

## Structure of 8-Ethyl-4,10,12-trimethoxy-6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one

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**Abstract.** C<sub>22</sub>H<sub>20</sub>O<sub>5</sub>, *M<sub>r</sub>* = 364.40, triclinic, *P* $\bar{1}$ , *a* = 11.60 (1), *b* = 20.44 (2), *c* = 7.657 (6) Å,  $\alpha$  = 91.19 (8),  $\beta$  = 95.53 (8),  $\gamma$  = 89.55 (7)°, *V* = 1806 (3) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.340 g cm<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.71069 Å,  $\mu$  = 0.88 cm<sup>-1</sup>, *F*(000) = 768, *T* = 296 K, *R* = 0.051, 1594 unique observed reflections. This compound possesses a methoxy group at C-4 instead of a hydroxyl group at C-1 in the benzonaphthopyrone unit of antibiotic gilvocarcins. The primary stereochemical difference in the two chemically identical molecules present in the asymmetric cell is the ethyl group orientation, which is within the plane of the fused rings in the first molecule but is rotated nearly 90° out of plane in the second.

**Experimental.** A method similar to that reported previously (Hua, Saha, Maeng & Bensoussan, 1990) was followed in the preparation of the title compound. The compound, recrystallized from methanol, melted at 432–433 K. Crystal used for data collection 0.26 × 0.25 × 0.20 mm, yellow prism. Rigaku AFC5S diffractometer, graphite-monochromated Mo *K* $\alpha$  radiation,  $\omega$  scans, scan speed 6° min<sup>-1</sup> (in  $\omega$ ), weak reflections [*I* < 10.0 $\sigma$ (*I*)] rescanned (max. of 2 rescans) and the counts accumulated to assure good counting statistics. Lattice parameters‡ from least-squares fit of 25 strong reflections in 2 $\theta$  range 20–25°. A total of 6353 reflections measured (*h* 0 to 13, *k* -24 to 24, *l* -9 to 9), 4759 reflections considered unobserved with [*I* < 3 $\sigma$ (*I*)], data set comprised of 1594 unique reflections, *R*<sub>int</sub> (based on *F*<sup>2</sup>) = 0.043 (346 averaged reflections), ( $\sin\theta/\lambda$ )<sub>max</sub> = 0.60 Å<sup>-1</sup>. The percentage of observed reflections in the 0–40° 2 $\theta$  range was 43 but dropped sharply to 12.7 in the 40–45° shell and 5.3% in the

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

$$B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33} + 2U_{12}\cos\gamma + 2U_{13}\cos\beta + 2U_{23}\cos\alpha).$$

