International Tables for X-ray Crystallography (1968). Vol. III, p. 276. Birmingham: Kynoch Press.

JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

ROBERTS, P. & SHELDRICK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.

SCHMALLE, H. W., JARCHOW, O. H., HAUSEN, B. M. & SCHULZ, K. H. (1983*a*). *Funkt. Biol. Med.* **2**, 9–17.

SCHMALLE, H. W., JARCHOW, O. H., HAUSEN, B. M. & SCHULZ, K. H. (1983*b*). Abstr. Eighth Eur. Crystallogr. Meet., Liège, Belgium, p. 30.

SCHMALLE, H. W., JARCHOW, O. H., HAUSEN, B. M. & SCHULZ, K. H. (1984). *Acta Cryst.* C**40**, 1084–1087.

SCHULZ, K. H., GARBE, I., HAUSEN, B. M. & SIMATUPANG, M. H. (1979). *Arch. Dermatol. Forsch.* **264**, 275–286.

SHELDRICK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1984). C**40**, 1090–1092

Structure of (*R*)-3,4-Dimethoxydalbergione,* $C_{17}H_{16}O_4$

BY HELMUT W. SCHMALLE AND OTTO H. JARCHOW

Mineralogisch-Petrographisches Institut der Universität Hamburg, Grindelallee 48, *D*-2000 *Hamburg* 13, *Federal Republic of Germany*

AND BJÖRN M. HAUSEN AND KARL-HEINZ SCHULZ

Universitäts-Hautklinik Hamburg-Eppendorf, Martinistrasse 52, *D*-2000 *Hamburg* 20, *Federal Republic of Germany*

(*Received* 5 *December* 1983; *accepted* 24 *February* 1984)

Abstract. $M_r = 284{\cdot}31$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}462$ (1), $b = 7{\cdot}961$ (1), $c = 25{\cdot}254$ (2) Å, $V = 1500{\cdot}2$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}259$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $T = 296$ K, $F(000) = 600$, $\mu = 0{\cdot}745$ mm^{-1}, final $R = 0{\cdot}095$ for 885 observed reflections. The quinone ring is almost planar with a maximum out-of-plane deviation of $-0{\cdot}02$ (1) Å for C(3). The average values of the C–C distances and corresponding angles of the chiral atom C(7) are 1·51 (2) Å and 112·1 (1·3)°. The mean dimensions of the quinone ring are C–C = 1·485 (11), C=C = 1·346 (16), C=O = 1·206 (14) Å and C–C–C = 118 (1), C=C–C = 121 (1), O=C–C = 121 (1)°. The methylene distance is 1·306 (13) Å. The structure consists of discrete molecules.

Introduction. The structure determination of the title compound (*R*-3,4-DMD) was undertaken in order to compare its conformation with those of related dalbergiones causing contact dermatitis (Schmalle, Jarchow, Hausen & Schulz, 1984*b*). *R*-3,4-DMD possesses the highest sensitizing power of all dalbergiones; its chemical structure and absolute configuration have been established by Eyton, Ollis, Fineberg, Gottlieb, Salignac de Souza Guimarães & Taveira Magalhães (1965). The results of an X-ray analysis are given in this paper as part II of a series on dalbergiones.

Experimental. For additional details see part I (Schmalle *et al.*, 1984*b*). *R*-3,4-DMD from the heartwood of Brazilian Pao ferro (*Machaerium sclerox-ylum* Tul.). Very soft red needle- and plate-shaped crystals, m.p. 314–316 K. Crystal 0·49 × 0·37 × 0·09 mm. Unit cell: 13 reflections in the interval $4° < \theta < 36°$. $(\sin\theta/\lambda)_{max} = 0{\cdot}531$ Å^{-1}, $-7 \le h \le 0$, $-8 \le k \le 0$, $-26 \le l \le 17$. 1893 reflections measured, $R_{int} = 0{\cdot}076$, 1148 unique reflections, 886 with $I \ge 3\sigma(I)$, 262 unobserved. The crystal changed its quality during the measurement; because of the resulting poor data set the molecule was refined as a fixed model. H-atom positions calculated and their distances fixed at 1·08 Å within an error of 0·015 Å in the full-matrix least-squares refinement. Number of reflections in final refinement cycle, $m = 885$ (002 omitted, because secondary extinction was suspected); parameters refined, $n = 225$; unit weight, $R = 0{\cdot}095$. $(\Delta/\sigma)_{max} = 1{\cdot}67$ (H-atom positional parameter) in final refinement cycle. Max. and min. heights in final difference Fourier synthesis 0·26 and $-0{\cdot}29$ e Å^{-3}.

