

die gegenseitige Überlappung der Bänder ist analog dem vergleichbaren Packungsmotiv in der α -Modifikation (Gieren & Lamm, 1982). Eine weitere Analogie in der Packung der α - und β -Modifikation als auch zur Kristallstruktur des TTF-Komplexes (Gieren, Lamm, Hübner, Rabben, Neidlein & Droste, 1984) besteht in der Bildung zentrosymmetrischer Paare mit mehr oder minder stark überlappenden Molekülteilen, wobei bedingt durch die Symmetriezentren sich die Moleküle der Paare Kopf-Schwanz überlagern. Aus den in Fig. 1 dargestellten beiden Bändern kann man zwei Typen solcher Kopf-Schwanz-Paare herausgreifen, die analog im 1. Schichttyp der α -Modifikation vorkommen. Auch in den Schichten vom 2. Typ der α -Modifikation und im TTF-Komplex kommen zentrosymmetrische Kopf-Schwanz-Paare von CHIN vor, bei denen sich die einzelnen Moleküle aber wesentlich stärker überlappen. Die Ausbildung der Bänder führt offensichtlich zu einer Reduzierung der Molekülüberlappung.

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Structural Studies of Colchicine Derivatives. III. Structure of 7-Deacetamidocolchicine, $C_{19}H_{20}O_5$

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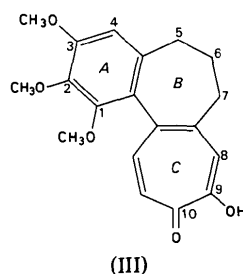
Abstract. $M_r = 328.37$, triclinic, $P\bar{1}$, $a = 14.462$ (3), $b = 8.185$ (2), $c = 7.864$ (2) Å, $\alpha = 62.50$ (3), $\beta = 82.18$ (3), $\gamma = 78.34$ (3)°, $V = 808$ (6) Å³, $Z = 2$, $D_m = 1.34$ (2), $D_x = 1.35$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 7.620$ cm⁻¹, $F(000) = 348$, $T = 293$ K. Final $R = 0.060$ for 2170 unique reflections. The troponoid ring exhibits an arrangement corresponding to an isocolchicine-like structure. The benzene ring is almost planar while the troponoid ring has a skew-boat conformation and the other seven-membered ring a

boat conformation. There is a possible intermolecular hydrogen bond between the O= and OH- groups on the troponoid ring but no other short intermolecular distances exist.

Introduction. In our laboratories we are engaged in a systematic study of colchicine derivatives. The crystal structures of colchicine acetate (Miravittles, Solans, Bladé-Font, Germain & Declercq, 1982), colchicine *O,N*-diacetate (Busetta, Leroy, Hospital, Elguero & Bladé-Font, 1979) and acetyl anhydrocolchicine (Miravittles, Rius, Bladé-Font & Germain, 1983) have

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been recently determined. Bladé-Font (1977a,b, 1978, 1979) has synthesized the title compound (III) among the other new derivatives of colchicine.



In the relationship between the molecular geometry of colchicine derivatives and their biological activity (antimitotics) (Rösner *et al.*, 1981; Santavý, 1979), the arrangement of the oxygen substituents on the tropolonic ring may be relevant. In this respect, contrary to previous ideas, colchicine (Silverton, 1979) has been found to exist in the solid state in the colchicine form (I), but 7-oxodeacetamidocolchicine exists as an unusual 3:2 mixture of the possible tautomers (Iorio, Brossi & Silverton, 1978). Now, the results of the present work indicate that the simpler derivative, 7-deacetamidocolchicine, belongs to the isocolchicine series (II).

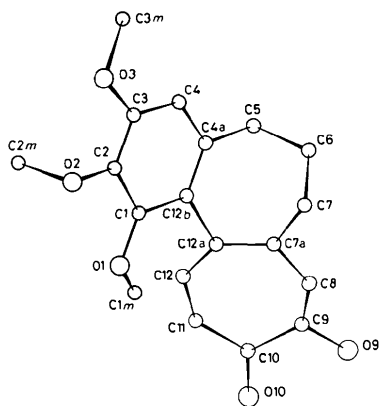
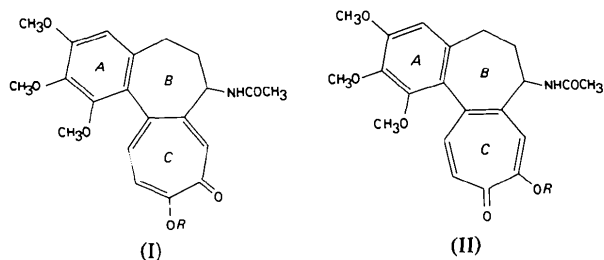


Fig. 1. View of the molecule with the atom numbering.

