1, 159 (1929) pointed out that the name *Dalbergia retusa* Hemsley had already been given to a Panamanian *Dalbergia* (cocobolo) and that the Madagascar species, which he renamed *Dalbergia obtusa*, must not be confused with this ('... D'après les règles de la nomenclature, l'espèce de Baillon, postérieure à celle de Hemsley et ne confondant pas avec cette Dernière, doit recevoir un nom spécifique nouveau et nous proposons celui de *D. obtusa*').

Dalbergia obtusa Lecomte heartwood contains obtusaquinone, (*R*)-4-methoxydalbergione and its quinol stereochemistry unspecified), and the cinnamyl phenol, obtustastyrene. *Dalbergia retusa* Hemsley contains obtusaquinone which may indicate a close relationship to *D. obtusa* Lecomte. The Hemsley species does differ, however, in that the 4-methoxydalbergione and its quinol are *racemic* and in that the heartwood does not appear to contain the cinnamyl phenol, obtustastyrene.

¹ T. R. SESHADRI, *Phytochem.* 11, 881 (1972).

² A. BRAGA DE OLIVEIRA, O. R. GOTTLIEB, W. D. OLLIS and C. T. RIZZINI, *Phytochem.* 10, 1863 (1971).

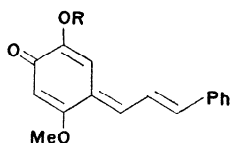
³ C. R. SOUTHWELL and J. D. BULTMAN, *Biotropica* 3, 81 (1971).

⁴ L. JURD, A. D. KING, JR., K. MIHARA and W. L. STANLEY, *Appl. Microbiol.* 21, 507 (1971).

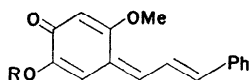
RESULTS AND DISCUSSION

The heartwood of *Dalbergia retusa* is intensely orange in color. Long extraction of heartwood sawdust with low boiling petroleum yields the principal pigment as an orange-red, crystalline compound, m.p. 178–179°, and minor quantities of a blue-black, crystalline pigment, m.p. 102–103°. The orange pigment, which constitutes approx. 3% of the weight of the undried heartwood, may be the primary active constituent of *Dalbergia retusa* heartwood. It is highly toxic to fish, lethal concentrations being as low as 200 ppb for the species studied, and its effects on marine boring organisms are currently being investigated in some detail by Dr. Bultman and his group.

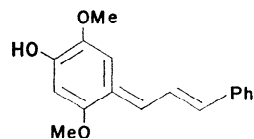
The orange pigment has a molecular formula of $C_{16}H_{14}O_3$, and contains one methoxyl and one hydroxyl group. In ethanol it has $\lambda_{\max}$ 397 nm ($\epsilon_{\max}$ 37 000) with low intensity inflections at 268 nm and 253 nm. Its 100 MHz NMR spectrum in $CDCl_3$ shows the presence of the methoxyl as a singlet at δ 3.85 (3H), two uncoupled quinoidal protons as singlets at δ 5.88 (1H) and δ 6.83 (1H), an hydroxyl proton as a sharp singlet at δ 6.96 (1H), and three highly deshielded olefinic and five phenyl protons as an 8H multiplet at δ 7.0–7.6. The pigment is readily reduced by sodium dithionite in aqueous methanol or in aqueous acetic acid to yield a mixture of *o*-diphenolic compounds. These spectral properties are indicative of a quinone-methide structure, the data being in close agreement with those reported⁵ for obtusaquinone, a novel *p*-quinone-methide recently isolated from *Dalbergia obtusa*. However, although the *D. retusa* pigment and obtusaquinone appeared spectrally equivalent, the reported m.p. (155°) and stability to sodium dithionite reduction of obtusaquinone were contrary to the observed behavior of the *D. retusa* pigment. Thus, these discrepancies initially suggested the orange pigment to be an isomer of obtusaquinone. Further investigation of the *D. retusa* pigment, however, eliminated the possibility of structural isomerism and firmly established its structure as Ia or IIa. Direct comparison with obtusaquinone has now confirmed their identity,⁶ and Dr. W. D. Ollis has indicated that the m.p. description of obtusaquinone should be corrected to read "m.p. 174–175°, with preliminary softening at 155–160°".