| Molecule 1 | <i>x</i>   | <i>y</i>    | <i>z</i>   | <i>B<sub>eq</sub></i> (Å <sup>2</sup> ) |
|------------|------------|-------------|------------|---|
| C(1)       | 0.875 (1)  | 0.7017 (5)  | 0.495 (1)  | 5.1 (6)                                 |
| C(2)       | 0.761 (1)  | 0.7156 (5)  | 0.446 (1)  | 5.3 (6)                                 |
| C(3)       | 0.677 (1)  | 0.6703 (6)  | 0.468 (1)  | 5.3 (6)                                 |
| C(4)       | 0.7037 (9) | 0.6108 (6)  | 0.541 (1)  | 4.8 (6)                                 |
| C(4a)      | 0.8225 (8) | 0.5934 (5)  | 0.593 (1)  | 4.0 (6)                                 |
| C(4b)      | 0.865 (1)  | 0.5329 (5)  | 0.667 (1)  | 4.0 (6)                                 |
| O(5)       | 0.7799 (6) | 0.4853 (4)  | 0.6744 (9) | 5.0 (4)                                 |
| C(6)       | 0.8020 (9) | 0.4250 (6)  | 0.741 (1)  | 5.0 (6)                                 |
| C(6a)      | 0.9227 (8) | 0.4099 (5)  | 0.806 (1)  | 4.2 (6)                                 |
| C(7)       | 0.9445 (8) | 0.3471 (5)  | 0.868 (1)  | 4.6 (6)                                 |
| C(8)       | 1.056 (1)  | 0.3297 (5)  | 0.934 (1)  | 4.8 (6)                                 |
| C(9)       | 1.1418 (9) | 0.3760 (6)  | 0.934 (1)  | 4.9 (6)                                 |
| C(10)      | 1.1204 (9) | 0.4367 (5)  | 0.868 (1)  | 4.2 (6)                                 |
| C(10a)     | 1.0078 (8) | 0.4576 (5)  | 0.798 (1)  | 4.0 (5)                                 |
| C(10b)     | 0.9782 (8) | 0.5205 (5)  | 0.721 (1)  | 3.7 (5)                                 |
| C(11)      | 1.0585 (8) | 0.5703 (5)  | 0.699 (1)  | 4.1 (5)                                 |
| C(12)      | 1.0253 (9) | 0.6286 (6)  | 0.628 (1)  | 4.6 (6)                                 |
| C(12a)     | 0.9079 (9) | 0.6410 (6)  | 0.571 (1)  | 4.2 (6)                                 |
| C(13)      | 1.088 (1)  | 0.2617 (6)  | 0.998 (1)  | 7.4 (7)                                 |
| C(14)      | 0.993 (1)  | 0.2171 (5)  | 1.026 (2)  | 9.6 (8)                                 |
| O(15)      | 0.6220 (6) | 0.5659 (3)  | 0.575 (1)  | 6.1 (4)                                 |
| C(16)      | 0.5035 (8) | 0.5845 (5)  | 0.534 (2)  | 7.7 (7)                                 |
| O(17)      | 0.7227 (6) | 0.3881 (4)  | 0.741 (1)  | 7.5 (5)                                 |
| O(18)      | 1.2049 (6) | 0.4837 (3)  | 0.8776 (9) | 6.1 (4)                                 |
| C(19)      | 1.3224 (8) | 0.4664 (5)  | 0.936 (1)  | 7.5 (7)                                 |
| O(20)      | 1.0982 (6) | 0.6783 (4)  | 0.605 (1)  | 6.6 (4)                                 |
| C(21)      | 1.214 (1)  | 0.6712 (6)  | 0.682 (2)  | 8.6 (8)                                 |
| Molecule 2 |            |             |            |   |
| C(22)      | 0.4308 (9) | -0.1853 (5) | 0.474 (1)  | 4.8 (6)                                 |
| C(23)      | 0.323 (1)  | -0.2055 (4) | 0.412 (1)  | 5.0 (6)                                 |
| C(24)      | 0.2270 (8) | -0.1664 (6) | 0.431 (1)  | 5.0 (6)                                 |
| C(25)      | 0.2377 (8) | -0.1051 (5) | 0.507 (1)  | 4.0 (6)                                 |
| C(25a)     | 0.3497 (7) | -0.0817 (4) | 0.578 (1)  | 3.0 (5)                                 |
| C(25b)     | 0.3722 (7) | -0.0202 (5) | 0.665 (1)  | 3.3 (5)                                 |
| O(26)      | 0.2770 (5) | 0.0206 (3)  | 0.6783 (8) | 4.2 (3)                                 |
| C(27)      | 0.2826 (8) | 0.0808 (5)  | 0.760 (1)  | 4.2 (6)                                 |
| C(27a)     | 0.3968 (8) | 0.1021 (5)  | 0.835 (1)  | 3.7 (5)                                 |
| C(28)      | 0.3990 (8) | 0.1634 (5)  | 0.917 (1)  | 4.4 (5)                                 |
| C(29)      | 0.4999 (9) | 0.1882 (5)  | 1.000 (1)  | 4.8 (6)                                 |
| C(30)      | 0.5993 (9) | 0.1494 (5)  | 0.999 (1)  | 4.7 (6)                                 |
| C(31)      | 0.5986 (8) | 0.0886 (5)  | 0.919 (1)  | 3.7 (5)                                 |
| C(31a)     | 0.4943 (8) | 0.0618 (5)  | 0.832 (1)  | 3.3 (5)                                 |
| C(31b)     | 0.4802 (8) | -0.0014 (4) | 0.741 (1)  | 3.4 (5)                                 |
| C(32)      | 0.5734 (7) | -0.0458 (5) | 0.717 (1)  | 3.9 (5)                                 |
| C(33)      | 0.5575 (8) | -0.1033 (5) | 0.631 (1)  | 4.0 (6)                                 |
| C(33a)     | 0.4464 (8) | -0.1235 (5) | 0.560 (1)  | 3.3 (5)                                 |
| C(34)      | 0.504 (1)  | 0.2552 (6)  | 1.091 (1)  | 8.3 (8)                                 |
| C(35)      | 0.513 (2)  | 0.3068 (6)  | 0.987 (2)  | 16 (1)                                  |
| O(36)      | 0.1458 (5) | -0.0649 (3) | 0.527 (1)  | 6.0 (4)                                 |
| C(37)      | 0.0341 (8) | -0.0904 (5) | 0.467 (2)  | 9.0 (8)                                 |
| O(38)      | 0.1929 (6) | 0.1111 (3)  | 0.760 (1)  | 7.1 (4)                                 |
| O(39)      | 0.6930 (5) | 0.0480 (3)  | 0.9257 (8) | 5.1 (4)                                 |
| C(40)      | 0.8034 (8) | 0.0733 (5)  | 0.993 (1)  | 7.3 (7)                                 |
| O(41)      | 0.6451 (5) | -0.1472 (3) | 0.6079 (8) | 5.3 (4)                                 |
| C(42)      | 0.7575 (8) | -0.1303 (5) | 0.689 (1)  | 6.3 (6)                                 |