Table 1. Fractional atomic coordinates ($\times 10^4$) with *e.s.d.*'s in parentheses and equivalent isotropic temperature factors

| | x | y | z | $B_{\text{eq}}^*(\text{Å}^2)$ |
|--------|----------|-----------|-----------|-------------------------------|
| C(1) | 1896 (2) | 4195 (4) | 3156 (4) | 2.8 |
| C(1m) | 2781 (2) | 5202 (6) | 4692 (6) | 5.4 |
| C(2) | 1356 (2) | 5770 (4) | 1817 (5) | 2.9 |
| C(2m) | 080 (2) | 7700 (5) | 2527 (6) | 5.0 |
| C(3) | 1177 (2) | 5834 (4) | 93 (5) | 3.1 |
| C(3m) | 456 (3) | 7563 (5) | -2941 (5) | 4.6 |
| C(4) | 1507 (2) | 4301 (4) | -270 (4) | 3.2 |
| C(4a) | 2036 (2) | 2711 (4) | 1083 (4) | 3.0 |
| C(5) | 2395 (2) | 1070 (5) | 634 (5) | 3.8 |
| C(6) | 3457 (2) | 876 (5) | 147 (5) | 4.3 |
| C(7) | 3990 (2) | 1297 (5) | 1422 (5) | 3.4 |
| C(7a) | 3695 (2) | 258 (4) | 3520 (4) | 3.0 |
| C(8) | 4322 (2) | -1398 (5) | 4586 (5) | 3.8 |
| C(9) | 4346 (2) | -2627 (5) | 6477 (5) | 3.9 |
| C(10) | 3721 (2) | -2612 (4) | 8072 (5) | 3.4 |
| C(11) | 2839 (2) | -1342 (4) | 7755 (5) | 3.1 |
| C(12) | 2484 (2) | 136 (4) | 6131 (5) | 2.9 |
| C(12a) | 2851 (2) | 944 (4) | 4209 (4) | 2.7 |
| C(12b) | 2247 (2) | 2641 (4) | 2792 (4) | 2.6 |
| O(1) | 2065 (1) | 4157 (3) | 4855 (3) | 3.3 |
| O(2) | 1071 (1) | 7305 (3) | 2165 (3) | 3.9 |
| O(3) | 670 (1) | 7454 (3) | -1153 (3) | 3.6 |
| O(9) | 5074 (2) | -4066 (4) | 7009 (4) | 5.6 |
| O(10) | 3948 (1) | -3779 (3) | 9735 (3) | 4.4 |

$$* B_{\text{eq}} = \frac{1}{3} \pi^2 \sum_i U_{ij} a_i^* a_j^* a_i \cdot a_j$$

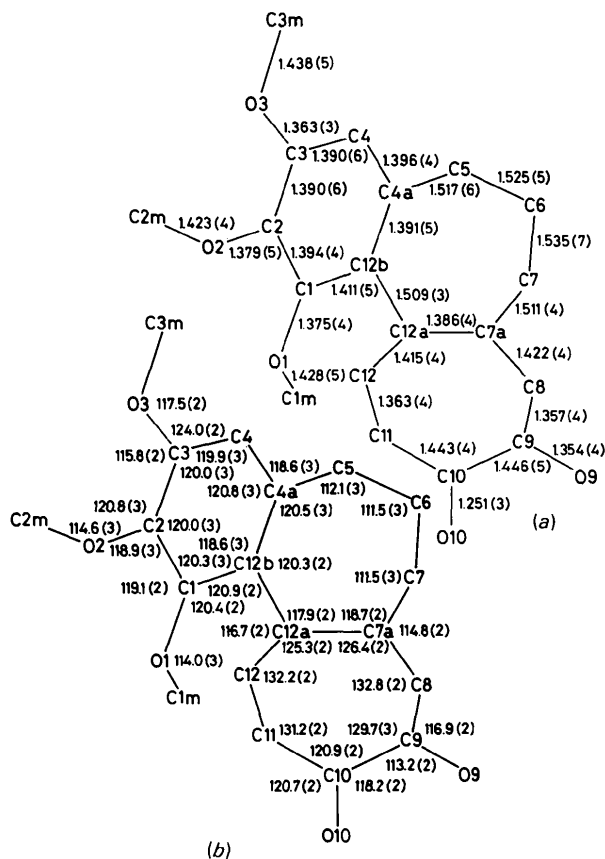


Fig. 2. (a) Bond lengths (Å), (b) bond angles ($^\circ$).

