

conduit à 0,75 environ. Cette compacité est due à l'existence, dans le plan (100) ou au voisinage de ce plan, de nombreuses liaisons de van der Waals se formant soit entre deux molécules de benzonitrile, soit entre un atome d'halogène et une molécule de benzonitrile.

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Senepoxide

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Abstract. $C_{18}H_{18}O_7$, monoclinic, $P2_1$, $a=7.225$, $b=10.386$, $c=12.191$ Å, $\beta=106.7^\circ$. $R=4.5\%$. 1629 reflexions.

Introduction. A single crystal of senepoxide, grown from methanol, was mounted on a PW 1100 4-circle automatic diffractometer. We measured 1629 reflexions with Cu $K\alpha$ radiation, monochromated with a graphite crystal. The structure was solved by symbolic addition (Karle & Karle, 1966) and the phase function (Riche, 1973). The E map corresponding to the highest maximum of the phase function gave all the heavy atoms. Refinement was carried out by full-matrix

least squares using a modified version of *ORFLS* (Busing, Martin & Levy, 1962). The thermal parameters of the non-hydrogen atoms were anisotropic. The hydrogen atoms were situated at theoretical positions (C–H: 1.0 Å; C–C–H: 109 or 120°), except those of the two methyl groups which were located on difference series maps; their thermal factors were kept isotropic and given the values of the carbon atoms to which they were bonded.

The scattering factors were those of Doyle & Turner (1968) for heavy atoms, and those of Stewart, Davidson & Simpson (1965) for hydrogen atoms.

The final R is 4.5%. Fractional coordinates and

Table 1. Atomic positional and thermal parameters ($\times 10^4$) of heavy atoms

The temperature factors are given by the expression: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + \beta_{23}kl)]$.

| | x | y | z | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} | B |
|-------|-----------|-----------|-----------|--------------|--------------|--------------|--------------|--------------|--------------|-----|
| C(1) | -1276 (5) | 1937 (3) | 6100 (3) | 231 (7) | 82 (3) | 70 (2) | -10 (4) | 52 (3) | -1 (2) | 3.8 |
| C(2) | 564 (5) | 1397 (3) | 5959 (2) | 220 (7) | 82 (3) | 68 (2) | -20 (4) | 40 (3) | -7 (2) | 3.8 |
| C(3) | 483 (5) | 902 (3) | 4767 (3) | 255 (8) | 83 (3) | 71 (2) | -4 (4) | 54 (4) | -5 (2) | 4.0 |
| C(4) | -1418 (6) | 337 (4) | 4134 (3) | 296 (10) | 122 (4) | 73 (2) | -19 (6) | 33 (4) | -21 (3) | 5.0 |
| C(5) | -3037 (6) | 631 (4) | 4377 (3) | 275 (9) | 133 (4) | 82 (3) | -25 (6) | 31 (4) | -15 (3) | 5.3 |
| C(6) | -3106 (5) | 1547 (4) | 5274 (3) | 229 (8) | 111 (4) | 87 (3) | -11 (5) | 41 (4) | 2 (2) | 4.6 |
| C(7) | -1300 (5) | 2315 (4) | 7286 (3) | 254 (8) | 100 (3) | 90 (3) | -21 (5) | 67 (4) | -17 (3) | 4.5 |
| O(8) | 408 (3) | 3076 (2) | 7747 (2) | 242 (5) | 104 (2) | 69 (2) | -9 (3) | 54 (2) | -17 (2) | 4.2 |
| C(9) | 536 (5) | 3667 (3) | 8745 (2) | 263 (8) | 93 (3) | 66 (2) | 28 (5) | 58 (4) | 3 (2) | 4.1 |
| O(9) | -614 (4) | 3503 (3) | 9273 (2) | 333 (7) | 158 (3) | 92 (2) | -41 (4) | 103 (3) | -21 (2) | 5.7 |
| C(10) | 2219 (5) | 4529 (3) | 9086 (2) | 240 (8) | 89 (3) | 58 (2) | 14 (4) | 41 (3) | 4 (2) | 3.8 |
| C(11) | 3807 (5) | 4392 (3) | 8656 (3) | 249 (8) | 96 (3) | 67 (2) | 22 (5) | 42 (3) | -4 (2) | 4.2 |
| C(12) | 5351 (5) | 5225 (4) | 8978 (3) | 218 (8) | 156 (5) | 87 (3) | -3 (6) | 43 (4) | 13 (3) | 5.2 |
| C(13) | 5282 (6) | 6229 (4) | 9723 (4) | 270 (10) | 116 (4) | 113 (4) | -23 (5) | 38 (5) | -9 (3) | 5.5 |
| C(14) | 3715 (7) | 6370 (4) | 10153 (4) | 357 (12) | 123 (4) | 111 (4) | -14 (7) | 61 (5) | -40 (3) | 6.1 |
| C(15) | 2189 (6) | 5521 (4) | 9831 (3) | 288 (9) | 124 (4) | 89 (3) | -4 (6) | 63 (4) | -27 (3) | 5.1 |
| O(16) | -2236 (4) | 2807 (2) | 5198 (2) | 282 (6) | 93 (2) | 96 (2) | 14 (4) | 50 (3) | 8 (2) | 4.9 |
| O(17) | 1012 (3) | 322 (2) | 6744 (2) | 204 (5) | 99 (2) | 76 (2) | 2 (3) | 33 (2) | 7 (2) | 4.1 |
| C(18) | 2902 (6) | 37 (4) | 7178 (3) | 251 (9) | 152 (5) | 76 (3) | 33 (6) | 35 (4) | 3 (3) | 5.2 |
| O(18) | 4150 (4) | 615 (4) | 6949 (3) | 221 (6) | 246 (5) | 126 (3) | -6 (6) | 50 (3) | 43 (3) | 7.2 |
| C(19) | 3111 (7) | -1135 (5) | 7929 (4) | 351 (12) | 178 (6) | 97 (3) | 67 (8) | 32 (5) | 25 (4) | 6.7 |
| O(20) | 947 (4) | 1999 (2) | 4155 (2) | 337 (7) | 98 (2) | 85 (2) | 6 (4) | 94 (3) | 0 (2) | 4.8 |
| C(21) | 1688 (6) | 1750 (4) | 3285 (3) | 259 (9) | 136 (5) | 89 (3) | 11 (5) | 74 (4) | 0 (3) | 5.0 |
| O(21) | 1937 (5) | 677 (3) | 2994 (3) | 388 (9) | 151 (4) | 126 (3) | -11 (5) | 133 (4) | -29 (3) | 6.5 |
| C(22) | 2239 (9) | 2982 (6) | 2799 (5) | 510 (18) | 176 (6) | 158 (5) | 15 (10) | 182 (8) | 35 (5) | 8.0 |