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‡ The reduced triclinic cell is *a* = 7.657 (6), *b* = 11.60 (1), *c* = 20.44 (2) Å,  $\alpha$  = 89.55 (7),  $\beta$  = 88.81 (8),  $\gamma$  = 84.47 (8)°. The transformation matrix to the working cell is 001, -100, 0-10.

Table 2. Selected bond distances (Å), bond angles (°) and their e.s.d.'s

|       |        |        | Molecule 1 | Molecule 2* |        |        |        | Molecule 1 | Molecule 2* |
|-------|--------|--------|------------|-------------|--------|--------|--------|------------|-------------|
| C(1)  | C(2)   |        | 1.36 (1)   | 1.36 (1)    | C(7)   | C(8)   |        | 1.39 (1)   | 1.37 (1)    |
| C(1)  | C(12a) |        | 1.42 (1)   | 1.42 (1)    | C(8)   | C(9)   |        | 1.38 (1)   | 1.39 (1)    |
| C(2)  | C(3)   |        | 1.38 (1)   | 1.38 (1)    | C(8)   | C(13)  |        | 1.52 (1)   | 1.52 (1)    |
| C(3)  | C(4)   |        | 1.37 (1)   | 1.37 (1)    | C(9)   | C(10)  |        | 1.36 (1)   | 1.38 (1)    |
| C(4)  | C(4a)  |        | 1.44 (1)   | 1.44 (1)    | C(10)  | C(10a) |        | 1.43 (1)   | 1.43 (1)    |
| C(4)  | O(15)  |        | 1.37 (1)   | 1.36 (1)    | C(10)  | O(18)  |        | 1.37 (1)   | 1.366 (9)   |
| C(4a) | C(4b)  |        | 1.43 (1)   | 1.43 (1)    | C(10a) | C(10b) |        | 1.45 (1)   | 1.46 (1)    |
| C(4a) | C(12a) |        | 1.42 (1)   | 1.42 (1)    | C(10b) | C(11)  |        | 1.41 (1)   | 1.43 (1)    |
| C(4b) | O(5)   |        | 1.40 (1)   | 1.388 (9)   | C(11)  | C(12)  |        | 1.36 (1)   | 1.34 (1)    |
| C(4b) | C(10b) |        | 1.36 (1)   | 1.38 (1)    | C(12)  | C(12a) |        | 1.41 (1)   | 1.41 (1)    |
| O(5)  | C(6)   |        | 1.36 (1)   | 1.37 (1)    | C(12)  | O(20)  |        | 1.35 (1)   | 1.37 (1)    |
| C(6)  | C(6a)  |        | 1.47 (1)   | 1.46 (1)    | C(13)  | C(14)  |        | 1.47 (1)   | 1.34 (1)    |
| C(6)  | O(17)  |        | 1.19 (1)   | 1.21 (1)    | O(15)  | C(16)  |        | 1.43 (1)   | 1.43 (1)    |
| C(6a) | C(7)   |        | 1.39 (1)   | 1.39 (1)    | O(18)  | C(19)  |        | 1.44 (1)   | 1.43 (1)    |
| C(6a) | C(10a) |        | 1.40 (1)   | 1.40 (1)    | O(20)  | C(21)  |        | 1.43 (1)   | 1.43 (1)    |
| C(2)  | C(1)   | C(12a) | 121 (1)    | 120.2 (9)   | C(9)   | C(8)   | C(13)  | 119 (1)    | 121 (1)     |