Table 2. Selected torsion angles ($^{\circ}$)

| E.s.d.'s are in the range 0.3–0.4 $^{\circ}$. | | | | | |
|--|--------|---------------------------|------|--------------------------|-------|
| C(2)–C(1)–O(1)–C(1m) | –77.8 | C(7)–C(7a)–C(12a)–C(12b) | 3.2 | C(10)–C(11)–C(12)–C(12a) | –0.4 |
| C(1)–C(2)–O(2)–C(2m) | –112.3 | C(7a)–C(12a)–C(12b)–C(4a) | 49.1 | C(11)–C(12)–C(12a)–C(7a) | 4.5 |
| C(4)–C(3)–O(3)–C(3m) | 0.8 | C(12a)–C(12b)–C(4a)–C(5) | 1.1 | C(12)–C(12a)–C(7a)–C(8) | 2.4 |
| C(12b)–C(4a)–C(5)–C(6) | –72.2 | C(12a)–C(7a)–C(8)–C(9) | –7.0 | C(4)–C(4a)–C(5)–C(6) | 106.6 |
| C(4a)–C(5)–C(6)–C(7) | 39.0 | C(7a)–C(8)–C(9)–C(10) | –1.3 | C(12)–C(12a)–C(12b)–C(1) | 52.6 |
| C(5)–C(6)–C(7)–C(7a) | 48.6 | C(8)–C(9)–C(10)–C(11) | 11.2 | O(9)–C(9)–C(10)–O(10) | 6.0 |
| C(6)–C(7)–C(7a)–C(12a) | –78.6 | C(9)–C(10)–C(11)–C(12) | –9.7 | | |

Experimental. Title compound obtained according to previously reported methods (Van Tamelen, Spencer, Allen & Orvis, 1961). Pale-greenish crystal obtained by evaporation at room temperature, 0.2 mm edges. Syntex four-circle diffractometer, graphite-monochromatized $\text{Cu K}\alpha$ radiation. Unit-cell parameters by least squares from 15 reflections with θ between 35 and 65 $^{\circ}$. No systematic absences: 2170 unique reflections collected, $(\sin\theta/\lambda)_{\text{max}} = 0.544 \text{ \AA}^{-1}$, range of hkl : $-15 < h < 15$, $-7 < k < 8$, $0 < l < 8$; for weak intensities, *i.e.* $I < \sigma(I)$, the most probable intensity was assumed to be $I = [I + \sigma(I)]/2$. One standard reflection measured after every 50 reflections, no systematic or significant variation. Lorentz and polarization but no absorption correction. Straightforward option of MULTAN11/82 direct-methods program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) furnished 14 C atoms; others determined using phases calculated by Karle recycling. Refinement on F carried out using a local version of CRYSTAN (Burzlaff, Böhme & Gomm, 1977). Isotropic and anisotropic block-matrix least-squares refinement without H atoms except in final cycle. Only one H atom [H(91)] could not be located using difference Fourier synthesis. Final $R = 0.060$, $wR = 0.050$ with $w = 1/\sigma^2(F_o)$ [$\sigma(F_o)$ derived from counting statistics], $S = 1.54$. $(\Delta/\sigma)_{\text{max}} = 0.60$. Max. and min. height in final difference F synthesis 0.26 and -0.21 e \AA^{-3} . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1; * Fig. 1 shows a view of the molecule with the numbering system. The chemical structure of 7-deacetamidocolchicine as defined by the X-ray crystallographic results corresponds to scheme (III).

The bond lengths and angles are shown in Fig. 2. The benzene ring is nearly planar $\{\chi^2 = 44.2 [= \sum(\delta/\sigma)^2]$, r.m.s.d. = 0.008 (6) \AA , $\delta_{\text{max}} = 0.012 \text{ \AA}$ for C(2) and C(3)}.

* Lists of anisotropic thermal parameters, structure factors and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39154 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The methoxy group C(3m)–O(3)–C(3) is approximately contained in the plane of ring *A* [1.4 (3) $^{\circ}$], while the other two, C(2)–O(2)–C(2m) and C(1)–O(1)–C(1m), form dihedral angles of 110.0 (3) and 103.4 (3) $^{\circ}$ respectively with ring *A*, pointing in opposite directions.

The conformation of ring *B* is similar to that found in other colchicine derivatives as shown by the sum of the torsion angles of this ring (Table 2): colchicine = 305, isocolchicine = 300, colchicine acetate = 291, colchicine = 296 and 7-deacetamidocolchicine = 292 $^{\circ}$.