Table 2. Atomic coordinates ($\times 10^3$) and isotropic temperature factors for hydrogen atoms

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> |
|--------|----------|----------|----------|----------|
| H(12) | 384 | 368 | 811 | 4.2 |
| H(13) | 649 | 510 | 868 | 5.2 |
| H(14) | 637 | 686 | 995 | 5.5 |
| H(15) | 369 | 709 | 1070 | 6.1 |
| H(16) | 106 | 563 | 1014 | 5.1 |
| H(A7) | -247 | 284 | 727 | 4.5 |
| H(B7) | -126 | 154 | 778 | 4.5 |
| H(2) | 160 | 206 | 619 | 3.8 |
| H(3) | 150 | 23 | 485 | 4.0 |
| H(4) | -162 | -29 | 349 | 5.0 |
| H(5) | -420 | 17 | 389 | 5.3 |
| H(6) | -408 | 129 | 567 | 4.6 |
| H(A19) | 421 | -108 | 843 | 5.9 |
| H(B19) | 251 | -96 | 841 | 5.9 |
| H(C19) | 282 | -188 | 745 | 5.9 |
| H(A22) | 219 | 287 | 211 | 7.0 |
| H(B22) | 359 | 305 | 328 | 7.0 |
| H(C22) | 166 | 380 | 296 | 7.0 |

thermal parameters for heavy atoms are given in Table 1 and those for hydrogen in Table 2.*

Discussion. Senepoxide, which was isolated from the medicinal plant *Uvaria catocarpa* (*Annonacea*), belongs to a small group of naturally occurring, highly oxygenated cyclohexane derivatives containing, amongst others, crotepoxide (I) (Kupchan, Hemingway & Smith, 1969) and pipoxide (II) (Singh, Dhar & Atal, 1970). The molecular structure and absolute stereochemistry (III) have been proposed for senepoxide (1*S*, 2*S*, 3*R*, 6*S*-1-benzoyloxymethyl-2,3-diacetoxy-1,6-epoxycyclohex-4-ene) on the basis of chemical and spectroscopic evidence (Hollands, Becher, Gaudemer & Polonsky, 1968).

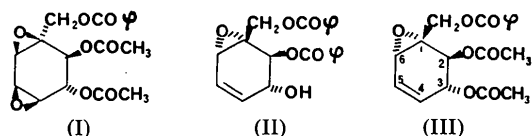


Fig. 1, which shows the *ORTEP* (Johnson, 1965) drawing of the molecule as obtained from our X-ray results, confirms fully the proposed formula. Tables 3 and 4 give the bond distances between heavy atoms and their valency angles.

