C(1)—C(1) bond, 1·438 (2) Å, and the C(2)—C(10) bond, 1·465 (2) Å, are shortened (compared to the sum of single-bond covalent radii for carbon, 1·544 Å, Pauling, 1960). Likewise, in (2), the C(1)—C(1) bond, 1·446 (2) Å, and the C(2)—C(11) bond, 1·477 (2) Å, are shortened; and in (3), the C(1)—C(1) bond, 1·454 (4) Å, and the C(2)—C(12) bond, 1·481 (4) Å, are shortened. There is, however, only a slight lengthening of the C(1)—C(2) double bond: in (1), 1·345 (2) Å; in (2), 1·353 Å; and in (3), 1·355 (4) Å (the sum of double-bond covalent radii for carbon is 1·334 Å).

In (1), the cyclopentene ring is planar within 0·008 Å. In (2), the cyclohexene ring is not planar, with C(4) 0·69 Å out of the plane of C(2), C(3), C(5), C(6) and C(11).

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# Structure of Dimethyl (1*S*,3*S*)-1-Methoxycarbonylmethyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indole-1,3-dicarboxylate at 165 K

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**Abstract.** $C_{18}H_{20}N_2O_6$, $M_r = 360{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}999\,(1)$, $b = 13{\cdot}693\,(1)$, $c = 10{\cdot}612\,(1)$ Å, $V = 1743{\cdot}6\,(2)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}37$ Mg m$^{-3}$, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}83$ mm$^{-1}$, $F(000) = 712$, $T = 165\,(1)$ K, $R = 0{\cdot}028$, $wR = 0{\cdot}033$ for 1362 observed reflections. The $CO_2Me$ and $CH_2CO_2Me$ groups attached to C(3) and C(5) are both equatorial and the $CO_2Me$ group at C(3) is axial. The six-membered heterocyclic ring is in a half-chair conformation. The crystal packing is determined by an intermolecular hydrogen bond between N(1) and O(52) [N···O = 2·857 (3) Å] and by several short contacts involving the carbonyl O atoms of the substituents at C(3) and C(5).

**Introduction.** The tetrahydro-β-carboline moiety occurs in many indole alkaloids, and the assignment of stereochemistry to these systems is often a crucial step in the structure elucidation of natural products of this type. The synthesis of these compounds also

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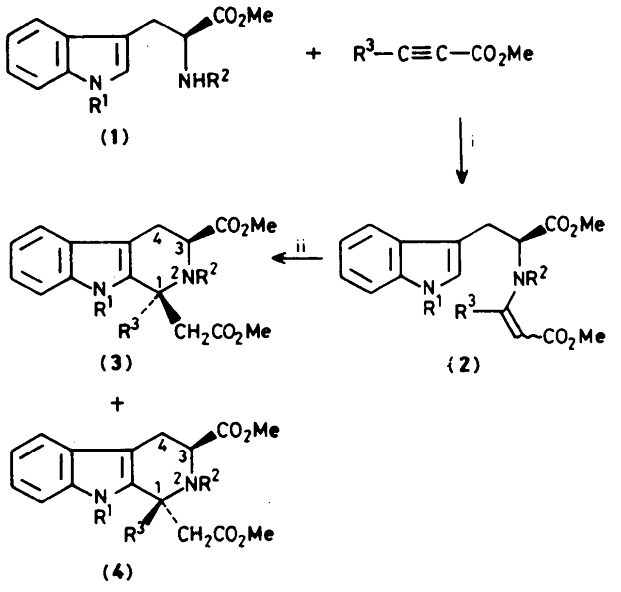
relies upon the determination of the stereochemistry of key intermediates, and spectroscopic methods often yield the required information.

Bailey, Hollinshead & Dauter (1985) showed that (*S*)-tryptophan methyl esters (1) react with conjugated alkynoates to produce 1,3-disubstituted or 1,1,3-trisubstituted tetrahydro-$\beta$-carbolines (3,4). These compounds are potential precursors to a range of bridged indole alkaloids, but NMR analysis ($^1H$ or $^{13}C$) fails to give unambiguous information about the stereochemistry of the trisubstituted derivatives. However, for the triester (4) ($R^1 = H$, $R^2 = H$, $R^3 = CO_2Me$) one of the diastereoisomers could be crystallized from ethanol, and its structure was initially reported at room temperature (Bailey *et al.*, 1985). We report here the refinement of this structure using intensity data collected at 165K.



