

As can be seen from Table 6 and Fig. 5(a), crystal (I) has an extended three-dimensional network of intermolecular hydrogen bonds involving the waters of hydration. The Na ions and their waters of hydration form layers between columns of DNT. The two DNT molecules themselves are stacked over one another with C(6)—C(4*) (3.24 Å) being the closest contact. The two molecules are rotated with respect to each other in such a way that the nitro groups do not lie directly over the ring. The DNT form alternating layers with a head-to-head or tail-to-tail arrangement.

In crystal (II) (Fig. 5b), the DNT molecules also form the same alternating pattern; however, they are more compact. The DNT are also oriented in such a way that the nitro groups lie over the ring. The closest contacts between the layers are within the normal charge-transfer distances with C(2)—O(511) 3.23 Å, C(3)—O(512) 3.31 Å and C(6)—O(311) 3.19 Å. The nitro group at C(5) may be rotated so far from coplanarity to facilitate these close contacts.

The authors wish to thank Mrs Mary Erman, Miss Elaine DeJarnette and Miss Gloria Del Bel for their technical assistance and Dr Jane Griffin for her helpful discussions. This research was supported in part by grant AM-15051 from the National Institute of Arthritis, Metabolism and Digestive Diseases, DHEW.

References

- BAITINGER, W. F., VON SCHLEYER, R., MURTY, T. S. S. R. & ROBINSON, L. (1964). *Tetrahedron*, **20**, 1635–1647.
CODY, V., DUAX, W. L. & HAUPTMAN, H. A. (1973). *Int. J. Peptide Protein Res.* **5**, 297–308.

- CODY, V., DUAX, W. L. & NORTON, D. A. (1971). *Am. Crystallogr. Assoc. Meeting. Abstracts*.
DETTITA, G. T., EDMONDS, J. W., LANGS, D. A. & HAUPTMAN, H. A. (1975). *Acta Cryst.* **A31**, 472–479.
GERDIL, R. (1972). *Helv. Chim. Acta*, **55**, 2159–2167.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
GREEN, W. L. (1968). *Endocrinology*, **83**, 336–347.
GREER, M. A. & GRIMM, Y. (1968). *Endocrinology*, **83**, 405–410.
HAIBACH, H. (1971). *Endocrinology*, **88**, 1277–1279.
HAMILTON, J. A. & STEINRAUF, L. K. (1967). *Acta Cryst.* **23**, 817–825.
HERBSTEIN, F. H. & KAFTORY, M. (1976). *Acta Cryst.* **B32**, 387–396.
HOLDEN, J. R. & DICKINSON, C. (1977). *J. Phys. Chem.* **81**, 1505–1514.
HUGHES, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1737–1752.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
JENSEN, B. (1975). *Acta Chem. Scand. Ser. B*, **29**, 891–903.
LANGS, D. A. & DETTITA, G. T. (1977). *Am. Crystallogr. Assoc. Meeting. Abstracts*.
MAARTMANN-MOE, K. (1969). *Acta Cryst.* **B25**, 1452–1460.
MANDEL, N. S. & MANDEL, G. S. (1976). *J. Am. Chem. Soc.* **98**, 2319–2323.
RAO, S. T. & MALLIKARJUNAN, M. (1975). *Acta Cryst.* **A31**, S48.
SORIANO-GARCIA, M., SRIKRISHNAN, T. & PARTHASARATHY, R. (1978). *Acta Cryst.* **A34**, S114.
STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*. New York: Macmillan.
THEWALT, U. & BUGG, C. E. (1972). *Acta Cryst.* **B28**, 82–92.
VAN DER HELM, D. & TATSCH, C. E. (1972). *Acta Cryst.* **B28**, 2307–2312.
VERBIST, J., PUTZEYS, J. P., PIRET, P. & VAN MEERSSCHE, M. (1971). *Acta Cryst.* **B27**, 1190–1194.

