

References

- CROMER, D. T. & LIBERMAN, D. (1970). Los Alamos Scientific Laboratory, Univ. of California Report, LA-4403 UC-34.
- CRUICKSHANK, D. W. J., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In *Computing Methods and the Phase Problem in Crystal Structure Analysis*, edited by R. PEPINSKY & J. M. ROBERTSON. New York: Pergamon Press.
- FILIPPAKIS, S. E. & SCHMIDT, G. M. J. (1967). *J. Chem. Soc. (B)*, pp. 229–234.
- GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). Univ. of California program UCLALS 1.
- GOPALAKRISHNAN, T. & RAO, L. M. (1973). *Ind. J. Pure Appl. Phys.* **11**, 360–361.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KARLE, I. L., BRITTS, K. & GUM, P. (1964). *Acta Cryst.* **17**, 496–500.
- PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 746–751.
- SHONO, R. (1968). *Block-Diagonal Least-Squares Program for the IBM/1130*. Department of Crystallography, Univ. of Pittsburgh.
- SMITH, G., KENNARD, C. H. L. & WHITE, A. H. (1976). *J. Chem. Soc. Perkin II*, pp. 791–792.

Acta Cryst. (1977). **B33**, 1260–1263

Tetra-*O*-methyldehydrodicaffeic Acid Dilactones, (+) and (–) Isomers

BY HIKARU NAKAMURA AND YOICHI IITAKA

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo 113, Japan

AND YOSHIKI KUMADA, TOMIO TAKEUCHI AND HAMAO UMEZAWA

Institute of Microbial Chemistry, Kamiosaki, Shinagawa-ku, Tokyo 141, Japan

(Received 22 October 1976; accepted 29 November 1976)

Abstract. $C_{22}H_{22}O_8$, $M_r = 414.4$. Orthorhombic, $P2_12_1$, $a = 10.343$ (3), $b = 34.014$ (10), $c = 5.597$ (2) Å, $Z = 4$, $D_x = 1.398$ g cm $^{-3}$. The absolute configuration was determined for the (+) and (–) compounds from the anomalous dispersion effect of O atoms for Cu $K\alpha$ radiation.

Introduction. Dehydrodicaffeic acid dilactone was isolated, with caffeic acid, from a mushroom culture as a result of the inhibitory activity against catechol-*O*-methyltransferase. Both (+) and (–) compounds were produced by the mushroom and they exhibit nearly the same power of inhibition to catechol-*O*-methyltransferase, dopamine β -hydroxylase and dopa decarboxylase (Kumada, Naganawa, Iinuma, Matsuzaki, Takeuchi & Umezawa, 1976).

The crystals were grown from acetone solution as colourless prisms. The crystal, $0.35 \times 0.27 \times 0.05$ mm, used for the present analysis was the (–) compound. The lattice constants and intensity data were obtained by a Philips four-circle X-ray diffractometer with graphite-monochromated Cu $K\alpha$ radiation. Intensities of 1879 of 2476 possible reflexions were measured as having $I_o \geq 2\sigma(I_o)$, within the 2θ range of 6–156°, by the θ – 2θ scanning method. The scans were repeated twice when the total counts during a single scan were

less than 10^4 . The scan speed was $2\theta = 4^\circ$ min $^{-1}$ and the background was measured at each end of the scan for 10 s. The intensities were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by the direct method with *MULTAN* (Main, Woolfson & Germain, 1971). Starting with 10 reflexions, including three origin-defining and three known phases obtained by the Σ_1 relations, the phases of 305 structure factors with $E \geq 1.3$ were assigned, but first attempts to arrive at the correct solution were unsuccessful. Reassignment of the starting set by eliminating the five strongest reflexions yielded a reasonable E map in which 28 of the 30 heavy atoms could be located. The structure determination was completed by the Fourier method and the refinement was carried out by the block-diagonal least-squares method with *HBL5* (Okaya & Ashida, 1967). Unit weight was applied for each reflexion. The final R value was 0.043 including all the H atoms with isotropic temperature factors. The final atomic parameters are given in Table 1.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32334 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