The troponoid ring *C* exhibits a definite bond-length alternation with an arrangement corresponding to an isocolchicine-like structure (II). The torsion angles of this ring define a skew-boat conformation with the carbonyl at the prow of the boat as in colchicine acetate [r.m.s.d. of the plane = 0.045 (12) \AA , $\delta_{\text{max}} = 0.079 \text{ \AA}$ for C(10)].

The overall shape of this molecule is characterized by the angles between the normals to the three rings [$A-B = 40.2$ (4), $B-C = 38.1$ (4), $A-C = 48.6$ (4) $^{\circ}$] as well as by the twisting between ring *A* and ring *C* given by the torsion angle C(12)–C(12a)–C(12b)–C(1) = 52.6 (4) $^{\circ}$.

The crystal structure probably contains an intermolecular hydrogen bond O(9)···O(10)' = 2.733 (4) \AA . No other short intermolecular distances below 3.20 \AA are found.

From our results and those published by other authors (Silverton, 1979; Iorio, Brossi & Silverton, 1978; Margulis, 1982) it seems that the absence of any substitution at position 7 in colchicine derivatives may favour, in the solid state, the isocolchicine-like arrangement of the oxygen substituents on the troponoid ring *C*.

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9-Methylthioxanthenium-10-bis(methoxycarbonyl)methylide 10-Oxide, C₁₉H₁₈O₅S

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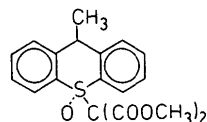
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Abstract. $M_r = 358.42$, $P\bar{1}$, $a = 15.159(3)$, $b = 8.672(2)$, $c = 7.178(1)$ Å, $\alpha = 93.80(2)$, $\beta = 101.12(2)$, $\gamma = 104.91(2)^\circ$, $V = 888.0(3)$ Å³, $Z = 2$, $D_x = 1.340$ g cm⁻³, $\text{Cu } K\alpha$, $\lambda = 1.54178$ Å, $\mu = 18.08$ cm⁻¹, $F(000) = 376$, room temperature, $R = 0.051$ for 2016 unique reflections. The $^+S-C^-$ distance of 1.689(3) Å in the title oxysulfonium ylide is shorter than the average $^+S-C^-$ distance of 1.718(8) Å observed for a series of sulfonium ylides. The two $^+S-C(sp^2)$ distances are 1.760(4) and 1.768(4) Å while the ^+S-O distance is 1.445(3) Å. The central ring in the tricyclic system is in a boat conformation with the methyl and carbanion moieties occupying axial sites. The C(17) carbanion carbon atom is 0.11(1) Å out of the plane of the attached atoms and toward the C(15) methyl group. An intramolecular interaction between the π cloud of the carbanion and the methyl hydrogen, $C(17)\cdots H(15b) = 2.56$ Å, may lead to a slight pyramidalization of C(17).

Introduction. Although the chemistry of organosulfur compounds has been of interest for many years, there still remains some controversy concerning the nature of the sulfur bonding (Bernardi, Csizmadia, Mangini, Schlegel, Whangbo & Wolfe, 1975; Minyav, Minkin, Sadikov & Naddaka, 1977; Tatsumi, Yoshioka, Yamaguchi & Fueno, 1976). Ylides derived from organosulfur compounds have added to the controversy (Block, 1981; Trost & Melvin, 1975; Borden, Davidson, Anderson, Denniston & Epiotis, 1978). In most

hypervalent compounds d orbitals need not be invoked to rationalize molecular geometry and bonding; however, many theoretical calculations include some d -orbital participation in order to correlate more accurately specific physical properties. When the sulfur atom possess a formal positive charge, the $3d$ orbitals are contracted and should provide a better opportunity for overlap with the s and p orbitals of second- and third-row elements. Sulfonium ylides and oxysulfonium ylides can be viewed as carbanions stabilized by an adjacent positively charged sulfur atom. These systems should provide the best opportunity for observing any effects of d -orbital participation. Recent structural studies of sulfonium ylides (Abbady, Craig, Ternay, Martin, Galloy & Watson, 1981; Abbady, Askari, Morgan, Ternay, Galloy & Watson, 1982; Galloy, Watson, Craig, Guidry, Ternay & Martin, 1983) did not require the inclusion of d orbitals although such interactions were not symmetry forbidden. We now present a structural investigation of an oxysulfonium ylide.



Experimental. Crystal $0.12 \times 0.17 \times 0.51$ mm, Syntex $P2_1$ diffractometer, data collected using $\theta:2\theta$ scan, $2\theta_{\max} = 115.0^\circ$, graphite-monochromated radiation, lattice parameters from least-squares refinement of 15 medium-angle reflections, angles measured by centering

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