(Ia) R = H
(Ib) R = Me



(IIa) R = H
(IIb) R = Me



Violastylene (III)

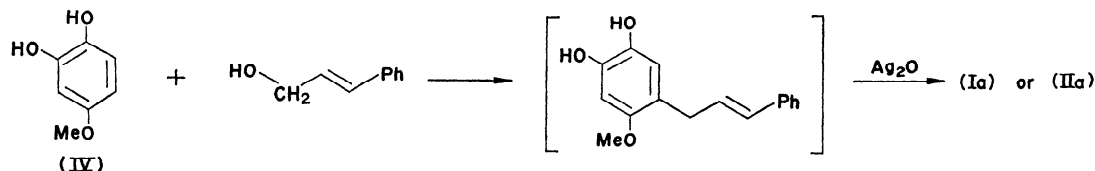
Obtusaquinone formed a methyl ether which was reduced with sodium borohydride to violastylene III, and to dihydroviolastylene on catalytic hydrogenation. The reduction of *O*-methylobtusaquinone to violastylene (and the reverse oxidation mentioned below) confirms the *trans* configuration of the ethylenic double bond attached to the phenyl ring, and with the NMR spectral data, confirms structure Ib or IIb for *O*-methylobtusaquinone.

Oxidation of violastylene by lead dioxide in benzene as previously reported,⁵ or better, by silver oxide in ether gives good yields of *O*-methylobtusaquinone, m.p. and m.m.p. 169°. This pigment, which was also formed from violastylene by oxidation with DDQ,

⁵ M. GREGSON, W. D. OLLIS, B. T. REDMAN, I. O. SUTHERLAND and H. H. DIETRICH, *Chem. Commun.* 1395 (1968).

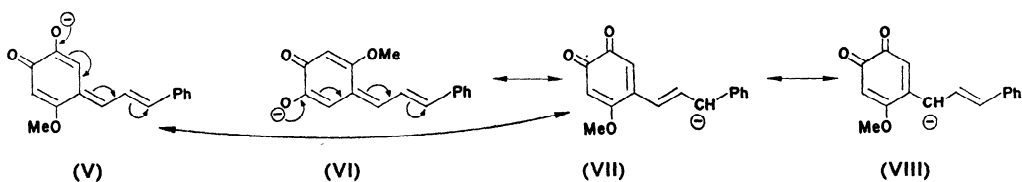
⁶ W. D. OLLIS, private communication.

can be synthesized quickly and conveniently by brief acid-catalyzed condensation of cinnamyl alcohol with 2,5-dimethoxyphenol and, without further separation, silver oxide oxidation of the crude mixture of alkylated products. *O*-methyl obtusaquinone readily crystallizes from the oxidation reaction mixture.



The *Dalbergia retusa* pigment is readily reduced by catalytic hydrogenation, by sodium borohydride in methanol, and by sodium dithionite to yield *o*-diphenolic products. The formation of catechol derivatives is in accord with structure Ia or IIa. This structural assignment was confirmed by a new and simple synthesis of the pigment, involving acid-catalyzed condensation of cinnamyl alcohol with 4-methoxycatechol (IV) and subsequent silver oxide oxidation of the crude condensation mixture.

The experimental evidence described above confirms the structure of obtusaquinone as Ia or IIa, and of *O*-methyl obtusaquinone as Ib or IIb. It does not, however, unambiguously distinguish these geometric isomers. Furthermore, although molecular models do indicate that there is less steric hindrance to planarity in forms Ia and Ib than in IIa and IIb, it would appear that obtusaquinone and its *O*-methyl derivative do not necessarily have the same geometric configuration. Thus, the anion formed from obtusaquinone in alkaline solution could be a resonance hybrid of canonical forms V, VI, VII, VIII, etc. which on methylation could lead to either geometric form.

