bond distance [1·499 (5) Å] appears very short for a C—C single bond value but exactly the same as found in other indolinone nuclei (Itai, Iitaka & Kubo, 1978; De, 1990; Chakraborty & Talapatra, 1985).

A stereoscopic view of the packing of the molecule is shown in Fig. 2. The amide N atom N(1), forms a hydrogen bond with the carbonyl O atom O(1) in the molecule related by the centre of symmetry at the origin [N(1)—H(N1) = 0·87 (4); N(1)···O(1) ($-x$, $-y$, $-z$) = 2·853 (4); H(N1)···O(1) ($-x$, $-y$, $-z$) = 2·01 (4) Å; N(1)—H(N1)···O(1) = 164°]. These bonds link the molecules in pairs around the centres of symmetry.

The authors thank Dr Frank D. Popp of University of Missouri, Kansas City, USA, for the gift of the sample used in this investigation. AD would like to thank all his colleagues at Khalisani College, Chandannagore, Hooghly, for their support and encouragement.

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Acta Cryst. (1991). C**47**, 2181–2183

Structure of Homovanillic Acid

BY NOBUO OKABE AND YASUO HATANAKA

Department of Pharmaceutical Sciences, Kinki University, Kowakae 3-4-1, *Higashi Osaka, Osaka* 577, *Japan*

AND YOH SASAKI

Department of Science and Engineering, Kinki University, Kowakae 3-4-1, *Higashi Osaka, Osaka* 577, *Japan*

(*Received* 14 *January* 1991; *accepted* 29 *April* 1991)

Abstract. 4-Hydroxy-3-methoxyphenylacetic acid, $C_9H_{10}O_4$, $M_r = 182{\cdot}18$, orthorhombic, *Pbca*, $a = 10{\cdot}571\ (5)$, $b = 32{\cdot}589\ (3)$, $c = 4{\cdot}973\ (5)$ Å, $V = 1713\ (3)$ Å^3, $Z = 8$, $D_x = 1{\cdot}413$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 0{\cdot}105$ mm^{-1}, $F(000) = 768$, $T = 296$ K, $R = 0{\cdot}040$ for 900 reflections with $I > 3\sigma(I)$. The molecule has the carboxyl side chain oriented perpendicular to the phenyl-ring plane as observed in catecholamines. A hydrogen bond between the carboxyl groups makes a centrosymmetric dimer, as usual.

Introduction. Homovanillic acid (HVA) is an important dopamine metabolite produced from a deaminated metabolite of dopamine, 3,4-dihydroxyphenylacetic acid, by the catalytic action of catechol-*o*-methyltransferase (Soares-da-Silva & Garrett, 1990; Kopin, 1985; Ishimitsu & Hirose, 1981). The crystal structures of dopamine (Bergin & Carlström, 1968; Giesecke, 1980) and other related compounds (Barlow, Johnson, Howard, Walton & Koellner, 1989; Seiler, Markstein, Walkinshaw & Boelsterli, 1989) have been determined. It is also important to determine the detailed structure of dopamine metabolites for understanding its metabolic pathway. For this reason, we report here the crystal structure of homovanillic acid.

Experimental. Crystallized from 50% methanol solution (0·2 *M*) as platelets, 0·4 × 0·4 × 0·2 mm. Rigaku AFC5R automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation; lattice parameters determined by least-squares fit of 2θ values of 25 reflections ($24{\cdot}99 < 2\theta < 38{\cdot}69°$); intensity data up to $2\theta = 55{\cdot}0°$ collected, ω scan, scan speed $32{\cdot}0°(\omega)$ min^{-1}, scan width $(0{\cdot}88 + 0{\cdot}30\tan\theta)°$, the ratio of peak counting time to background counting time was 2:1 at 50 kV and 180 mA; h 0–12,

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Table 1. *Atomic coordinates for non-*H *atoms with e.s.d.'s in parentheses*

	x	*y*	*z*	B_{eq}* (Å^2)
O(1)	0·6890 (2)	0·21324 (6)	−0·2823 (5)	4·3 (1)
O(2)	0·8619 (2)	0·20985 (6)	0·1062 (5)	4·1 (1)
O(3)	0·8903 (2)	0·00276 (6)	0·2793 (5)	5·4 (1)
O(4)	0·9294 (2)	0·04474 (6)	−0·0608 (5)	5·6 (1)
C(1)	0·7464 (3)	0·10267 (8)	0·1172 (6)	3·3 (1)
C(2)	0·6559 (3)	0·10627 (9)	−0·0809 (7)	3·9 (2)
C(3)	0·6371 (3)	0·1430 (1)	−0·2162 (7)	3·8 (2)
C(4)	0·7089 (3)	0·17678 (8)	−0·1509 (6)	3·1 (1)
C(5)	0·7991 (3)	0·17375 (8)	0·0536 (6)	3·0 (1)
C(6)	0·8185 (3)	0·13671 (8)	0·1843 (7)	3·3 (1)
C(7)	0·7679 (4)	0·06240 (9)	0·2608 (8)	4·0 (2)
C(8)	0·8707 (3)	0·03634 (8)	0·1420 (7)	3·7 (1)
C(9)	0·9634 (3)	0·2081 (1)	0·2967 (8)	3·8 (2)

* The *B* values are the equivalent isotropic temperature factors calculated from $B_{eq} = \frac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac\cos\beta)$.