$R^1$ = H or Me, $R^2$ = H or $CH_2Ph$, $R^3$ = H or $CO_2Me$

Scheme 1. Reagents: (i) $CHCl_3$, room temperature 1–10 d ($R^3$ = H) or 5–10 min ($R^3 = CO_2Me$); (ii) TFA (2·4 mol eq.), $CHCl_3$, room temperature, 5–10 min.

**Experimental.** Colourless needles (from ethanol) elongated along **b**, crystal 0·17 × 0·38 × 0·21 mm. Enraf–Nonius CAD-4 diffractometer, Ni-filtered Cu $K\alpha$ radiation; $\theta$–$2\theta$ scans; lattice parameters from 25 reflections with $43 < 2\theta < 60°$, Lp corrections, no absorption correction, $\theta_{max} = 57·5°$, $h$ −1 to 14, $k$ −1 to 15, $l$ 0 to 12; four standard reflections after every 96 data, variation ± 3%; intensity data measured and saved as profiles of 96 intervals for each scan; profile intensity data coverted into integrated net intensities (Blessing, 1986) and structure-factor amplitudes. 1767 data, 1385 unique ($R_{int} = 0·0178$), 1362 observed with $I > 2\sigma(I)$.

Table 1. *Final positional and equivalent isotropic temperature parameters for non-*H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| N(1) | 0·1659 (2) | 0·8575 (1) | 0·4500 (2) | 2·4 (1) |
| C(2) | 0·0823 (2) | 0·8360 (2) | 0·5340 (2) | 2·2 (1) |
| C(3) | 0·0451 (2) | 0·7335 (2) | 0·5674 (2) | 2·1 (1) |
| N(4) | −0·0626 (2) | 0·7418 (2) | 0·6308 (2) | 2·2 (1) |
| C(5) | −0·0719 (2) | 0·8181 (2) | 0·7270 (2) | 2·2 (1) |
| C(6) | −0·0634 (2) | 0·9192 (2) | 0·6659 (2) | 2·4 (1) |
| C(7) | 0·0337 (2) | 0·9192 (2) | 0·5775 (2) | 2·3 (1) |
| C(8) | 0·0883 (2) | 0·9992 (2) | 0·5148 (2) | 2·3 (1) |
| C(9) | 0·0746 (2) | 1·1012 (2) | 0·5163 (3) | 2·6 (1) |
| C(10) | 0·1402 (2) | 1·1563 (2) | 0·4363 (3) | 3·1 (1) |
| C(11) | 0·2180 (2) | 1·1137 (2) | 0·3566 (3) | 3·2 (1) |
| C(12) | 0·2348 (2) | 1·0138 (2) | 0·3546 (3) | 2·9 (1) |
| C(13) | 0·1695 (2) | 0·9580 (2) | 0·4348 (2) | 2·4 (1) |
| C(31) | 0·0297 (2) | 0·6730 (2) | 0·4455 (2) | 2·4 (1) |
| C(32) | −0·0007 (2) | 0·5689 (2) | 0·4717 (2) | 2·4 (1) |
| O(33) | −0·0145 (2) | 0·5352 (1) | 0·5733 (2) | 3·0 (1) |
| O(34) | −0·0117 (2) | 0·5177 (1) | 0·3656 (2) | 3·3 (1) |
| C(35) | −0·0514 (3) | 0·4180 (2) | 0·3815 (3) | 3·8 (1) |
| C(36) | 0·1335 (2) | 0·6863 (2) | 0·6528 (2) | 2·2 (1) |
| O(37) | 0·1241 (1) | 0·6760 (1) | 0·7644 (2) | 2·7 (1) |
| O(38) | 0·2248 (1) | 0·6608 (1) | 0·5888 (2) | 2·8 (1) |
| C(39) | 0·3139 (2) | 0·6216 (2) | 0·6645 (3) | 3·4 (1) |
| C(51) | −0·1823 (2) | 0·8073 (2) | 0·7909 (2) | 2·3 (1) |
| O(52) | −0·2548 (1) | 0·7510 (1) | 0·7618 (2) | 3·3 (1) |
| O(53) | −0·1934 (2) | 0·8706 (1) | 0·8859 (2) | 3·1 (1) |
| C(54) | −0·2994 (3) | 0·8688 (2) | 0·9499 (3) | 3·8 (1) |