Acta Cryst. (1979). **B35**, 1835–1839

Structure of *cis*-3-(4-Bromophenyl)-4a,7a-dihydro-6,7a-dimethyl-4a,5-diphenyl-7H-cyclopenta-1,4,2-dioxazine, the Product of a Regio- and Stereospecific Isomerization

BY CHUNG CHIEH AND DONALD MACKAY

Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

(Received 4 October 1978; accepted 10 April 1979)

Abstract

The adduct of 1,4-dimethyl-2,3-diphenylcyclopentadiene and *p*-bromonitrosocarbonylbenzene underwent a regio- and stereospecific isomerization leading to the title compound, C₂₆H₂₂BrNO₂. The colorless crystals

grown from ethanol (with a trace of benzene) are monoclinic with $a = 13.949$ (4), $b = 10.588$ (2), $c = 16.753$ (3) Å, $\beta = 119.1$ (1)°, space group $P2_1/c$ and $Z = 4$. The structure was determined from 2105 observed reflections measured by the θ - 2θ scan technique using graphite-monochromated Mo $K\alpha$ radiation

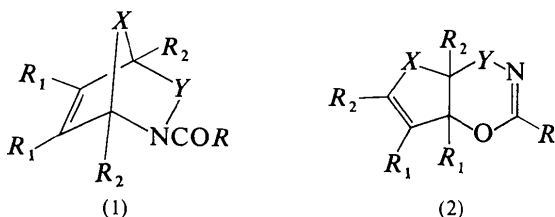
0567-7408/79/081835-05\$01.00

© 1979 International Union of Crystallography

and was refined by the full-matrix least-squares method to a final R value of 0.072. The six-membered dioxazine ring has a half-chair conformation with $N=C = 1.26$ (2), $C-O = 1.37$ (1), $O-C = 1.45$ (1), $C-C = 1.55$ (2), $C-O = 1.48$ (1) and $O-N = 1.40$ (1) Å. The mean COC angle is 119 (1°). Other angles of interest in the ring are $ONC = 118$ (1), $NCO = 127$ (1°). The $C=C$ double bond in the five-membered ring is 1.32 (2) Å.

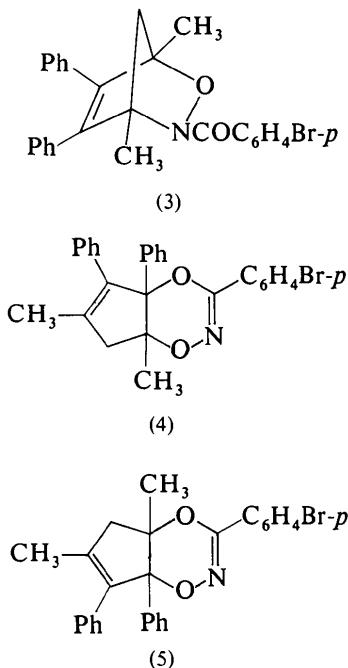
Introduction

In a study of the thermal rearrangement of compounds of the general type (1), the most widely encountered process was the [3,3] sigmatropic rearrangement to the *cis*-1,3,4-oxadiazines (2), when $Y = NCOR$ (Campbell, Harris, Mackay & Sauer, 1975).



In some cases, alternative pathways were possible (Chieh, Mackay & Wong, 1972).

In the thermal rearrangement of (3), both regioisomers (4) and (5) are possible. Only the former can arise as a result of a [3,3] sigmatropic rearrangement of (3) but either can arise by a dissociation-recombination mechanism.



A clear distinction between (4) and (5) was not possible by IR, UV or NMR spectroscopy. Structure elucidation by chemical means did not hold great promise. Thus hydrogenolysis of the $N-O$ bond was expected to be accompanied by saturation of the alkene link; acid cleavage of the dioxazine ring would be ambiguous owing to probable double-bond migration in the cyclopentene ring. Accordingly an X-ray analysis was undertaken of a representative member of the dioxazines, the product from the oxidation of *p*-bromohydroxamic acid in the presence of dimethyldiphenylcyclopentadiene. It is now shown to be the title compound (4). It provides the first crystal structure determination of a dioxazine ring system.

Experimental

Equivalent amounts of 1,4-dimethyl-2,3-diphenylcyclopentadiene and *p*-bromobenzohydroxamic acid were stirred in benzene with an excess of silver oxide for 4 h at room temperature. The solution was filtered, and heated near the b.p. for 15 min to complete the isomerization of (3) to (4). Evaporation and treatment of the residue with cold methanol caused crystallization of (4), isolated in 50–60% yield.

Recrystallization of the product from ethanol or benzene alone did not give good crystals. The compound was too soluble in the latter, and not soluble enough in the former. About 50 mg of the product suspended in 15 ml ethanol was dissolved by adding a few drops of benzene. Evaporation of this clear solution at room temperature (298 K) gave beautiful prismatic colorless crystals. The space group and cell constants were determined by photographic methods, and then the latter were refined by least squares along with the orientation matrix from 15 reflections, automatically centered on a Syntex $P2_1$ diffractometer. Crystal data are given in Table 1.