Table 2. *Bond lengths* (Å) *and angles* (°) *between non-*H *atoms, and hydrogen bonds* (Å)

O(1)—C(4)	1·372 (3)	C(1)—C(7)	1·511 (4)
O(2)—C(5)	1·376 (3)	C(2)—C(3)	1·388 (4)
O(2)—C(9)	1·433 (4)	C(3)—C(4)	1·376 (4)
O(3)—C(8)	1·306 (3)	C(4)—C(5)	1·397 (4)
O(4)—C(8)	1·216 (4)	C(5)—C(6)	1·386 (4)
C(1)—C(2)	1·378 (4)	C(7)—C(8)	1·500 (4)
C(1)—C(6)	1·387 (4)		

C(5)—O(2)—C(9)	116·9 (2)	O(2)—C(5)—C(4)	114·0 (2)
C(2)—C(1)—C(6)	119·0 (3)	O(2)—C(5)—C(6)	125·7 (3)
C(2)—C(1)—C(7)	121·1 (3)	C(4)—C(5)—C(6)	120·2 (3)
C(6)—C(1)—C(7)	119·9 (3)	C(1)—C(6)—C(5)	120·2 (3)
C(1)—C(2)—C(3)	121·3 (3)	C(1)—C(7)—C(8)	114·5 (3)
C(2)—C(3)—C(4)	119·8 (3)	O(3)—C(8)—O(4)	122·8 (3)
O(1)—C(4)—C(3)	119·7 (3)	O(3)—C(8)—C(7)	112·6 (3)
O(1)—C(4)—C(5)	120·8 (2)	O(4)—C(8)—C(7)	124·7 (3)
C(3)—C(4)—C(5)	119·4 (3)		

D	*A*	Symmetry	*D*···*A*
O(1)	O(2)	*x*, *y*, *z*	2·662 (3)
O(3)	O(4)	−*x*, −*y*, −*z*	2·686 (3)

k 0–40, *l* 0–5. 2348 independent reflections measured, 900 with $I > 3\sigma(I)$ used for the structure determinations; three reference reflections monitored at 100 reflection intervals showed no crystal deterioration; Lorentz–polarization and absorption corrections (max. and min. transmission factors 1·00, 0·95) applied. Structure solved by direct methods with *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984), refined by least-squares method (on *F*) with anisotropic thermal parameters for all non-H atoms; H atoms located from difference Fourier map, included in refinement with isotropic thermal parameters. Final $R = 0{\cdot}040$, $wR = 0{\cdot}043$, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 4F_o^2/\sigma^2(F_o^2)$, $(\Delta/\sigma)_{max} = 0{\cdot}07$, $S = 1{\cdot}41$; max. and min. peaks on the final difference Fourier map 0·16 and −0·17 e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV); all numerical calculations performed using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985).

Discussion. Final atomic parameters of non-H atoms are listed in Table 1.* The bond lengths and angles are given in Table 2. A perspective view of the molecule is shown in Fig. 1 with the atomic numbering scheme. The carboxyl side chain is oriented perpendicular to the phenyl ring {torsion angle, TOR1 [C(2)—C(1)—C(7)—C(8)] = 94·0 (4)°} and the O(3) atom of the side chain is oriented in the *trans* conformation with respect to the C(1) atom {TOR2 [O(3)—C(8)—C(7)—C(1)] = 177·0 (3)°}. When the O(3) atom of HVA is replaced with an amino group, the overall orientation of the side chain resembles that in catecholamines, whose side chains are oriented approximately perpendicular to the phenyl-ring plane [dopamine hydrochloride, TOR1 = −100·4 (3), TOR2 = 173·2 (2)° (Giesecke, 1980); adrenaline, TOR1 = 80·5, TOR2 = 171·6° (Andersen, 1975*a*); noradrenaline, TOR1 = 94·2, TOR2 = 167·5° (Andersen, 1975*b*)]. The 3-methoxy

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54212 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

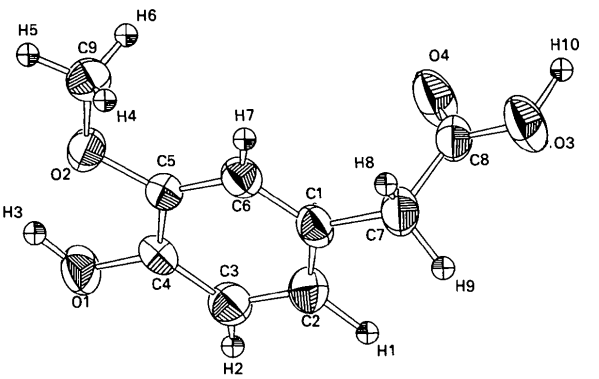

Fig. 1. Perspective view of homovanillic acid, along with the atomic numbering used.