Discussion. The atomic parameters of the C and O atoms are listed in Table 1.† The atom-numbering

*IUPAC name: (*R*)-2,3-dimethoxy-5-(1-phenylallyl)-1,4-benzoquinone.

† Lists of structure factors, anisotropic thermal parameters of the C and O atoms, positional H-atom parameters and some selected torsion angles of the dalbergiones have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39300 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/84/061090-03$01.50

Table 1. *Final atomic coordinates and B_{eq} values for R-3,4-DMD with e.s.d.'s in parentheses*

B_{eq} values are given in the form $4\,[(b_{11}/a^{*2})(b_{22}/b^{*2})(b_{33}/c^{*2})]^{1/3}$.

	x	y	z	B_{eq}(Å^2)
O(1)	0·842 (1)	0·840 (2)	0·6400 (4)	6·7 (6)
O(2)	0·972 (1)	0·875 (1)	0·7359 (4)	6·3 (6)
O(3)	0·754 (1)	0·765 (1)	0·8231 (3)	4·8 (5)
O(4)	0·446 (1)	0·600 (1)	0·7958 (4)	5·6 (4)
C(1)	0·581 (2)	0·694 (2)	0·6634 (5)	4·6 (6)
C(2)	0·759 (2)	0·781 (2)	0·6752 (5)	4·9 (7)
C(3)	0·816 (2)	0·790 (2)	0·7299 (5)	5·0 (7)
C(4)	0·717 (2)	0·735 (2)	0·7721 (5)	4·4 (6)
C(5)	0·540 (2)	0·648 (2)	0·7589 (5)	4·5 (7)
C(6)	0·488 (2)	0·636 (2)	0·7039 (4)	4·2 (6)
C(7)	0·537 (2)	0·680 (2)	0·6068 (6)	6·2 (8)
C(8)	0·638 (1)	0·541 (1)	0·5807 (4)	4·8 (8)
C(9)	0·726 (1)	0·573 (1)	0·5330 (4)	6·3 (9)
C(10)	0·821 (1)	0·444 (1)	0·5078 (4)	8·5 (9)
C(11)	0·828 (1)	0·285 (1)	0·5305 (4)	9 (1)
C(12)	0·740 (1)	0·253 (1)	0·5782 (4)	7 (1)
C(13)	0·645 (1)	0·381 (1)	0·6033 (4)	6·1 (8)
C(14)	0·327 (2)	0·674 (3)	0·6009 (8)	9 (1)
C(15)	0·243 (3)	0·554 (3)	0·5758 (8)	10 (1)
C(16)	1·083 (2)	0·841 (3)	0·7822 (7)	8 (1)
C(17)	0·784 (2)	0·625 (2)	0·8573 (6)	6·7 (9)

Table 2. *Bond distances* (Å) *and angles* (°) *of R-3,4-DMD to complete* Fig. 1

E.s.d.'s are given in parentheses.

C(7)–C(8)	1·490 (17)	C(1)–C(7)–C(8)	111·9 (1·2)
		C(1)–C(7)–C(14)	108·4 (1·3)
Phenyl ring		C(8)–C(7)–C(14)	116·0 (1·4)
C–C	1·395 } fixed	C(7)–C(14)–C(15)	122·8 (1·9)
C–C–C	120·0 }		

scheme and some bond lengths and angles are shown in the *ORTEP* drawing of Fig. 1. Further bond distances and angles are given in Table 2. The *bc* projection of the unit cell is shown in Fig. 2. The quinone ring is almost planar with torsion angles C(1)–C(2)–C(3)–C(4) −4·2 (1·5), C(2)–C(3)–C(4)–C(5) 4·3 (1·4) and C(3)–C(4)–C(5)–C(6) −2·2 (1·5)°. The maximum out-of-plane deviation of the quinone ring C(1) to C(6) is −0·02 (1) Å for C(3); atoms O(1), O(2), O(3), O(4), C(7), C(16) and C(17) deviate 0·08 (1), 0·05 (1), 0·19 (1), 0·06 (1), −0·05 (2), −0·50 (3) and −0·84 (3) Å from this plane. The angle between the planes of the quinone ring and of the phenyl ring is 83 (1)°. Atom C(7) is chiral with configuration *S* in the enantiomer found as the *MULTAN* solution and used for the refinement. As the title compound displays configuration *R* in the enantiomer of naturally occurring *Machaerium* species (Eyton *et al.*, 1965; Ollis, Redman, Roberts, Sutherland & Gottlieb, 1968; Ogiyama & Yasue, 1973; Ollis, Redman, Roberts, Sutherland, Gottlieb & Taveira Magalhães, 1978) the atom parameters have been transformed (Table 1) and used for the *ORTEP* drawing in Fig. 1.