Table 1. *Crystal data*

Formula	$C_{26}H_{22}BrNO_2$
M_r	460.1
Crystal system	Monoclinic
a (Å)	13.949 (4)
b (Å)	10.588 (2)
c (Å)	16.753 (3)
β ($^\circ$)	119.1 (1)
Systematic absences	$h0l, l = 2n + 1$ $0k0, k = 2n + 1$
Space group	$P2_1/c$
V (Å ³)	2162.0
D_o (floatation in KI solution) (Mg m ⁻³)	1.42
Z	4
D_x ($\lambda_{Mo K\alpha} = 0.71069$ Å) (Mg m ⁻³)	1.413
μ (Mo $K\alpha$) (mm ⁻¹)	2.05
m.p. (decomposition) (K)	432–433

The crystal used had a prismatic shape with maximum and minimum dimensions of 0.30 and 0.14 mm respectively. Intensities were measured by the θ - 2θ scan method on a computer-controlled Syntex $P2_1$ diffractometer which was equipped with a graphite monochromator, a scintillation counter and a pulse-height analyzer. The slowest scan speed of $2.02^\circ \text{ min}^{-1}$ was used for reflections with peak intensities less than 150 c.p.s. Higher speeds up to $29.3^\circ \text{ min}^{-1}$ were used for strong reflections. Scan ranges were 1° below $K\alpha_1$ (0.70926 Å) and above $K\alpha_2$ (0.71354 Å). The time for the background count was half that of the scan. Between each 50 reflections scanned, two strong ones were repeatedly measured. The intensities of these reflections fluctuated within 5%. Among 2815 independent reflections with $2\theta \leq 45^\circ$ measured ($298 \pm 2 \text{ K}$), 2105 had a positive net count. Lorentz and polarization factors, including correction for the monochromator, were applied to derive the structure amplitude. The unobserved reflections were not included in the refinement.

The structure was solved by the heavy-atom method and refined by full-matrix least squares. When all non-hydrogen atoms were included, the R factor $[\sum (|F_o| - |F_c|) / \sum |F_o|]$ was 0.13 with isotropic temperature factors. The atomic scattering factors of Cromer & Waber (1965) were used with anomalous-dispersion correction for Br (Cromer, 1965). Anisotropic thermal

parameters were then introduced and refined to an R of 0.09. A difference Fourier map calculated at this stage had peaks with maximum electron density of $0.5 \text{ e } \text{Å}^{-3}$. Some corresponded to the positions of H atoms. H atoms of the three phenyl groups were included at the positions calculated based on $\text{C-H} = 1.0 \text{ Å}$. Scattering factors of the bonded atom (Stewart, Davidson & Simpson, 1965) were used for H. Further refinement of non-hydrogen atomic parameters gave a final R of 0.072. A weighting function, $w = (60 - F + 0.022F^2)^{-1}$, was used for all 2105 observed reflections so that the errors $[\sum w(|F_o| - |F_c|)^2 / (n)]^{1/2}$ were approximately equal for the ten ranges based on F_o at the final stage. At the final cycle, the maximum shift of parameters was less than 0.25 of the e.s.d.'s. The final atomic coordinates are given in Table 2.* The residual electron density in the final difference map did not exceed $\pm 0.5 \text{ e } \text{Å}^{-3}$.

Results and discussion

The standard chemical numbering is adopted for atoms of the two-ring system. This is shown in Fig. 1 together with bond lengths and angles. Standard deviations are 0.01 Å for the Br-C bond, 0.01–0.02 Å and 0.5° for other bonds and angles. Since the coordinates of the H atoms were not refined, bond lengths involving them are not given. The positions of the H atoms were calculated, by assuming $\text{C-H} = 1.00 \text{ Å}$, just before the final stage of refinement. An arbitrary isotropic temperature factor of 3.0 Å^2 was assigned to all H atoms. Finally, the H atoms were included in the structure factor calculations and the parameters of the other atoms were refined. The final results gave a mean C-H bond length of 1.02 Å . This lengthening is rather uniform for all C-H bonds and thus indicates that the