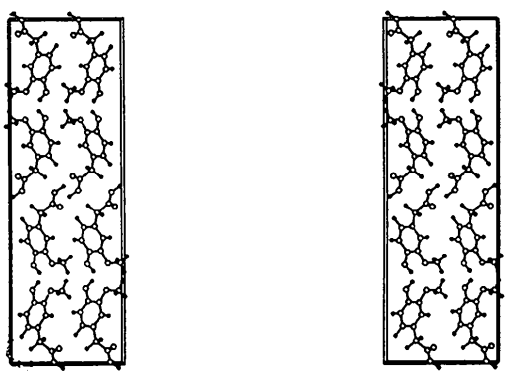

Fig. 2. A stereoscopic view of the structure viewed approximately down the *c* axis. **b** is vertical and **a** is horizontal.

group is in the phenyl-ring plane [C(4)—C(5)—O(2)—C(9) = −174·6 (3)°]. Fig. 2 shows a stereoscopic drawing of the crystal packing. HVA molecules are arranged with alternations of the hydrogen-bonded carboxyl-group layer and the hydrophobic phenyl-ring layer along the *y* axis. An intermolecular hydrogen bond is formed between the carboxyl groups and an intramolecular one between the phenolic hydroxyl group and the O atom of the methoxy group. These hydrogen bonds are listed in Table 2.

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Acta Cryst. (1991). C**47**, 2183–2185

(18*R*)-18-Méthoxycarbonyl-17-oxo-1-(*p*-tolylsulfonyl)aspidofractinine

PAR P. TOFFOLI ET N. RODIER

Laboratoire de Chimie minérale, Faculté des Sciences pharmaceutiques et biologiques, 5 Rue J.-B. Clément, 92296 Châtenay-Malabry CEDEX, France

ET P. LE MÉNEZ ET N. KUNESCH

Laboratoire de Chimie des substances thérapeutiques naturelles, Faculté des Sciences pharmaceutiques et biologiques, 5 Rue J.-B Clément, 92296 Châtenay-Malabry CEDEX, France

(*Reçu le* 26 *octobre* 1990, *accepté le* 18 *janvier* 1991)

Abstract. (18*R*)-18-Methoxycarbonyl-17-oxo-1-(*p*-tolylsulfonyl)aspidofractinine, $C_{28}H_{30}N_2O_5S$, M_r = 506·6, monoclinic, $P2_1/c$, a = 9·059 (2), b = 21·625 (3), c = 12·898 (2) Å, β = 94·62 (1)°, V = 2519 (1) Å^3, Z = 4, D_x = 1·336 Mg m^{-3}, λ(Cu $K\bar{\alpha}$) = 1·5418 Å, μ = 1·45 mm^{-1}, $F(000)$ = 1072, T = 296 (1) K, R = 0·039 for 3705 observed independent reflections. The aromatic *A* and *H* rings belonging to the indoline and tosyl groups, respectively, are planar. Ring *B* shows a half-chair conformation, while a boat conformation has been determined for the six-membered rings *C*, *D* and *E*, which share the carbon atoms, C(2) and C(20). An envelope conformation is observed for the pyrrolidine ring *F* and a chair conformation for the piperidine ring *G*. The ring-junction configurations are *cis* for *B*/*D*, *C*/*F* (or *D*/*F*), *C*/*G* and *E*/*F* and *trans* for *B*/*C* and *D*/*G*. Some longer than usual C—N and C—C bond lengths are due to steric hindrance around C(2), C(7) and C(20). The cohesion of the structure is due to van der Waals interactions.

Introduction. De nombreux alcaloïdes de type biogénétique *Aspidosperma* possèdent le squelette pentacyclique de l'aspidospermidine (1). Les alcaloïdes hexacycliques de la même famille, dont un représentant caractéristique est la kopsinine (2), diffèrent principalement de l'aspidospermidine (1) par la présence d'un cycle supplémentaire dû à la formation d'une liaison entre les atomes de carbone 2 et 18.

L'intérêt pharmacologique de ces composés, conjugué à leur présence en faible quantité dans les plantes, a suscité de nombreux efforts de synthèse. Le composé étudié au cours de ce travail a été préparé en élaborant, par voie stéréospécifique, un intermédiaire possédant le squelette de base pentacyclique, puis en soumettant celui-ci à une réaction de Diels–Alder à l'aide de l'acrylate de méthyle (Le Ménez, Sapi, Kunesch, Angell & Wenkert, 1989). La géométrie de sa molécule, au niveau des atomes de carbone 2 et 20, n'a pu être déduite de la comparaison de ses spectres de RMN de ^{1}H et de ^{13}C avec

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