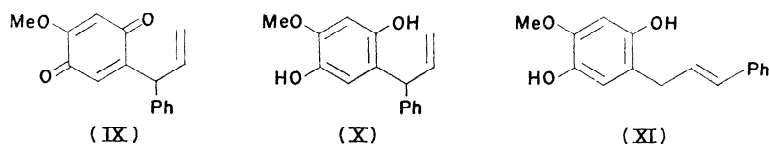


The optically inactive, blue-black pigment is an easily dissociated molecular complex (quinhydrone) of an optically inactive, yellow quinone, $\text{C}_{16}\text{H}_{14}\text{O}_3$ (m.p. 125°), identical with racemic⁷ 4-methoxydalbergione IX, and a colorless, dihydric phenol, $\text{C}_{16}\text{H}_{16}\text{O}_3$ (m.p. 98° ; dibenzoate, m.p. $146\text{--}147^\circ$). The NMR spectra of the phenol and its diacetate (m.p. 104°) are in accord with structure X, and this was confirmed by the synthesis of the crystalline phenol by, (a) sodium dithionite reduction of 4-methoxydalbergione IX and of the natural quinhydrone, and (b) acid-catalyzed condensation of methoxyquinol with cinnamyl alcohol. The latter reaction leads to an easily separable mixture of the cinnamylquinol XI and X. The synthetic quinhydrone, prepared by crystallizing equimolecular quantities of synthetic IX and X, was identical in all respects with the blue-black pigment from *Dalbergia retusa* extracts. The co-occurrence of IX and X is interesting, because quinones and their corresponding quinols have rarely⁸ been isolated from the same source. The occurrence

⁷ L. JURD, *Tetrahedron Letters* 2863 (1969).

⁸ W. B. EYTON, W. D. OLLIS, M. FINEBERG, O. R. GOTTLIEB, I. S. S. GUIMARÃES and M. T. MAGALHÃES, *Tetrahedron* 21, 2697 (1965).

of antipodes in the same plant is also rare⁹ and racemic dalbergiones have not previously been isolated from plants.² In 1968 it was briefly mentioned that a substance (obtusaquinol)¹⁰ of structure X co-occurs with (*R*)-4-methoxydalbergione in *Dalbergia obtusa*. Since the physical properties (m.p., rotation, etc.) of obtusaquinol have not been reported, it is not known whether it is identical with the racemic *Dalbergia retusa* product or is one of the optically active forms.



EXPERIMENTAL

Extraction of *Dalbergia retusa* heartwood. Sawdust of *Dalbergia retusa* heartwood (2500 g) was extracted continuously with warm, low-boiling light petrol. for 7 days. The solid which separated in the extract was collected, warmed with Et₂O and filtered to yield crude obtusaquinone as an orange crystalline solid (71.0 g). The light petrol. filtrate was concentrated to 400 ml, decanted from an oil (A), concentrated further to 150 ml and allowed to stand. The quinhydrone of 4-methoxydalbergione and 4-methoxydalbergioquinol separated as blue-black prisms (0.93 g). Additional quantities (1.12 g) of the quinhydrone were obtained by re-extraction of the oil (A) with low boiling light petrol.

Obtusaquinone (Ia or IIa). (a) The major orange pigment from *Dalbergia retusa* crystallized from acetone or ethyl acetate as glistening, orange-red needles, m.p. 178–179°, and from benzene as orange-red needles, m.p. 176–177°. (Found: C, 75.7; H, 5.52; MeO-, 12.2. Calc. for C₁₆H₁₄O₃: C, 75.6; H, 5.55; MeO-, 12.2%.) It gave an intense olive-green color with alcoholic FeCl₃. Silicic acid TLC, *R_f* 0.34 (benzene–EtOH, 9:1), 0.75 (CHCl₃–MeOH, 10:1), 0.78 (CHCl₃–MeOH, 4:1). (b) A mixture of 4-methoxycatechol (1.4 g) and cinnamyl alcohol (1.3 g) was heated under reflux with 2% aq. oxalic acid (50 ml) for 20 hr. The oily product was extracted with Et₂O and after washing with H₂O the dried Et₂O solution was treated with silver oxide (3.0 g). The mixture was heated for 10 min and filtered. The filtrate was evaporated to an oil which was dissolved in warm benzene. On cooling, obtusaquinone crystallized (0.71 g). Recrystallized from benzene and from acetone synthetic obtusaquinone separated as orange-red needles, m.p. 178–179°, identical in all respects with the natural product. (Found: C, 75.7; H, 5.65. Calc. for C₁₆H₁₄O₃: C, 75.6; H, 5.55%.)