Table 2. Fractional atomic coordinates and their e.s.d.'s

	x	y	z
O(1)	0.5054 (4)	0.3103 (5)	0.3544 (4)
N(2)	0.4424 (5)	0.3922 (6)	0.3762 (4)
C(3)	0.3418 (6)	0.3680 (8)	0.3438 (5)
O(4)	0.2854 (4)	0.2699 (5)	0.2875 (4)
C(4a)	0.3444 (6)	0.1817 (8)	0.2606 (5)
C(5)	0.3454 (6)	0.2242 (6)	0.1735 (5)
C(6)	0.4410 (7)	0.1982 (8)	0.1788 (5)
C(7)	0.5212 (7)	0.1416 (9)	0.2711 (6)
C(7a)	0.4684 (7)	0.1780 (7)	0.3302 (5)
C(31)	0.2677 (6)	0.4504 (7)	0.3598 (5)
C(32)	0.1548 (7)	0.4423 (8)	0.3047 (6)
C(33)	0.0843 (6)	0.5165 (8)	0.3210 (5)
C(34)	0.1293 (7)	0.6011 (8)	0.3936 (6)
C(35)	0.2416 (7)	0.6116 (8)	0.4490 (6)
C(36)	0.3107 (8)	0.5378 (8)	0.4319 (5)
Br	0.03122 (9)	0.6992 (1)	0.41648 (8)
C(41)	0.2882 (6)	0.0554 (7)	0.2524 (5)
C(42)	0.2795 (7)	-0.0343 (7)	0.1884 (6)
C(43)	0.2311 (8)	-0.1504 (8)	0.1841 (7)
C(44)	0.1965 (8)	-0.1805 (9)	0.2473 (7)
C(45)	0.2049 (8)	-0.093 (1)	0.3093 (7)
C(46)	0.2496 (7)	0.0256 (8)	0.3117 (6)
C(51)	0.2507 (6)	0.2861 (8)	0.0957 (5)
C(52)	0.2277 (8)	0.4127 (9)	0.1028 (7)
C(53)	0.146 (1)	0.478 (1)	0.0316 (8)
C(54)	0.0832 (9)	0.417 (1)	-0.0495 (8)
C(55)	0.1018 (8)	0.291 (1)	-0.0573 (6)
C(56)	0.1848 (8)	0.2282 (8)	0.0148 (6)
C(M)	0.4753 (8)	0.2205 (9)	0.1078 (6)
C(M2)	0.5048 (7)	0.1050 (9)	0.4185 (5)

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34399 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

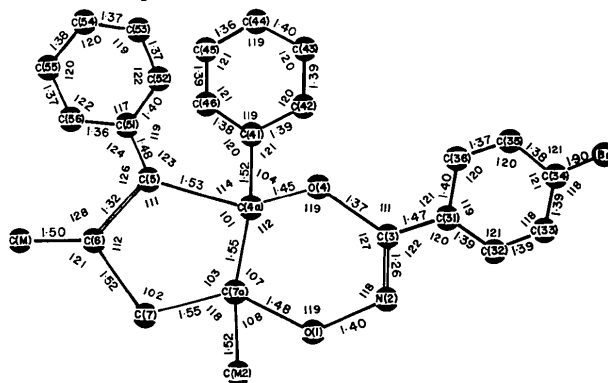


Fig. 1. Atomic numbering, bond lengths (Å) and angles ($^\circ$). Four angles not shown for clarity are C(41)-C(4a)-C(7a) 113° , O(4)-C(4a)-C(5) 112° , C(M2)-C(7a)-C(4a) 118° , and O(1)-C(7a)-C(7) 102° . Standard deviations are discussed in the text.

phenyl C atoms moved toward the centers of the rings by 0.02 Å in the last stage of refinement.

The distances of C(4a), C(5), C(6), C(7) and C(7a) from the least-squares plane of the five-membered ring are: -0.17, 0.08, 0.04, -0.16 and 0.21 Å respectively. The dioxazine ring adopts a half-chair conformation. The shape of the molecule can be seen from the stereoview (Fig. 2). Torsion angles, planes and interplanar angles are given in Table 3. Many torsion angles of the dioxazine ring are small and this indicates that part of the ring is flat owing to the presence of the double bond, C=N. The structure around C(4a) and C(7a) is under strain. The conformation of these two sp^3 carbon atoms is neither eclipsed nor staggered. A diagram showing this with the torsion angles indicated is given in Fig. 3.