To determine the absolute configuration, small crystals of the (+), 0.4 × 0.2 × 0.025 mm, and (-), 0.2 × 0.1 × 0.06 mm, compounds were chosen for the intensity measurement. The five reflexions shown in Table 2 were chosen for the intensity measurement. They are of medium intensity and have a large difference between $|F_c|$ values of hkl and $\bar{h}\bar{k}\bar{l}$. The integrated intensities of these reflexions were carefully

Table 1. *Final atomic coordinates*

The coordinates for non-hydrogen atoms are ×10⁴ and those for H atoms are ×10³.

	x	y	z
C(1)	3096 (4)	2375 (1)	1335 (7)
C(2)	3295 (4)	2096 (1)	3480 (7)
O(3)	2450 (3)	2268 (1)	5349 (5)
C(4)	2282 (4)	2658 (1)	4952 (7)
C(5)	2788 (3)	2768 (1)	2514 (7)
C(6)	4115 (4)	2982 (1)	2598 (8)
O(7)	4833 (3)	2805 (1)	601 (5)
C(8)	4335 (4)	2452 (1)	-35 (8)
O(9)	1787 (3)	2869 (1)	6418 (6)
O(10)	4843 (3)	2250 (1)	-1527 (5)
C(11)	2975 (4)	1671 (1)	3193 (7)
C(12)	3519 (4)	1412 (1)	4864 (8)
C(13)	3263 (4)	1014 (1)	4741 (8)
C(14)	2445 (4)	868 (1)	2944 (8)
C(15)	1894 (4)	1125 (1)	1340 (9)
C(16)	2164 (4)	1526 (1)	1451 (8)
O(17)	3777 (3)	734 (1)	6248 (7)
C(18)	4637 (5)	864 (1)	8071 (10)
O(19)	2272 (3)	467 (1)	2948 (6)
C(20)	1538 (6)	303 (1)	1015 (10)
C(21)	4046 (4)	3415 (1)	2328 (8)
C(22)	3297 (4)	3583 (1)	508 (7)
C(23)	3151 (4)	3987 (1)	379 (8)
C(24)	3760 (4)	4232 (1)	2090 (9)
C(25)	4532 (4)	4063 (1)	3831 (9)
C(26)	4670 (4)	3654 (1)	3936 (9)
O(27)	2412 (3)	4180 (1)	-1265 (6)
C(28)	1643 (5)	3944 (1)	-2820 (10)
O(29)	3498 (3)	4623 (1)	1880 (7)
C(30)	3976 (6)	4875 (1)	3759 (14)
H(C1)	244 (4)	225 (1)	40 (8)
H(C2)	422 (4)	208 (1)	390 (8)
H(C5)	216 (4)	295 (1)	173 (8)
H(C6)	463 (4)	293 (1)	412 (8)
H(C12)	408 (4)	152 (1)	605 (9)
H(C15)	127 (4)	104 (1)	16 (9)
H(C16)	175 (4)	171 (1)	30 (7)
H(C18)	432 (5)	112 (1)	908 (11)
H'(C18)	549 (5)	100 (1)	749 (10)
H''(C18)	479 (4)	60 (1)	943 (9)
H(C20)	194 (4)	38 (1)	-69 (8)
H'(C20)	153 (5)	-1 (1)	122 (10)
H''(C20)	55 (5)	37 (1)	153 (10)
H(C22)	283 (4)	340 (1)	-57 (8)
H(C25)	497 (4)	425 (1)	506 (9)
H(C26)	527 (4)	349 (1)	524 (9)
H(C28)	216 (5)	374 (1)	-384 (9)
H'(C28)	100 (4)	371 (1)	-200 (9)
H''(C28)	111 (5)	415 (1)	-362 (11)
H(C30)	368 (4)	478 (1)	573 (9)
H'(C30)	369 (5)	514 (1)	340 (11)
H''(C30)	494 (5)	492 (1)	339 (10)