O-Methylobtusaquinone (Ib or IIb). (a) The orange pigment (5.0 g) from *Dalbergia retusa* was heated under reflux with Me₂SO₄ (8.0 g), anhydrous K₂CO₃ (25 g) and dry acetone (200 ml) for 1 hr. The mixture was concentrated and diluted with H₂O. The product crystallized from EtOAc. O-Methylobtusaquinone was thereby obtained as long, orange needles, m.p. 169° (3.70 g). (Found: C, 75.9; H, 6.27; MeO-, 23.2. Calc. for C₁₇H₁₆O₃: C, 76.1; H, 6.01; 2 MeO-, 23.1.) 100 MHz NMR spectrum in CDCl₃: 3H, *s*, δ 3.78; 3H, *s*, δ 3.85; 1H, *s*, δ 5.81; 1H, *s*, δ 6.56; 8H, *m*, δ 6.95–7.55. (b) 2,5-Dimethoxyphenol (2.8 g) and cinnamyl alcohol (3.0 g) were heated in formic acid (10 ml) and H₂O (5 ml) for 40 min. Excess of H₂O was added and the oily product was extracted with Et₂O. The ether solution was washed with sat. aq. Na₂CO₃ and treated with silver oxide (3.0 g). The mixture was allowed to stand with occasional shaking and warming for 10 min. The filtered ether solution was then concentrated with the slow addition of low boiling light petrol. until yellow crystals began to separate. After cooling the product was collected and recrystallized from EtOAc. O-Methylobtusaquinone (1.6 g) was thereby obtained as orange needles, m.p. 169°, identical in all respects with the product from (a). (Found: C, 76.1; H, 6.10. Calc. for C₁₇H₁₆O₃: C, 76.1; H, 6.01%.) O-Methylobtusaquinone (0.45 g) was also synthesized by oxidation of pure violastylene (1.0 g) in Et₂O (100 ml) with silver oxide (2.0 g) under similar conditions.

Violastylene III. (a) A suspension of O-methylobtusaquinone (0.30 g) in MeOH (10.0 ml) was treated at room temp. with NaBH₄ (0.15 g). After 5 min excess of H₂O was added and the colorless, solid product was collected (0.30 g). Recrystallized successively from 50% aq. HOAc and from low boiling light petrol., violastylene separated as glistening, colorless needles, m.p. 83–84°, identical with authentic material.¹¹ (Found: C, 75.8; H, 6.84. Calc. for C₁₇H₁₈O₃: C, 75.5; H, 6.71%.) 100 MHz NMR spectrum in CDCl₃: 2H, *d*, δ 3.47, *J* = 6.0 Hz; 3H, *s*, δ 3.78; 3H, *s*, δ 3.82; 1H, *s*, δ 5.56 (OH); 2H, *m*, δ 6.32–6.40; 1H, *s*, δ 6.58; 1H, *s*, δ 6.71; 5H, *m*, δ 7.15–7.38. Treated with benzoyl chloride and pyridine the product formed

⁹ B. J. DONNELLY, D. M. X. DONNELLY and C. B. SHARKEY, *Phytochem.* 4, 337 (1965).

¹⁰ M. GREGSON, K. KUROSAWA, W. D. OLLIS, B. T. REDMAN, R. J. ROBERTS, I. O. SUTHERLAND, A. BRAGA DE OLIVEIRA, W. B. EYTON, O. R. GOTTLIEB and H. H. DIETRICH, *Chem. Commun.* 1390 (1968).

¹¹ S. MAGESWARAN, W. D. OLLIS, R. J. ROBERTS and I. O. SUTHERLAND, *Tetrahedron Letters* 2897 (1969).

a *monobenzoate*, colorless needles from MeOH, m.p. 101–102°. Violastylene (0.70 g) was dissolved in tetrahydrofuran (20 ml) and hydrogenated at atmospheric pressure and room temp. in the presence of 5% Pd-*C* *dihydroviolastylene* crystallized from low boiling light petrol. as glistening, colorless needles, m.p. 59–60° (0.50 g). 100 MHz NMR spectrum in CDCl_3 : 2H, *m*, δ 1.91; 4H, *m*, δ 2.63; 3H, *S*, δ 3.75; 3H, *S*, δ 3.83; 1H, *S*, δ 5.51; 1H, *S*, δ 6.54; 1H, *S*, δ 6.64; 5H, *m*, δ 7.10–7.35. Catalytic hydrogenation of *O*-methylobtusaquinone under similar conditions gave dihydroviolastylene, m.p. and m.m.p. 59°.