| C(1)  | C(2)   | C(3)   | 120 (1)    | 120.9 (9)   | C(8)   | C(9)   | C(10)  | 121.9 (9)  | 122.3 (9)   |
| C(2)  | C(3)   | C(4)   | 121 (1)    | 121.3 (9)   | C(9)   | C(10)  | C(10a) | 123 (1)    | 121.1 (9)   |
| C(3)  | C(4)   | C(4a)  | 120 (1)    | 120.1 (9)   | C(9)   | C(10)  | O(18)  | 122 (1)    | 123.4 (9)   |
| C(3)  | C(4)   | O(15)  | 123 (1)    | 123.3 (9)   | C(10a) | C(10)  | O(18)  | 115 (1)    | 115.3 (9)   |
| C(4a) | C(4)   | O(15)  | 116 (1)    | 116.5 (9)   | C(6a)  | C(10a) | C(10)  | 113.4 (9)  | 115.0 (9)   |
| C(4)  | C(4a)  | C(4b)  | 127 (1)    | 125.8 (9)   | C(6a)  | C(10a) | C(10b) | 120.3 (9)  | 117.7 (8)   |
| C(4)  | C(4a)  | C(12a) | 117 (1)    | 117.3 (9)   | C(10)  | C(10a) | C(10b) | 126 (1)    | 127.3 (9)   |
| C(4b) | C(4a)  | C(12a) | 115.6 (9)  | 117.0 (8)   | C(4b)  | C(10b) | C(10a) | 118 (1)    | 119.9 (8)   |
| C(4a) | C(4b)  | O(5)   | 114 (1)    | 116.1 (8)   | C(4b)  | C(10b) | C(11)  | 117.2 (9)  | 116.0 (9)   |
| C(4a) | C(4b)  | C(10b) | 124 (1)    | 123.8 (8)   | C(10a) | C(10b) | C(11)  | 125 (1)    | 124.0 (9)   |
| O(5)  | C(4b)  | C(10b) | 121.4 (9)  | 120.0 (9)   | C(10b) | C(11)  | C(12)  | 122 (1)    | 122.5 (9)   |
| C(4b) | O(5)   | C(6)   | 123.4 (8)  | 123.9 (7)   | C(11)  | C(12)  | C(12a) | 121 (1)    | 121.4 (9)   |
| O(5)  | C(6)   | C(6a)  | 117 (1)    | 116.5 (9)   | C(11)  | C(12)  | O(20)  | 124 (1)    | 123.7 (9)   |
| O(5)  | C(6)   | O(17)  | 118 (1)    | 116.6 (9)   | C(12a) | C(12)  | O(20)  | 115 (1)    | 115 (1)     |
| C(6a) | C(6)   | O(17)  | 125 (1)    | 127 (1)     | C(1)   | C(12a) | C(4a)  | 119.7 (9)  | 120.1 (9)   |
| C(6)  | C(6a)  | C(7)   | 116 (1)    | 114.9 (9)   | C(1)   | C(12a) | C(12)  | 120 (1)    | 121 (1)     |
| C(6)  | C(6a)  | C(10a) | 119 (1)    | 121.8 (9)   | C(4a)  | C(12a) | C(12)  | 120 (1)    | 119.3 (9)   |
| C(7)  | C(6a)  | C(10)  | 124.1 (9)  | 123.2 (9)   | C(8)   | C(13)  | C(14)  | 118 (1)    | 116 (1)     |
| C(6a) | C(7)   | C(8)   | 119.7 (9)  | 121.0 (9)   | C(4)   | O(15)  | C(16)  | 116.7 (8)  | 116.1 (8)   |
| C(7)  | C(8)   | C(9)   | 118 (1)    | 117 (1)     | C(10)  | O(18)  | C(19)  | 119.6 (8)  | 118.9 (8)   |
| C(7)  | C(8)   | C(13)  | 123 (1)    | 122 (1)     | C(12)  | O(20)  | C(21)  | 116.6 (8)  | 116.4 (8)   |