measured, with their symmetry-equivalent reflexions. In order to estimate the absorption effect, the ψ -scan method was employed. For each reflexion, intensities were measured by varying the ψ angle (azimuthal angle about the reflexion vector) from -90° to +90° (for some reflexions the angles were limited to a narrower range because of a mechanical conflict) in steps of 5°, and for each step the integrated intensity was measured by adopting the same procedure as in the running measurement of intensities described before. The mean intensity value of each reflexion was obtained by taking the average of the intensities for various ψ 's. The two extreme values were excluded from the averaging since they might be affected by multiple reflexions. There was no systematic variation in intensity for different ψ angles; they agree within the limit of experimental error estimated on the basis of counting statistics. Hence, the absorption effect seemed to be negligible. The sequence of the measurement was hkl and its three equivalent reflexions followed by their Friedel pairs. The mean intensities obtained for the four symmetry-equivalent reflexions were then averaged to give the values of hkl and $\bar{h}\bar{k}\bar{l}$ separately. In Table 2, the observed intensity ratios between the Friedel pairs are listed, measured for both (+) and (-) compounds. These values may be compared with the ratios of $|F_c|^2$ calculated by assuming that the atomic coordinates are as given in Table 1 and the dispersion corrections of the atomic scattering factor of O for Cu $K\alpha$ radiation are $\Delta f' = 0.047$, $\Delta f'' = 0.032$ (*International Tables for X-ray Crystallography*, 1974). The result indicates clearly that the absolute configuration of (-)-tetra-*O*-methyldehydrodicafeic acid dilactone is *R* for all asymmetric C atoms as shown in Fig. 1, or as presented by the atomic parameters given in Table 1 with a right-handed coordinate system. The (+) compound has, naturally, the opposite configuration *S*.

Discussion. The molecule possesses a pseudo diad axis through the midpoint of the C(1)–C(5) bond. The bond lengths and angles are given in Fig. 1, which shows that most of the values correspond well between the two halves of the molecule. The only marked difference is found in the torsion angles about the bonds connecting the lactone ring and the benzene ring, and the associated bond angles subtended at C(11) and C(21). It is noted that the bond angles subtended at the methoxyl-substituted C atoms of the benzene rings, O(17)–C(13)–C(14), O(19)–C(14)–C(13), O(27)–C(23)–C(24) and O(29)–C(24)–C(23), which are found between the two methoxyl groups, are appreciably smaller than the other bond angles. Endocyclic torsion angles calculated for each ring are shown in Fig. 2 with some other torsion angles. Both lactone rings have a diad axis passing through C(4) and the midpoint of C(1)–C(2) [C(8) and the midpoint of C(5)–C(6) in the other ring]; thus, the conformation of

Table 2. Comparison of calculated and observed intensity ratios for the selected Friedel-pair reflexions

$F_c(+)$ and $I_o(+)$: calculated structure factors and observed intensities for hkl -type reflexions. $F_c(-)$ and $I_o(-)$: same for $\bar{h}\bar{k}\bar{l}$ -type reflexions. The standard deviations calculated from the dispersion of the observed values are listed in parentheses. N : number of observations from which the average value of $I_o(+)$ was derived. The same number of observations were used to obtain $I_o(-)$.