Racemic quinhydrone of 4-methoxydalbergione and 4-methoxydalbergiquinol. (a) The blue-black crystalline product from *Dalbergia retusa* was recrystallized from Et_2O -low boiling light petrol. to yield the *quinhydrone* as hard, glistening, blue-black needles, m.p. 102–103° (to an orange liquid). (Found: C, 75.3; H, 5.98; MeO, 12.2. Calc. for $\text{C}_{32}\text{H}_{30}\text{O}_6$: C, 75.3; H, 5.92; 2 MeO-, 12.2%.) The quinhydrone is optically inactive (measured in benzene), and on silicic acid TLC it dissociates into a fast-moving yellow component (R_f 0.81, benzene-EtOH, 9:1) and a colorless component (R_f 0.43). The quinhydrone (0.93 g) was chromatographed on a silicic acid column (55×2.5 cm) with benzene as eluent. Evaporation of the high R_f fraction gave racemic 4-methoxydalbergione as a yellow, crystalline solid (0.43 g) which on recrystallization from MeOH gave racemic 4-methoxydalbergione, m.p. and m.m.p. 125°. Evaporation of the low R_f fraction gave 4-methoxydalbergiquinol as an oil which rapidly crystallized (0.41 g). (b) A solution in ether of synthetic 4-methoxydalbergione (0.12 g) and 4-methoxydalbergiquinol (0.12 g), prepared as described below, was diluted with low boiling light petrol. and concentrated until blue-black crystals began to separate. After cooling the product was collected (0.21 g) and recrystallized from Et_2O -light petrol. The synthetic quinhydrone of 4-methoxydalbergione and 4-methoxydalbergiquinol was obtained as brittle, blue-black needles, m.p. and m.m.p. with the product in (a), 102–103°.

Racemic 4-methoxydalbergiquinol. (a) The colorless product from the natural quinhydrone was recrystallized from Et_2O -light petrol. 4-Methoxydalbergiquinol from the quinhydrone separated as colorless needles from Et_2O -light petrol., m.p. 98–99°, undepressed with the synthetic specimens described below. (Found: C, 75.1; H, 6.42. Calc. for $\text{C}_{16}\text{H}_{16}\text{O}_3$: C, 75.0; H, 6.29%.) If formed a *diacetate*, m.p. and m.m.p. with synthetic 4-methoxydalbergiquinol diacetate, 104–105°. 100 MHz NMR spectrum in CDCl_3 : 3H, *S*, δ 2.08; 3H, *S*, δ 2.35; 3H, *S*, δ 3.80; 1H, sextet, δ 4.76; 1H, sextet, δ 4.80; 1H, sextet, δ 5.18; 1H, octet, δ 6.17; 1H, δ 6.68; 1H, *S*, δ 6.85; 5H, *m*, δ 7.00–7.40. The *dibenzoate* crystallized from MeOH as colorless, glistening needles, m.p. 146–147°. (Found: C, 77.5; H, 5.15; Calc. for $\text{C}_{30}\text{H}_{24}\text{O}_5$: C, 77.6; H, 5.21%.) (b) An ethereal solution of natural 4-methoxydalbergione was decolorized by shaking with 5% aq. sodium dithionite. Crystallization of the product from Et_2O -light petrol. gave 4-methoxydalbergiquinol, m.p. and m.m.p. 98–99°.