The coordinates of the previously reported structure (Bailey *et al.*, 1985) were used as a starting point. Structure refined on $F$ by full-matrix least squares; $\sum w(|F_o| - |F_c|)^2$ minimized. Final refinement cycles included anisotropic thermal parameters for the non-H atoms. All 20 H atoms were located from a difference map and were refined with isotropic thermal factors. 315 parameters consisting of a scale factor, 138 positional, 150 anisotropic thermal factors, 20 isotropic thermal factors. $R$ = 0·028, $wR$ = 0·033, $S$ = 2·25 for 1362 observed data, $w = 1/\sigma^2(F_o)$, $(\Delta/\sigma)_{max} = \pm 0·1$; max. and min. heights in final difference Fourier synthesis ± 0·1 e Å$^{-3}$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Programs used include the data-reduction package *DREAM* (Blessing, 1987), a modified version of the Enraf–Nonius (1979) *SDP* refinement package and the plotting program *ARTIST* (Vallely, 1983).

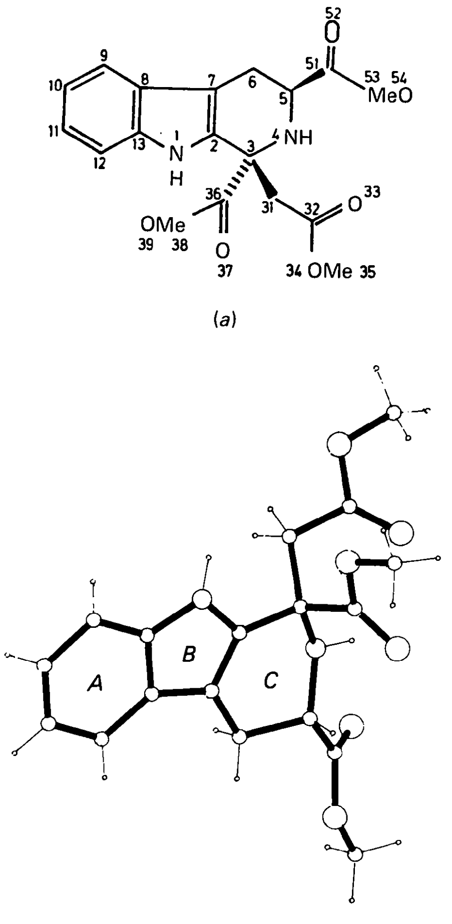
**Discussion.** The title compound was originally determined by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined with relatively poor room-temperature data to $R$ = 8·7% for 1077 reflections. These data gave a final model with an average $B_{eq}$ of 4·2 Å$^2$ (range 2·8 to 6·1 Å$^2$) and an average e.s.d. for bond lengths of 0·012 Å. Since X-ray studies on a series of related derivatives are planned, the diffraction data were recollected at 165 K and this has provided a more accurate description of the structure.

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* The atomic labelling scheme, stereochemistry and molecular structure are shown in Fig. 1. The heterocyclic ring *C* is in a half-chair conformation with C(5) 0·443 Å above and N(4) 0·285 Å below the least-squares plane defined by the other four atoms (r.m.s. deviation, $\sigma_C = 0{\cdot}002$ Å). Rings *A* and *B* are essentially planar ($\sigma_A = 0{\cdot}006$, $\sigma_B = 0{\cdot}008$ Å). The angle between planes *A* and *B* is 2·8°.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsional angles* (°)