The double bonds in the bicyclic rings are localized, as seen from the short C=C and C=N distances (Fig. 1). The C=N bond length, 1.26 (2) Å, is between the accepted value for C(sp^2)-N(sp^2) of 1.24 Å (*International Tables for X-ray Crystallography*, 1968) and that [1.279 (10) Å] of an oxazine derivative (Garbassi & Giarda, 1973). For a conjugated C=N in an oxazine a value of 1.29 Å is found (Abramovitch, Shinkai, Cue,

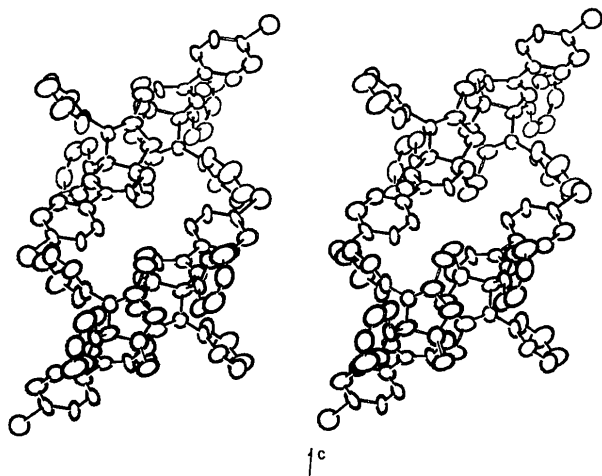


Fig. 2. Stereoview of the packing diagram.

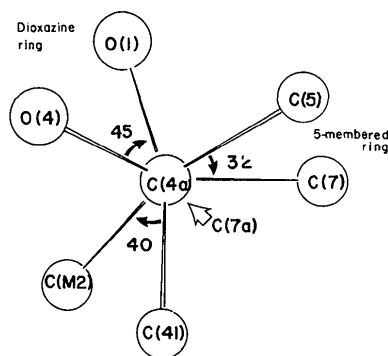


Fig. 3. Conformation viewed from C(4a) to C(7a), with torsion angles ($^\circ$).

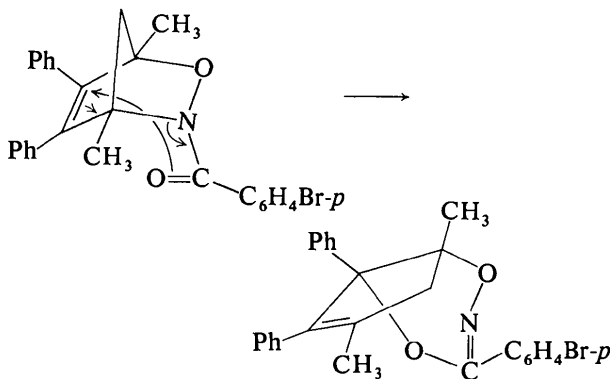
Table 3. Torsion angles ($^\circ$) and interplanar angles ($^\circ$)

The torsion angle $A-B-C-D$ is viewed along $B-C$, with a clockwise rotation of A to D taken to be positive.

Torsion angles of dioxazine ring	
O(1)-N(2)-C(3)-O(4)	1
N(2)-C(3)-O(4)-C(4a)	0
C(3)-O(4)-C(4a)-C(7a)	-24
C(4a)-C(7a)-O(1)-N(2)	-47
C(7a)-O(1)-N(2)-C(3)	25
Selected torsion angles related to the five-membered ring	
C(4a)-C(5)-C(6)-C(7)	3
C(4a)-C(5)-C(6)-C(M)	-178
Interplanar angles	
N(2),C(3),O(4),C(31) \wedge C(31),C(32)...C(36)	17
C(4a),C(5),C(6),C(51) \wedge C(51),C(52)...C(56)	76

Aagan & Atwood, 1976). The C(3)-C(31) bond length, 1.47 (2) Å, is typical for a C(sp^2)-C(sp^2) distance, 1.47-1.48 Å (Lide, 1962). The plane of the phenyl group attached to C(3) is rotated only slightly out of the plane defined by N(2), C(3), O(4), C(31), the angle being 17° (Table 3). Therefore, conjugation with a contribution from the phenyl ring as well as the C=N bond may cause the C(3)-O(4) distance, 1.37 (1) Å, to be shorter than other C-O bonds in the molecule (Fig. 1). The plane of the phenyl ring attached to C(5) intersects that defined by C(4a), C(5), C(6), C(51) at an angle of 76° . There is no conjugation between the phenyl and the C(5)=C(6) groups, giving a value of 1.48 (1) Å for C(5)-C(51). The C(4a)-C(41) bond length, 1.52 (1) Å, is also longer than the values obtained by methods other than X-ray diffraction (Lide, 1962). On the other hand, these values are reasonable when compared with those obtained by X-ray diffraction for phenyl groups attached to a ring. For example, the C(sp^3)-C(sp^2) (phenyl) bond lengths range from 1.53 to 1.57 Å in 2,2,7,7-tetraphenyl-6-oxabicyclo[3.2.1]octan-5-ol (Wei & Hawkinson, 1978).