Some torsion angles of *R*-3,4-DMD have been compared with corresponding ones of *R,S*-4-MD and *S*-4,4′-DMD (Schmalle *et al.*, 1984*b*). In the solid state, all dalbergiones reveal similar conformations. The methylene group is in a *trans* position with respect to the quinone ring. The torsion angles involving chiral atom C(7) are similar in *R*-4-MD and *S*-4,4′-DMD: C(1)–C(7)–C(14)=C(15) −143·8 (5) and 144·5 (8)°, the only signficant difference being in the title compound, 125 (2)°. The planes of the allyl group and the phenyl ring are almost perpendicular to each other in *R*-3,4-DMD (Fig. 2), the torsion angle C(8)–C(7)–C(14)=C(15) being 1·5 (2·4)° (see deposition footnote). The position for the hapten(allergen)–protein coupling in the skin is believed to be C(6) in *R*-3,4-DMD (Byck & Dawson, 1968). The molecular model of *R*-3,4-DMD fits well into the strong allergenic 2,6-substituted 1,4-benzoquinone structure of primin (Schmalle, Jarchow, Hausen & Schulz, 1984*a*) and into the powerful sensitizing naphthoquinone structure of deoxylapachol (DOL) (Schulz, Garbe, Hausen &

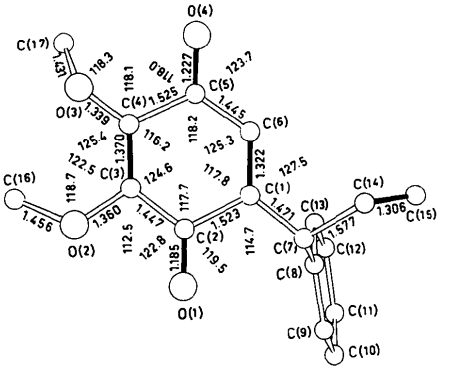

Fig. 1. *ORTEP* drawing of *R*-3,4-DMD with atom-numbering scheme and some bond distances (Å) and angles (°). The e.s.d.'s range from 0·010 to 0·018 Å and from 1·0 to 1·2°. Blackened bond lines denote C=C and C=O double bonds.

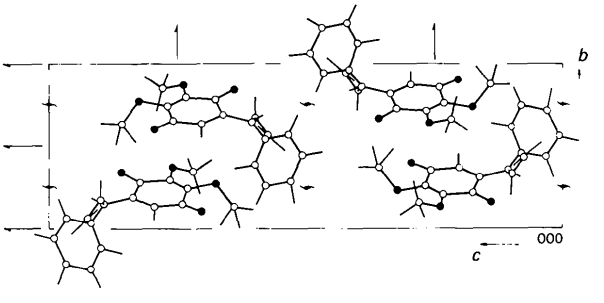

Fig. 2. The *bc* projection of the structure of *R*-3,4-DMD. Filled circles of the molecular models indicate O atoms and open circles C atoms.

Simatupang, 1977) and agrees with the cross-reactivities observed between primin and *R*-3,4-DMD as well as between primin and DOL (Hausen, 1981). Intermolecular distances were calculated up to 3·6 Å with *ORFFE*. The shortest O···H distances between neighbouring molecules are found in the [101] direction: O(3)···H(6^{i}) 2·57 (3), O(3)···C(6^{i}) 3·53 (2) Å, C(6)–H(6)···O(3^{i}) = 147 (6)°; these values are not characteristic of C–H···O hydrogen bonds and the structure therefore consists of discrete molecules.

This investigation was supported by a grant from the Deutsche Forschungsgemeinschaft, Bonn, Federal Republic of Germany. The authors thank Dr G. Adiwidjaja for the collection of the intensity data and Messrs B. Cornelisen, S. Mertig and W. Vogel for helpful assistance.

