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$\cdots$H distances between neighbouring molecules are found in the [101] direction: O(3)$\cdots$H($6^{\rm i}$) 2·57 (3), O(3)$\cdots$C($6^{\rm i}$) 3·53 (2) Å, C(6)—H(6)$\cdots$O($3^{\rm i}$) = 147 (6)°; these values are not characteristic of C—H$\cdots$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$\cdots$O interaction in the **b** direction the structure consists of discrete molecules.

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, $R_{\rm int} = 0{\cdot}018$, 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}.

---

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

0108-2701/84/061092-03$01.50

Table 1. *Final atomic coordinates and* B_{eq} *values for* *S*-4,4′-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)	0·6970 (6)	0·0970 (8)	0·2138 (3)	5·3 (2)
O(2)	0·1945 (5)	0·3671 (9)	0·0464 (2)	4·2 (2)
O(3)	0·3663 (5)	0·7243	0·0548 (2)	4·6 (2)
O(4)	0·7174 (5)	0·557 (1)	0·5878 (2)	5·4 (2)
C(1)	0·7000 (7)	0·455 (1)	0·1853 (3)	3·5 (2)
C(2)	0·6168 (8)	0·244 (1)	0·1800 (3)	3·9 (2)
C(3)	0·4396 (7)	0·216 (1)	0·1332 (3)	3·6 (2)
C(4)	0·3551 (7)	0·372 (1)	0·0920 (3)	3·4 (3)
C(5)	0·4401 (7)	0·583 (1)	0·0932 (3)	3·6 (2)
C(6)	0·6169 (9)	0·606 (1)	0·1429 (5)	3·9 (3)
C(7)	0·8752 (7)	0·576 (1)	0·2427 (3)	3·7 (2)
C(8)	0·8238 (6)	0·499 (1)	0·3341 (3)	3·5 (2)
C(9)	0·8834 (7)	0·356 (1)	0·3942 (4)	4·0 (3)
C(10)	0·8447 (8)	0·381 (1)	0·4786 (4)	4·5 (3)
C(11)	0·7439 (6)	0·546 (1)	0·5035 (3)	4·1 (3)
C(12)	0·6786 (7)	0·690 (1)	0·4437 (3)	4·5 (2)
C(13)	0·7218 (8)	0·663 (1)	0·3599 (3)	4·4 (3)
C(14)	0·626 (1)	0·734 (2)	0·6190 (4)	7·3 (5)
C(15)	0·0921 (8)	0·175 (1)	0·0467 (4)	4·8 (3)
C(16)	1·0044 (8)	0·639 (1)	0·2122 (4)	5·1 (3)
C(17)	1·107 (1)	0·761 (2)	0·2530 (4)	7·6 (4)

Table 2. *Bond distances* (Å) *and angles* (°) *for* *S*-4,4′-DMD *to complete Fig.* 1

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

C(7)–C(16)	1·511 (8)	C(1)–C(7)–C(16)	112·3 (5)
C(7)–C(8)	1·522 (7)	C(1)–C(7)–C(8)	109·7 (4)
O(4)–C(11)	1·362 (6)	C(8)–C(7)–C(16)	115·0 (5)
O(4)–C(14)	1·424 (11)	C(11)–O(4)–C(14)	118·4 (5)
C(8)–C(9)	1·383 (7)	C(7)–C(8)–C(9)	120·3 (5)
C(9)–C(10)	1·391 (8)	C(7)–C(8)–C(13)	121·7 (5)
C(10)–C(11)	1·368 (8)	C(9)–C(8)–C(13)	118·0 (5)
C(11)–C(12)	1·393 (8)	C(8)–C(9)–C(10)	120·8 (6)
C(12)–C(13)	1·392 (7)	C(9)–C(10)–C(11)	120·5 (6)
C(8)–C(13)	1·368 (8)	C(10)–C(11)–C(12)	119·7 (5)
		C(11)–C(12)–C(13)	118·6 (5)
		C(12)–C(13)–C(8)	122·5 (5)
		O(4)–C(11)–C(10)	115·5 (5)
		O(4)–C(11)–C(12)	124·8 (6)
		C(7)–C(16)–C(17)	130·0 (6)