\* Atom designators refer to molecule 1. This column lists comparable distances and angles for molecule 2.

45–50° shell. Three standard reflections ( $\bar{1}\bar{1}2$ ,  $\bar{1}12$ ,  $\bar{1}22$ ) changed by  $-0.6$ ,  $-0.7$  and  $-0.1\%$ , respectively; no decay correction applied. Data corrected for Lorentz and polarization, no absorption correction. The direct methods program *MITHRIL* (Gilmore, 1984) provided the locations of most of the fused-ring atoms although the presence of many false peaks led to considerable initial confusion. The remaining non-H atoms were found by reiterative least-squares/difference Fourier methods. Full-matrix least-squares refinement was performed to minimize  $\sum w(|F_o| - |F_c|)^2$  where  $w = 4F_o^2/\sigma^2(F_o^2)$  and  $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$  ( $S$  = scan rate,  $C$  = total integrated peak count,  $R$  = ratio of scan time to background counting time,  $B$  = total background count,  $Lp$  = Lorentz-polarization factor and  $p = 0.03$ ). After convergence methyl, methylene and phenyl H atoms were placed at assumed positions ( $C-H = 0.95$  Å), methyl-group orientations were determined on the basis of H-atom positions obtained from a difference Fourier synthesis, H-atom positions not refined. Final stages of refinement performed with 488 variables including all non-H positional and anisotropic thermal parameters, one scale factor, and a secondary-extinction coefficient ( $0.56910 \times 10^{-6}$ ). Convergence yielded  $R = 0.051$ ,  $wR = 0.052$ ,  $S = 1.57$  and  $(\Delta/\sigma)_{\max} = 0.03$ .

Final difference synthesis produced  $(\Delta\rho)_{\max} = 0.18$  and  $(\Delta\rho)_{\min} = -0.20 e \text{ \AA}^{-3}$ . Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71, 148). All computer programs from *TEXSAN* (Molecular Structure Corporation, 1985). Table 1\* lists the final atomic coordinates and equivalent isotropic temperature factors while Table 2 presents selected interatomic distances and angles. Fig. 1 shows the atom-numbering scheme and thermal motion of the two molecules and Fig. 2 illustrates the molecular packing. Least-squares-plane calculations show that C(35) is  $1.17$  Å out of the plane of the fused rings while its equivalent [C(14)] is within the planar array. Also, the unusually high thermal motion of C(35) may indicate some degree of disorder. These features may explain why this compound adopts triclinic symmetry with two chemically identical molecules in the asymmetric unit.