References

BYCK, J. S. & DAWSON, C. R. (1968). *Anal. Biochem.* **25**, 123–135.
EYTON, W. B., OLLIS, W. D., FINEBERG, M., GOTTLIEB, O. R., SALIGNAC DE SOUZA GUIMARÃES, I. & TAVEIRA MAGALHÃES, M. (1965). *Tetrahedron*, **21**, 2697–2705.
HAUSEN, B. M. (1981). *Woods Injurious to Human Health*. Berlin, New York: Walter de Gruyter.
OGIYAMA, K. & YASUE, M. (1973). *Phytochemistry*, **12**, 2544–2545.
OLLIS, W. D., REDMAN, B. T., ROBERTS, R. J., SUTHERLAND, I. O. & GOTTLIEB, O. R. (1968). *Chem. Commun.* pp. 1392–1393.
OLLIS, W. D., REDMAN, B. T., ROBERTS, R. J., SUTHERLAND, I. O., GOTTLIEB, O. R. & TAVEIRA MAGALHÃES, M. (1978). *Phytochemistry*, **17**, 1383–1388.
SCHMALLE, H. W., JARCHOW, O. H., HAUSEN, B. M. & SCHULZ, K. H. (1984*a*). *Acta Cryst.* C**40**, 1084–1087.
SCHMALLE, H. W., JARCHOW, O. H., HAUSEN, B. M. & SCHULZ, K. H. (1984*b*). *Acta Cryst.* C**40**, 1087–1090.
SCHULZ, K. H., GARBE, I., HAUSEN, B. M. & SIMATUPANG, M. H. (1977). *Arch. Dermatol. Forsch.* **258**, 41–52.

Acta Cryst. (1984). C**40**, 1092–1094

Structure of (*S*)-4,4′-Dimethoxydalbergione,* $C_{17}H_{16}O_4$

BY HELMUT W. SCHMALLE AND OTTO H. JARCHOW

Mineralogisch-Petrographisches Institut der Universität Hamburg, Grindelallee 48, *D*-2000 *Hamburg* 13, *Federal Republic of Germany*

AND BJÖRN M. HAUSEN AND KARL-HEINZ SCHULZ

Universitäts-Hautklinik Hamburg-Eppendorf, Martinistrasse 52, *D*-2000 *Hamburg* 20, *Federal Republic of Germany*

(*Received* 5 *December* 1983; *accepted* 24 *February* 1984)

Abstract. $M_r = 284{\cdot}31$, monoclinic, $P2_1$, $a = 7{\cdot}236$ (1), $b = 6{\cdot}479$ (1), $c = 15{\cdot}844$ (1) Å, $\beta = 93{\cdot}16$ (1)°, $V = 741{\cdot}7$ (3) Å^3, $Z = 2$, $D_x = 1{\cdot}273$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $T = 296$ K, $F(000) = 300$, $\mu = 0{\cdot}753$ mm^{-1}, final $R = 0{\cdot}052$ for 1184 observed reflections. The atoms of the quinone ring form an almost planar system with a maximum out-of-plane deviation of −0·022 (5) Å for C(2). The average values of the C_{sp^3}–C_{sp^2} bond lengths and corresponding angles are 1·519 (7) Å and 112·7 (5)°; the mean values of the quinone-ring dimensions are C–C = 1·483 (7), C=C = 1·328 (8), C=O = 1·215 (7) Å, C–C–C = 117·5 (5), C=C–C = 121·5 (5) and O=C–C = 121·3 (5)°. The methylene bond length is extremely short: 1·240 (9) Å. With the exception of a very weak C–H···O interaction in the **b** direction the structure consists of discrete molecules.

*IUPAC name: (*S*)-2-methoxy-5-[1-(4-methoxyphenyl)allyl]-1,4-benzoquinone.

Introduction. The structure determination of the title compound (*S*-4,4′-DMD) is part III of a series on dalbergiones. For parts I and II see preceding papers. (Schmalle, Jarchow, Hausen & Schulz, 1984*a*,*b*).

Experimental. For additional details see part I. *S*-4,4′-DMD from *Dalbergia nigra* All. Orange needles. Crystal 0·12 × 0·40 × 0·08 mm. Unit cell: 25 reflections in the interval $15° < \theta < 39°$. $(\sin\theta/\lambda)_{max} = 0{\cdot}588$ Å^{-1}, $-8 \le h \le 8$, $-7 \le k \le 0$, $-18 \le l \le 18$. 3·1% loss of intensities in standard reflections $20\bar{7}$ and $10\bar{5}$ monitored initially and then every hour. 2508 reflections measured, $R_{int} = 0{\cdot}018$, 1397 unique reflections, 1184 with $I > 3\sigma(I)$, 213 unobserved. Number of reflections in final refinement cycle, $m = 1184$; parameters refined, $n = 225$; unit weight, $R = 0{\cdot}052$. $(\Delta/\sigma)_{max} = 1{\cdot}91$ (H-atom positional parameter) in final refinement cycle. Max. and min. heights in final difference Fourier synthesis 0·17 and −0·19 e Å^{-3}.

0108-2701/84/061092-03$01.50