| | | | |
|---|---|---|---|
| N(1)—C(2) | 1·373 (3) | C(9)—C(10) | 1·381 (4) |
| N(1)—C(13) | 1·387 (3) | C(10)—C(11) | 1·388 (4) |
| C(2)—C(3) | 1·516 (3) | C(11)—C(12) | 1·382 (3) |
| C(2)—C(7) | 1·360 (3) | C(12)—C(13) | 1·386 (3) |
| C(3)—N(4) | 1·462 (3) | C(31)—C(32) | 1·498 (3) |
| C(3)—C(31) | 1·546 (3) | C(32)—O(33) | 1·203 (3) |
| C(3)—C(36) | 1·538 (3) | C(32)—O(34) | 1·333 (3) |
| N(4)—C(5) | 1·465 (3) | O(34)—C(35) | 1·455 (3) |
| C(5)—C(6) | 1·532 (3) | C(36)—O(37) | 1·198 (3) |
| C(5)—C(51) | 1·496 (3) | C(36)—O(38) | 1·335 (3) |
| C(6)—C(7) | 1·496 (3) | O(38)—C(39) | 1·441 (3) |
| C(7)—C(8) | 1·439 (3) | C(51)—O(52) | 1·202 (3) |
| C(8)—C(9) | 1·406 (3) | C(51)—O(53) | 1·335 (3) |
| C(8)—C(13) | 1·409 (3) | O(53)—C(54) | 1·442 (4) |
| | | | |
| C(2)—N(1)—C(13) | 108·1 (1) | C(8)—C(9)—C(13) | 118·0 (2) |
| N(1)—C(2)—C(3) | 124·4 (2) | C(9)—C(10)—C(11) | 121·8 (2) |
| N(1)—C(2)—C(7) | 110·8 (2) | C(10)—C(11)—C(12) | 121·6 (2) |
| C(3)—C(2)—C(7) | 124·8 (2) | C(11)—C(12)—C(13) | 116·9 (2) |
| C(2)—C(3)—N(4) | 107·2 (2) | N(1)—C(13)—C(8) | 107·8 (2) |
| C(2)—C(3)—C(31) | 109·6 (2) | N(1)—C(13)—C(12) | 129·5 (2) |
| C(2)—C(3)—C(36) | 108·9 (2) | C(8)—C(13)—C(12) | 122·7 (2) |
| N(4)—C(3)—C(31) | 108·7 (2) | C(3)—C(31)—C(32) | 112·5 (2) |
| N(4)—C(3)—C(36) | 111·8 (2) | C(31)—C(32)—O(33) | 124·6 (2) |
| C(31)—C(3)—C(36) | 110·5 (2) | C(31)—C(32)—O(34) | 111·6 (2) |
| C(3)—N(4)—C(5) | 116·3 (2) | O(33)—C(32)—O(34) | 123·7 (2) |
| N(4)—C(5)—C(6) | 110·1 (2) | C(32)—O(34)—C(35) | 115·3 (2) |
| N(4)—C(5)—C(51) | 108·2 (2) | C(3)—C(36)—O(37) | 124·6 (2) |
| C(6)—C(5)—C(51) | 109·8 (2) | C(3)—C(36)—O(38) | 112·1 (2) |
| C(5)—C(6)—C(7) | 108·5 (2) | O(37)—C(36)—O(38) | 123·3 (2) |
| C(2)—C(7)—C(6) | 123·2 (2) | C(36)—O(38)—C(39) | 115·0 (2) |
| C(2)—C(7)—C(8) | 106·6 (2) | C(5)—C(51)—O(52) | 125·9 (2) |
| C(6)—C(7)—C(8) | 130·1 (2) | C(5)—C(51)—O(53) | 111·5 (2) |
| C(7)—C(8)—C(9) | 134·2 (2) | O(52)—C(51)—O(53) | 122·5 (2) |
| C(7)—C(8)—C(13) | 106·8 (2) | C(51)—O(53)—C(54) | 115·6 (2) |
| C(9)—C(8)—C(13) | 119·0 (2) | | |
| | | | |
| N(1)—C(2)—C(3)—C(31) | −46·9 (3) | C(3)—N(4)—C(5)—C(6) | 66·5 (2) |
| N(1)—C(2)—C(3)—C(36) | 74·1 (3) | C(3)—N(4)—C(5)—C(51) | −173·4 (2) |
| C(3)—C(2)—C(7)—C(6) | 0·6 (4) | N(4)—C(5)—C(6)—C(7) | −47·2 (2) |
| C(7)—C(2)—C(3)—N(4) | 11·4 (3) | C(5)—C(6)—C(7)—C(2) | 17·3 (2) |
| C(2)—C(3)—N(4)—C(5) | −44·9 (2) | C(5)—C(6)—C(7)—C(8) | −167·9 (2) |