The epoxide and the C(2) acetoxy group are *trans*. The two acetoxy groups C(2) and C(3) are *trans* diaxial. The dihedral angle between H(2) and H(3) is 81.6°. Apparently, in solution, senepoxide adopts a similar conformation since the observed coupling constant $J_{2,3}$ in its NMR spectrum is small (2.5 Hz).

The cyclohexene ring adopts a 1-3 diplanar conformation, the torsion angle along the C(4)-C(5) bond being 0.9° while that of C(6)-C(1) is 1.5°. But

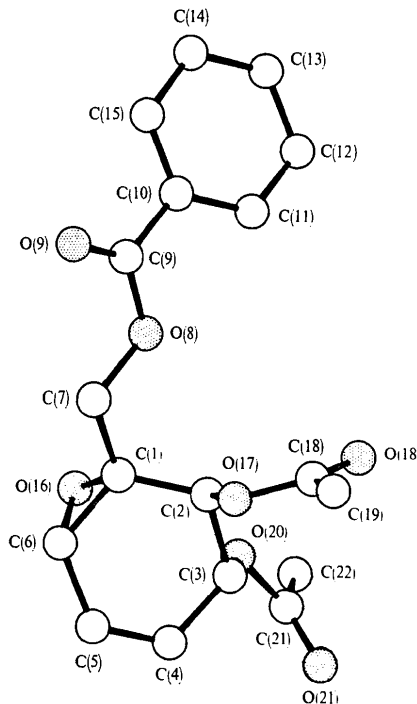
* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31599 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Intramolecular distances (Å)

| E.s.d.'s are in parentheses. | | | |
|------------------------------|-----------|-------------|-----------|
| C(1)-C(2) | 1.497 (5) | C(9)-C(10) | 1.470 (5) |
| C(1)-C(6) | 1.471 (5) | C(10)-C(11) | 1.399 (5) |
| C(1)-C(7) | 1.503 (5) | C(10)-C(15) | 1.378 (5) |
| C(1)-O(16) | 1.438 (4) | C(11)-C(12) | 1.377 (5) |
| C(2)-C(3) | 1.527 (4) | C(12)-C(13) | 1.393 (6) |
| C(2)-O(17) | 1.445 (4) | C(13)-C(14) | 1.384 (7) |
| C(3)-C(4) | 1.489 (5) | C(14)-C(15) | 1.378 (6) |
| C(3)-O(20) | 1.453 (4) | O(17)-C(18) | 1.348 (5) |
| C(4)-C(5) | 1.323 (6) | C(18)-O(18) | 1.181 (6) |
| C(5)-C(6) | 1.460 (5) | C(18)-C(19) | 1.504 (7) |
| C(6)-O(16) | 1.466 (5) | O(20)-C(21) | 1.344 (5) |
| C(7)-O(8) | 1.436 (5) | C(21)-O(21) | 1.198 (5) |
| O(8)-C(9) | 1.342 (4) | C(21)-C(22) | 1.511 (7) |
| C(9)-O(9) | 1.200 (5) | | |

Table 4. Bond angles (°)

| | | | |
|-----------------|-----------|-------------------|-----------|
| C(2)-C(1)-C(6) | 118.1 (3) | O(8)-C(9)-C(10) | 111.7 (3) |
| C(2)-C(1)-C(7) | 117.7 (3) | O(9)-C(9)-C(10) | 125.4 (3) |
| C(2)-C(1)-O(16) | 113.4 (3) | C(9)-C(10)-C(11) | 122.3 (3) |
| C(6)-C(1)-C(7) | 118.3 (3) | C(9)-C(10)-C(15) | 118.2 (3) |
| C(6)-C(1)-O(16) | 60.5 (2) | C(11)-C(10)-C(15) | 119.5 (3) |
| C(7)-C(1)-O(16) | 115.7 (3) | C(10)-C(11)-C(12) | 120.9 (3) |
| C(1)-C(2)-C(3) | 116.3 (3) | C(11)-C(12)-C(13) | 118.6 (4) |
| C(1)-C(2)-O(17) | 104.5 (3) | C(12)-C(13)-C(14) | 120.8 (4) |
| C(3)-C(2)-O(17) | 108.1 (3) | C(13)-C(14)-C(15) | 119.9 (4) |
| C(2)-C(3)-C(4) | 113.8 (3) | C(10)-C(15)-C(14) | 120.2 (4) |
| C(2)-C(3)-O(20) | 105.9 (3) | C(1)-O(16)-C(6) | 60.8 (2) |
| C(4)-C(3)-O(20) | 111.0 (3) | C(2)-O(17)-C(18) | 116.0 (3) |
| C(3)-C(4)-C(5) | 122.4 (4) | O(17)-C(18)-O(18) | 123.5 (4) |
| C(4)-C(5)-C(6) | 122.8 (4) | O(17)-C(18)-C(19) | 109.3 (4) |
| C(1)-C(6)-C(5) | 118.3 (3) | O(18)-C(18)-C(19) | 127.2 (4) |
| C(1)-C(6)-O(16) | 58.6 (2) | C(3)-O(20)-C(21) | 117.2 (3) |
| C(5)-C(6)-O(16) | 115.3 (3) | O(20)-C(21)-O(21) | 122.7 (4) |
| C(1)-C(7)-O(8) | 105.9 (3) | O(20)-C(21)-C(22) | 110.9 (4) |
| C(7)-O(8)-C(9) | 115.7 (3) | O(21)-C(21)-C(22) | 126.3 (4) |
| O(8)-C(9)-O(9) | 122.9 (3) | | |