Reaction of methoxyquinol with cinnamyl alcohol. Synthesis of X and XI. (a) A mixture of methoxyquinol (20 g), cinnamyl alcohol (20 g), ascorbic acid (5 g) and 5% aq. citric acid solution (500 ml) was heated under reflux for 20 hr. The oily product was separated by decantation and dissolved in warm benzene (200 ml). Addition of low boiling light petrol. to the dried benzene solution precipitated XIII as cream-colored crystals on cooling. Recrystallized from benzene-light petrol. the crystalline product (13.8 g) gave 5-cinnamyl-2-methoxyquinol as colorless needles, m.p. 108°. (Found: C, 74.9; H, 6.26; MeO-, 12.4. Calc. for $\text{C}_{16}\text{H}_{16}\text{O}_3$: C, 75.0; H, 6.29; 1 MeO-, 12.1%.) The *diacetate* separated from methanol as colorless needles, m.p. 103–104° (Found: C, 70.4; H, 5.92; MeO-, 9.14; CH_3CO -, 25.0. Calc. for $\text{C}_{20}\text{H}_{20}\text{O}_5$: C, 70.6; H, 5.92; 1 MeO-, 9.11, 2 CH_3CO -, 25.3%.) 100 MHz NMR spectrum of the diacetate in CDCl_3 : 6H, *S*, δ 2.40; 2H, *d*, δ 3.35, *J* = 6.0 Hz; 3H, *S*, δ 3.77; 1H, sextet, δ 6.16, *J* = 16.0–6.0 Hz; 1H, *d*, δ 6.43, *J* = 16.0 Hz; 1H, *S*, δ 6.68; 1H, *S*, δ 6.93; 5H, *m*, δ 7.14–7.40. Benzoylation of XIII gave the *dibenzoate*, colorless prisms from acetone-MeOH, m.p. 147–148°. (Found: C, 77.5; H, 5.25. Calc. for $\text{C}_{30}\text{H}_{24}\text{O}_5$: C, 77.6; H, 5.21%.) The benzene-light petrol. solution of the reaction product, after separation of the crude 5-cinnamyl-2-methoxyquinol, was evaporated to an oil. This was warmed with Ac_2O (20 ml) and pyridine (5 ml). The oily acetate readily crystallized from MeOH. 4-Methoxydalbergiquinol diacetate thereby separated as colorless needles, m.p. 104–105° (8.0 g), identical with the diacetate of natural 4-methoxydalbergiquinol. (Found: C, 70.8; H, 5.90. Calc. for $\text{C}_{20}\text{H}_{20}\text{O}_5$: C, 70.6; H, 5.92%.) The above diacetate (2.0 g) was suspended in MeOH and treated at boiling with a solution of sodium dithionite (3.0 g) in 10% aq. NaOH (20 ml). After 5 min H_2O was added, the clear solution was acidified, and the oily product was extracted with Et_2O . The dried ether solution was diluted with low boiling light petrol. and concentrated until colorless crystals began to separate. 4-Methoxydalbergiquinol was recrystallized from Et_2O -light petrol. to give colorless needles, m.p. 98–99° (1.02 g), identical with the natural product. (Found: C, 75.0; H, 6.34. Calc. for $\text{C}_{16}\text{H}_{16}\text{O}_3$: C, 75.0; H, 6.29%.) 100 MHz NMR spectrum in CDCl_3 : 3H, *S*, δ 3.81; broad singlet, δ 4.56 (OH); 4H, *m*, δ 4.78–5.34 (OH and 3 olefinic protons); 1H, octet, δ 6.32; 1H, *S*, δ 6.42; 1H, *S*, δ 6.64; 5H, *m*, δ 7.14–7.40. (b) A solution of synthetic 4-methoxydalbergiquinol (1.5 g) in Et_2O (100 ml) was shaken overnight with saturated aq. Na_2CO_3 (40 ml). The yellow solid obtained on evaporation of the Et_2O layer crystallized from MeOH to yield *racemic* 4-methoxydalbergione as yellow needles, m.p. 125° (lit. m.p. 125°) (0.55 g). (Found: C, 75.6; H, 5.58. Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_3$: C, 75.6; H, 5.55%.) This product was identical with the natural dalbergione. (c) A solution of 5-cinnamyl-2-methoxyquinol (1.6 g) in Et_2O (100 ml) was shaken with saturated aq. Na_2CO_3 as in (b). Yellow crystals separated at the interface. The ether layer was evaporated and the product, combined with the yellow crystals, was recrystallized from MeOH. 5-Cinnamyl-2-methoxybenzoquinone

separated as golden-yellow, glistening needles, m.p. 131–132° (0.60 g), $\lambda_{\text{max}}^{\text{EtOH}}$ 257 (4.45), 368 (3.24) nm (log ϵ). (Found: C, 75.4; H, 5.52. Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_3$: C, 75.6; H, 5.55%.) Better yields were obtained by oxidation of 5-cinnamyl-2-methoxyquinol (2.56 g) in 100 ml of Et_2O with silver oxide (7.0 g). After 20 min the filtered Et_2O solution was evaporated and the product was crystallized from MeOH to give the cinnamylquinone as yellow needles, m.p. and m.m.p. 131–132° (1.60 g).

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