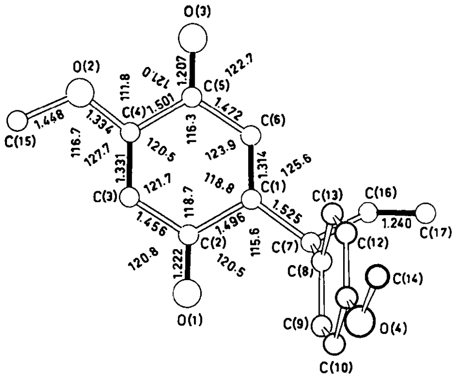

Fig. 1. *ORTEP* drawing of *S*-4,4′-DMD with some bond distances (Å) and angles (°). The e.s.d.'s range from 0·006 to 0·008 Å and from 0·4 to 0·5°. Blackened bond lines indicate C=C and C=O double bonds.

Discussion. The atomic coordinates and equivalent isotropic temperature factors of the C and O atoms are given in Table 1.* The atom-numbering scheme and some bond distances and angles are shown in the *ORTEP* drawing of Fig. 1. Further bond lengths and angles are listed in Table 2. The *ac* projection of the unit cell is shown in Fig. 2. The atoms of the quinone ring form an almost planar system with torsion angles C(1)–C(2)–C(3)–C(4) 3·3 (7), C(2)–C(3)–C(4)–C(5) 0·0 (6), and C(3)–C(4)–C(5)–C(6) −1·0 (6)°. The maximum out-of-plane deviation of the quinone ring C(1) to C(6) is −0·022 (5) Å for C(2); atoms O(1), O(2), O(3), C(15) and C(7) deviate −0·034 (4), −0·092 (4), 0·022 (3), 0·155 (6) and 0·131 (5) Å from the plane. The angle between the planes of the quinone ring and of the methoxyphenyl ring is 78·4 (4)°. Atom C(7) is chiral with configuration *R* in the enantiomer used for the refinement. However, the absolute configuration is found to be *S* in the enantiomer of *Dalbergia nigra* All. (Eyton, Ollis, Sutherland, Gottlieb, Taveira Magalhães & Jackman, 1965). Therefore, the final atom parameters have been transformed into the *S* form (Table 1) and used for the *ORTEP* drawing in Fig. 1. The average values of the C_{sp^3}–C_{sp^2} distances and corresponding angles are 1·519 (7) Å and 112·7 (5)°. The distance of 1·240 (9) Å is the shortest methylene bond length observed in the dalbergiones. Disorder in this structure could not be observed; C(17)—H distances are 1·238 (7) and 0·805 (7) Å after the final refinement cycle, the angle H—C—H being 118·1 (8)°.

---

* Lists of structure factors, anisotropic thermal parameters of the C and O atoms and positional H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39301 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

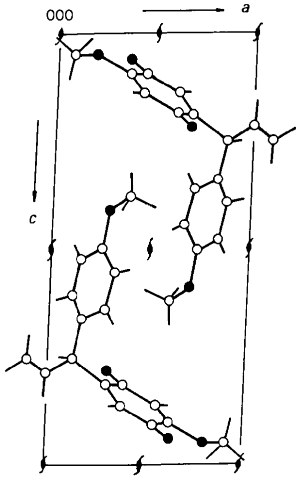

Fig. 2. The *ac* projection of the structure of *S*-4,4′-DMD. Filled circles of the molecular models mark O atoms and open circles C atoms.

The methoxy group O(4)—C(14) is found to be approximately in the phenyl plane; deviations for O(4) and C(14) are 0·044 (5) and 0·15 (1) Å respectively. The methyl C atom deviations of the methoxy groups bonded to quinone rings are 0·214 (5) Å for *R*-4-MD and 0·155 (6) Å for *S*-4,4′-DMD. In *R*-3,4-DMD, however, the C(16) methyl is twisted out of the plane of the quinone ring, as is the C(17) methyl group: deviations are −0·50 (3) and −0·84 (2) Å. The mean C—H distance for the title compound is 0·96 (5) Å. Intermolecular distances were calculated up to 3·6 Å with *ORFFE*. The shortest O···H distance between neighbouring molecules is found in the **b** direction: O(1)···H(3$^{\rm i}$) 2·43 (5), O(1)···C(3$^{\rm i}$) 3·45 (1), C(3)—H(3) 1·15 (5) Å, the angle C(3)—H(3)···O(1$^{\rm i}$) being 147 (3)°. This C—H···O interaction may be considered as a very weak hydrogen bond. Otherwise, the structure consists of discrete molecules like those in *R*-3,4-DMD and *R*-4-MD.