The intramolecular dimensions involving the non-H atoms are listed in Table 2. The various types of bonds generally have lengths in good agreement with the expected values and with those found in other 1,2,3,4-tetrahydro-β-carbolines (Ungemach *et al.*, 1980; Codding, 1983). The carbonyl bond lengths C(32)—O(33), C(36)—O(37) and C(51)—O(52) are 1·203 (3), 1·198 (3) and 1·202 (3) Å, respectively, in the range normally observed in esters (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The N atom N(4) makes three short intramolecular contacts with the carbonyl O atoms O(33), O(37) and O(52) of each of the three substituents: N(4)—O(33) 2·947 (3), N(4)—O(37) 2·801 (3), and N(4)—O(52) 2·696 (3) Å. The shortest intramolecular contact involving N(1) is to O(38) at 3·150 (3) Å.



(*a*)

(*b*)

Fig. 1. (*a*) Structual formula and atom-labelling scheme. (*b*) Perspective view of the molecular structure.

The protonated N atom N(1) is involved in an intermolecular hydrogen bond with O(52) at (0·5 + *x*, 1·5 − *y*, 1·0 − *z*): N(1)···O(52) 2·857 (3), N(1)—H(1) 0·93 (3), O(52)···H(1) 2·01 (3) Å, N(1)—H(1)···O(52) 151 (2)°. There are also several significant intermolecular contacts which are important in the molecular packing: C(12)···O(33) (0·5 + *x*, 1·5 − *y*, 1·0 − *z*) 3·171 (3); O(37)···C(54) (0·5 + *x*, 1·5 − *y*, 2·0 − *z*) 3·226 (4); C(6)···O(33) (−*x*, 0·5 +

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52081 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$y$, 1·5 − $z$) 3·307 (3) and O(33)···O(53) (−$x$, −0·5 + $y$, 1·5 − $z$) 3·388 (2) Å.

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## Structure of $Mn_2SiS_4$

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**Abstract.** Manganese thiosilicate, $M_r$ = 266·22, orthorhombic, *Pnma*, $a$ = 12·688 (2), $b$ = 7·429 (2), $c$ = 5·942 (1) Å, $V$ = 560·1 (2) Å$^3$, $Z$ = 4, $D_x$ = 3·157 g cm$^{-3}$, λ(Mo $K\alpha$) = 0·71069 Å, $\mu$ = 57·86 cm$^{-1}$, $F$(000) = 512, $T$ = 298 K, $R$ = 0·041, $wR$ = 0·031 for 1734 unique reflections with $F_o > 4\sigma(F_o)$. $Mn_2SiS_4$ crystallizes in the olivine structure type. Mn—S bond lengths (octahedral coordination about Mn) are in the range 2·555 (1)–2·646 (1) Å, Si—S bond lengths (tetrahedral coordination about Si) 2·104 (2)–2·144 (1) Å. The mean bond distances in $Mn_2SiS_4$ agree well with values found in other thiosilicates.

**Experimental.** $Mn_2SiS_4$ crystals were grown by chemical transport using $I_2$ as transporting agent and MnS, Si and $S_8$ as starting materials. The reaction was carried out in sealed quartz ampoules at 923/873 K for two weeks. A dark-brown, transparent crystal, size 0·14 × 0.10 × 0·18 mm, was used for data collection on a Syntex $P2_1$ diffractometer operated in ω-scan mode (Mo $K\alpha$, graphite monochromator). Lattice constants were obtained from a least-squares fit of 15 reflections in the range $36 < 2\theta < 68°$. Two standard reflections, measured every 50 reflections, showed no significant change during data collection. 1919 reflections in the range $2 < 2\theta < 80°$, $0 \le h \le 22$, $0 \le k \le 13$, $0 \le l \le 9$ were measured and yielded 1734 unique reflections ($R_{\rm int}$ = 0·078), of which 1256 were considered as observed [$F_o > 4\sigma(F_o)$]. The data were corrected for Lorentz and polarization effects. A numerical absorption correction (transmission factors 0·5062 to 0·6200) with *SHELX76* (Sheldrick, 1976) was applied. Secondary-extinction effects were taken into account by refinement of an empirical extinction coefficient $X$ = 7·2 (2) × 10$^{-7}$, $F_o = F_o(1 - XF_o^2/\sin\theta)$. As starting set for the structure refinement, the coordinates of an earlier determination by Hardy, Perez & Serment (1965) were used, but yielded a rather high $R$ value

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