h	k	l	(-)-Compound				(+) -Compound					
			$ F_c $	$\frac{ F_c(+) ^2}{ F_c(-) ^2}$	$I_o(+)$	$I_o(-)$	$\frac{I_o(+)}{I_o(-)}$	N	$I_o(+)$	$I_o(-)$	$\frac{I_o(+)}{I_o(-)}$	N
6	2	1	19.03	1.081	645 (25) <	662 (24)	0.974	19	967 (16) >	943 (22)	1.025	11
6	5	1	23.26	0.938	807 (16) >	787 (22)	1.025	17	1183 (25) <	1194 (17)	0.991	10
2	6	1	40.84	1.075	5171 (79) <	5247 (80)	0.986	88	7995 (98) >	7855 (97)	1.018	81
3, 12,	1	1	19.90	0.909	948 (21) >	936 (16)	1.013	27	1311 (32) <	1338 (36)	0.980	20
2	2	2	23.28	0.918	1568 (27) >	1551 (28)	1.011	100	2261 (39) <	2301 (38)	0.983	100
Handedness of the coordinate system	(Intensity measurement) (Atomic coordinates given in Table 1)				left					left		
Absolute configuration at C(1), C(2), C(5), C(6)					right					left		
					<i>R,R,R,R</i>					<i>S,S,S,S</i>		

the rings can be described as a twist form. The deviations of atoms from the plane formed by O(3), C(4) and C(5) [O(7), C(8) and C(1) in the other ring] are given in Table 3. The methyl C atoms of the two methoxyl groups substituted at the *ortho* positions are turned out towards each other and they are almost coplanar with the benzene ring. The two benzene rings have different orientations with respect to the lactone ring, as stated before.

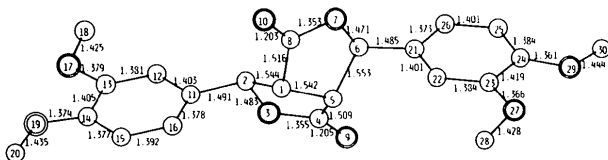


Fig. 1. Bond lengths (Å) and bond angles (°). The e.s.d.'s are 0.006 Å for C—C, 0.007 Å for methoxyl O—C bonds and 0.4° for C—C—C angles.

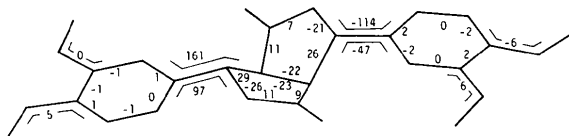


Fig. 2. Torsion angles (°). Endocyclic torsion angles are denoted in the rings.

Table 4 shows the intermolecular atomic contacts of less than 3.5 Å. The closest approaches are found between the carbonyl O atom, O(10), and the C and O atoms of the lactone ring [C(4), C(5) and O(3)].

Table 3. Deviations of atoms from the plane (Å)

Lactone ring A		Lactone ring B	
O(3)*	0.0	O(7)*	0.0
C(4)*	0.0	C(8)*	0.0
C(5)*	0.0	C(1)*	0.0
C(1)	-0.220	C(5)	-0.278
C(2)	0.265	C(6)	0.157
O(9)	-0.004	O(10)	-0.028

* Atoms forming the plane.

Table 4. Intermolecular interatomic distances less than 3.5 Å

Symmetry code: (i) $x, y, 1+z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, -z$.

C(2)—O(10 ⁱ)	3.263 (5) Å
O(3)—C(1 ⁱ)	3.436 (5)
O(3)—C(8 ⁱ)	3.297 (5)
O(3)—O(10 ⁱ)	3.031 (4)
O(9)—C(1 ⁱ)	3.498 (5)
C(18)—C(15 ⁱ)	3.490 (7)
O(19)—C(20 ⁱⁱⁱ)	3.366 (6)
O(7)—O(9 ⁱⁱⁱ)	3.482 (4)
C(8)—O(9 ⁱⁱⁱ)	3.424 (5)
C(18)—O(27 ⁱⁱⁱ)	3.385 (6)
C(18)—C(28 ⁱⁱⁱ)	3.435 (8)
O(10)—C(4 ^{iv})	3.184 (5)
O(10)—C(5 ^{iv})	3.097 (5)
O(10)—O(9 ^{iv})	3.421 (4)

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 KUMADA, Y., NAGANAWA, H., INUMA, H., MATSUZAKI, M., TAKEUCHI, T. & UMEZAWA, H. (1976). *J. Antibiot.* **29**. In the press.

MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN. A Computer Program for the Automatic Solution of Crystal Structures*, Univs. of York (England) and Leuven (Belgium).
 OKAYA, Y. & ASHIDA, T. (1967). *HBLS IV. The Universal Crystallographic Computing System* (I), p. 65. Tokyo: The Crystallographic Society of Japan.

Acta Cryst. (1977). **B33**, 1263–1266

Dichloro-1,4 *p*-Chlorophényl-1' Diméthylamino-4' Diaza-2,3 Butadiène

PAR F. CHENTLI-BENCHICKA, J. P. DECLERCQ, G. GERMAIN ET M. VAN MEERSSCHE

Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, Bâtiment Lavoisier, 1 place L. Pasteur, 1348 Louvain-la-Neuve, Belgique

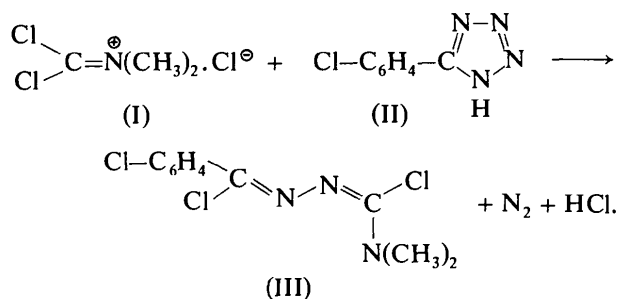
ET G. DUCHENE ET H. G. VIEHE

Laboratoire de Chimie Organique, Université de Louvain, Bâtiment Lavoisier, 1 place L. Pasteur, 1348 Louvain-la-Neuve, Belgique

(Reçu le 26 novembre 1976, accepté le 6 décembre 1976)

Abstract. C₁₀H₁₀N₃Cl₃, *M_r* = 277.5, monoclinic, space group *P*2₁/*c*; *a* = 27.559 (6), *b* = 7.165 (2), *c* = 12.716 (3) Å, β = 95.03 (2)°; *Z* = 8, *V* = 2501 Å³, *D_c* = 1.474 g cm⁻³; *F*(000) = 1136. The title compound is a derivative of the formaldazine formed from 5-chlorophenyltetrazole by reaction with dimethylphosgeneiminium chloride. The structure was solved by direct methods and refined by least squares to a final *R* value of 0.058 for the 2297 observed reflexions. One of the molecules of the asymmetric unit exhibits a nearly planar conformation corresponding to a *trans* position of the Cl atoms on (*E*)-diazabutadiene; the other shows a torsion of 12° around the N–N bond.

Introduction. L'attaque électrophile des chlorures d'acide sur les phényl-5 tétrazoles est généralement suivie d'une fragmentation et d'une transformation cyclique en oxadiazole (Huisgen & Seidel, 1961). Le diméthylphosgène-iminium mène à une fragmentation sans recyclisation et donne accès à une autre classe de composé, de structure C₆H₅-CCl=N=N=CCl-N<. L'étude par diffraction de rayons X a montré que, dans la réaction du chlorure de diméthylphosgène-iminium (I) avec le *p*-chlorophényl-5 tétrazole (II), il se forme bien un dérivé (III) de la *trans*-formaldazine H₂C=N=N=CH₂:



Les intensités de 3148 réflexions non équivalentes ont été mesurées sur un diffractomètre à quatre cercles Picker, commandé par cartes perforées; 851 de ces réflexions, répondant au critère *I* < 2,5σ(*I*), ont été considérées comme inobservées. La mesure des intensités a été faite en balayage ω-2θ jusqu'à 2θ_{max} = 110°, avec comme radiation Cu Kα, filtrée par Ni.

La structure a été déterminée par méthode directe, au moyen de la chaîne de programmes *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). L'utilisation de cette méthode nous a fourni les positions de tous les atomes sauf C(6) de la première molécule. Les facteurs de structure calculés à partir de cette première ébauche de la structure fournissent pour les 2297 réflexions observées une valeur de l'indice *R*