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 diffractometer data and Messrs B. Cornelisen, S. Mertig, B. Metz and W. Vogel for helpful assistance.

References

EYTON, W. B., OLLIS, W. D., SUTHERLAND, I. O., GOTTLIEB, O. R., TAVEIRA MAGALHÃES, M. & JACKMAN, L. M. (1965). *Tetrahedron*, **21**, 2683–2696.

SCHMALLE, H. W., JARCHOW, O. H., HAUSEN, B. M. & SCHULZ, K. H. (1984*a*). *Acta Cryst.* C**40**, 1087–1090.

SCHMALLE, H. W., JARCHOW, O. H., HAUSEN, B. M. & SCHULZ, K. H. (1984*b*). *Acta Cryst.* C**40**, 1090–1092.

Acta Cryst. (1984). C**40**, 1094–1096

Structure of *N*-Carboxy-L-valine Anhydride, $C_6H_9NO_3$

BY HITOSHI KANAZAWA*

Department of Education, Fukushima University, Asakawa-cho, Matsukawa, Fukushima City 960-12, *Japan*

AND YUJI OHASHI AND YOSHIO SASADA

Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Nagatsuta 4259, *Midori-ku, Yokohama* 227, *Japan*

(*Received* 23 *December* 1983; *accepted* 13 *February* 1984)

Abstract. M_r = 143·1, orthorhombic, $P2_12_12_1$, a = 5·787 (1), b = 22·740 (3), c = 5·395 (1) Å, V = 709·1 (1) Å^3, Z = 4, D_m = 1·33, D_x = 1·33 g cm^{-3}, T = 293 K, F(000) = 292, λ(Mo $K\alpha$) = 0·71069 Å, μ = 1·29 cm^{-1}, R = 0·056 for 845 observed reflections. The molecules are linked by intermolecular hydrogen bonds between N(1)—H(1) and O(1) along the *a* axis. The *N*-carboxy anhydride rings are arranged in a layer sandwiched by hydrophobic side chains, as observed in the crystal of *N*-carboxy-L-leucine anhydride.

Introduction. The polymerization of the *N*-carboxy anhydrides of α-amino acids (α-amino acid NCA's) has been useful in obtaining polypeptides with high molecular weight (Bamford, Elliott & Hanby, 1956). In a previous paper, it was revealed that polymerizability in the solid state was very different from that in solution (Kanazawa & Kawai, 1980). To elucidate the reaction mechanism in the solid state, the crystal structures of glycine NCA (Kanazawa, Matsuura, Tanaka, Kakudo, Komoto & Kawai, 1976*a*), L-alanine NCA (Kanazawa, Matsuura, Tanaka, Kakudo, Komoto & Kawai, 1976*b*), γ-benzyl-L-glutamate NCA (Kanazawa, Ohashi, Sasada & Kawai, 1978*a*) and L-leucine NCA (Kanazawa, Ohashi, Sasada & Kawai, 1978*b*) have been determined. The difference in polymerizability between L-leucine NCA and L-alanine NCA in the solid state was proved to be caused by the different molecular packing in the crystal (Kanazawa, Ohashi, Sasada & Kawai, 1982). In the present paper the crystal and molecular structure of L-valine NCA is compared with those of the related compounds so far determined.

Experimental. Colorless plate-like crystals obtained from an ethyl acetate solution in hexane vapor at 285 K, density by flotation in C_6H_{12}/CCl_4; systematic absences $h00$ $h = 2n + 1$, $0k0$ $k = 2n + 1$, $00l$ $l = 2n + 1$; approximate crystal dimensions 0·3 × 0·4 × 0·5 mm, Rigaku AFC-4 diffractometer, graphite monochromator; cell parameters refined by least squares on the basis of 21 independent 2θ values, Mo $K\alpha$ radiation

---

* To whom correspondence should be addressed.

0108-2701/84/061094-03$01.50