Fig. 1. *ORTEP* drawing of the senepoxide molecule.

it is very much flattened with respect to an unsubstituted 1-3 diplanar cyclohexene, the mean distance of all 6 atoms to the mean plane being 0.11 Å.

The bond distances are in good agreement with those found in the structure of crotepoixide (Coggon, McPhail & Sim, 1969).

The epoxide ring is inclined at 103° to the C(5)-C(6)-C(1)-C(2) plane. The two acetyl groups are planar within experimental error, but twisted around their bond to the benzene ring; the dihedral angle H(2)-C(2)-O(17)-C(18) is -34° and H(3)-C(3)-O(20)-C(21) is +39°.

The benzene ring makes an angle of 22° with C(9)-C(10) and is inclined at 29° to the cyclohexene ring mean plane.

The closest intermolecular distances are 3.18 Å for O(8)⋯O(21) and 3.14 Å for C(9)⋯O(21). The other distances for intermolecular contacts correspond to normal van der Waals interactions.

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Tris-(*p*-methoxyphenyl)chloromethane

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Abstract. C₂₂H₂₁O₃Cl, monoclinic, *P*2₁/*c*; *a* = 14.912 (8), *b* = 10.303 (4), *c* = 12.489 (4) Å, β = 98.27 (6)°; *Z* = 4, *D_m* = 1.300, *D_x* = 1.304 g cm⁻³. The structure was refined to an *R* of 0.08. The molecule has the expected propeller geometry with the restriction that one methoxyl group is oriented contrariwise to the other two.

Introduction. The title compound (Schuchardt, Munich) forms colourless elongated prisms by slow evaporation of a benzene/petroleum ether solution in a flow of dry nitrogen. The lattice parameters and the intensities were measured at room temperature on an automatic four-circle Philips PW1100 diffractometer with graphite-monochromatized Mo *K*α radiation (λ = 0.7107 Å). With a crystal, 0.10 × 0.21 × 0.20 mm, sealed in a Lindemann capillary, 1338 independent reflexions were scanned in the θ-2θ mode (scan width 1.2° in 2θ; scan speed 0.02° s⁻¹) out to a limit of sin θ/λ ≤ 0.55. The background was measured on each side of the peaks with a counting time of half the reflexion scan time. Three monitor reflexions were measured at intervals of 15 reflexions; no significant change in intensity was revealed. After the usual corrections, 862 reflexions with |*F_o*| > 2σ(*F_o*) were considered observed and used in the structure analysis. Absorption corrections

(μ = 2.28 cm⁻¹) were not applied. The structure was solved by the heavy-atom method and refined by full-matrix least squares with anisotropic temperature factors for the non-hydrogen atoms. All the H atoms could be seen on a difference map, but some of the maxima were too diffuse for a precise coordinate determination. Fortunately at least one peak around each methyl group had a high enough density for a satisfactory coordinate assignment. This was sufficient to define the orientation of all the methyl groups, assuming tetrahedral symmetry for the C atoms. The calculated positions of the H atoms (Table 2) with C-H length 1.09 Å were included in the latter stages of the refinement, but were not refined. All the observed reflexions were included in each cycle; the final *R* was 0.08 with the weighting scheme: *w* = 0.053|*F_o*| for |*F_o*| ≤ 13.0, *w* = 1.0 for 13.0 < |*F_o*| ≤ 64.0, and *w* = 75|*F_o*|⁻¹ for |*F_o*| > 64.0. The final atomic parameters are listed in Tables 1 and 2.* The atom numbering is as follows (the first digit of the two digit numbers refers to the phenyl ring):

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31647 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.