The structure determination indicated that the sigma-tropic rearrangement placed the carbonyl-derived O on the allylic ring carbon as shown.



The packing of the molecules is shown in Fig. 2. This is a stereoview looking down the *b* axis. There is no unusual intermolecular distance in this structure.

We thank the National Research Council of Canada for financial support and Dr Paul Moews for his help in using the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) at the University of Connecticut (where CC prepared part of the manuscript) to calculate the least-squares planes and angles.

References

- ABRAMOVITCH, R. A., SHINKAI, I., CUE, B. W., AAGAN, F. A. & ATWOOD, J. L. (1976). *J. Heterocycl. Chem.* **13**, 415–417.
 CAMPBELL, J. A., HARRIS, I., MACKAY, D. & SAUER, T. D. (1975). *Can. J. Chem.* **53**, 535–541.

- CHIEH, P. C., MACKAY, D. & WONG, L. L. (1972). *J. Chem. Soc. Perkin Trans. 2*, pp. 2094–2097.
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
 GARBASSI, F. & GIARDA, L. (1973). *Acta Cryst.* **B29**, 1190–1196.
International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed. Birmingham: Kynoch Press.
 LIDE, D. R. (1962). *Tetrahedron*, **17**, 125–134.
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 WEI, C. H. & HAWKINSON, S. W. (1978). *Acta Cryst.* **B34**, 170–175.

Acta Cryst. (1979). **B35**, 1839–1842

Calpurmenin and its 13 α -(2'-Pyrrolicarboxylic Acid) Ester

BY W. J. VERMIN, A. J. DE KOK AND C. ROMERS

Gorlaeus Laboratoria, Section X-ray and Electron Diffraction, University of Leiden, 2300 RA Leiden, The Netherlands

AND M. H. RADEMA AND J. L. VAN EIJK

Pharmaceutisch Laboratorium, University of Utrecht, 3511 GH Utrecht, The Netherlands

(Received 29 January 1979; accepted 11 April 1979)

Abstract

Calpurmenin and its 13 α -(2'-pyrrolicarboxylic acid) ester, C₂₀H₂₇N₃O₄, are alkaloids with a sparteine molecular framework, isolated from the South African *Leguminosa*, *Calpurnia aurea*. Crystals of the ester compound are orthorhombic with space group *P*2₁2₁2₁ and *Z* = 4. The lattice dimensions are *a* = 8.128 (4), *b* = 12.423 (3) and *c* = 18.467 (5) Å. The structure was solved with direct methods and refined with least squares using 1339 reflexions of which 805 had intensities with *I* > 2 σ (*I*). The keto oxygen atom is bound to C(2), the hydroxyl group is bound to C(12) in a β axial orientation, the ester moiety is bound to C(13) in an axial orientation. Ring *A* is a distorted sofa, rings *B* and *D* are slightly distorted chairs, while ring *C* has a nearly ideal boat conformation.

Introduction

During our research into the alkaloids of Ethiopian and South African *Leguminosae*, *inter alia* *Calpurnia*

aurea, we discovered in the South African *Calpurnia* two hitherto unknown alkaloids, which were not observed in the Ethiopian material (van Eijk & Radema, 1977). Thin-layer chromatography and column chromatography were employed to isolate these alkaloids. Mass spectroscopy (MS) showed one of them to be a pyrrolicarboxylic acid ester of the other compound (named calpurmenin); their molecular weights were 373 and 280, respectively (Radema, van Eijk, Vermin, de Kok & Romers, 1979). As was to be expected, MS proved these compounds to contain the sparteine skeleton with four six-membered fused rings *A*, *B*, *C* and *D* (see Fig. 1*a*). Furthermore, MS indicated that the keto oxygen atom is located either at C(2) in ring *A*, or at C(10) in ring *B*, while one hydroxyl group (or its corresponding ester moiety) is bound to C(13). According to MS and IR spectra the second hydroxyl group should be bound to C(12), C(11), C(15) or to C(17).

In the molecular framework of sparteine and its diastereoisomers, ring *C* (or *B*) can adopt either the chair or the boat conformation. The former occurs in α -