\* Lists of structure factors, H-atom parameters, anisotropic thermal parameters, intermolecular distances, torsion angles and selected least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54263 (50 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

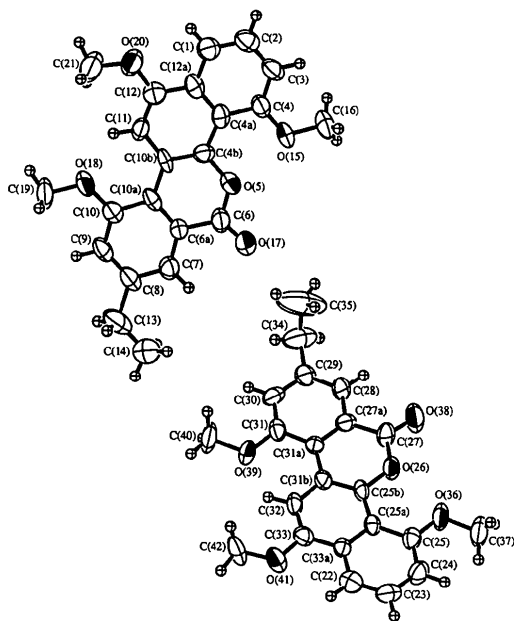


Fig. 1. Molecular configuration and atom-numbering scheme, thermal ellipsoids at the 50% probability level. H atoms are shown as isotropic spheres with  $B$ 's of 1.0 Å<sup>2</sup> and are unlabeled to improve clarity.

**Related literature.** The title compound was prepared as part of the studies of the synthesis of antibiotic gilvocarcins (Takahashi, Yoshida, Tomita & Shirahata, 1981). Despite many efforts with various kinds of NMR techniques including 2D NOESY (Homo-nuclear Nuclear Overhauser Effect correlated two dimensionally) experiments, we were unable to

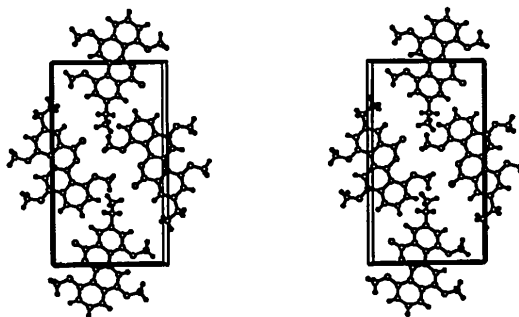


Fig. 2. Stereoscopic illustration of the molecular packing.  $b$  is vertical,  $a$  is horizontal and  $c$  is into the plane of the paper.

differentiate the title compound from its  $C$ -1 methoxy isomer, 8-ethyl-1,10,12-trimethoxy-6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one. This study allows us to characterize each isomer unequivocally. The structure of gilvocarcin M (possessing a  $C$ -1 hydroxy group) has been reported earlier (Hirayama, Takahashi, Shirahata, Ohashi & Sasada, 1981).

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## Structure of a Praziquantel Analogue\*

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**Abstract.** 2-(*m*-Nitrobenzoyl)-1,2,3,6,7,11*b*-hexahydro-4*H*-pyrazino[2,1-*a*]isoquinolin-4-one, C<sub>19</sub>H<sub>17</sub>N<sub>3</sub>O<sub>4</sub>,  $M_r = 351.4$ , monoclinic,  $P2_1/n$ ,  $a = 14.803$  (3),  $b = 7.991$  (1),  $c = 15.253$  (3) Å,  $\beta = 115.24$  (1)°,  $V = 1632.1$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.43$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha)$

$= 1.54178$  Å,  $\mu = 8.04$  cm<sup>-1</sup>,  $F(000) = 736$ ,  $T = 293$  K, final  $R = 0.038$  for 1821 unique observed reflections [ $F_o > 3\sigma(F_o)$ ]. The hydro-pyrazine ring adopts a half-chair conformation, while the tetrahydro-pyridine moiety has a sofa conformation with C(6) 0.66 Å out of the plane formed by C(7)—C(7*a*)—C(11*a*)—C(11*b*)—N(5). The nitrophenyl group is essentially planar [maximum deviation O(4)

\* Contribution No. 1066 of the Instituto de Química, UNAM.

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