

## Structure of 2-Methoxy Methyl $\beta$ -Orcinol Carboxylate (Methyl 4-Hydroxy-2-methoxy-3,6-dimethylbenzoate)

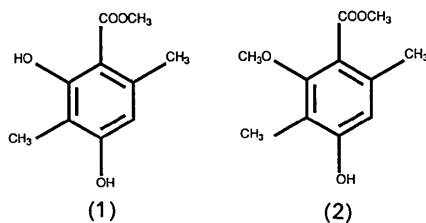
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**Abstract.**  $C_{11}H_{14}O_4$ ,  $M_r = 210.2$ , monoclinic,  $P2_1$ ,  $a = 7.931$  (1),  $b = 7.950$  (1),  $c = 8.929$  (1) Å,  $\beta = 102.81$  (1)°,  $V = 549.0$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m$  (floatation in KI/H<sub>2</sub>O) = 1.27,  $D_x = 1.272$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.09$  mm<sup>-1</sup>,  $F(000) = 224$ , room temperature,  $R = 0.040$ ,  $wR = 0.052$  for 1161 observed reflections. The phenyl ring is inclined to the carboxylate group by 71.7 (1)° and to the methoxy group by 75.3 (3)°, the latter two groups being inclined to one another by 53.4 (2)°. In the crystal, molecules related by the twofold screw axis are linked by a strong intermolecular hydrogen bond involving the 4-hydroxy substituent and the carboxylate carbonyl group.

**Experimental.** The title compound (2) is the 2-methoxy derivative of the natural product, methyl  $\beta$ -orcinol carboxylate (1) isolated from 'oak moss' *Evernia prunastri* (L.) Ach (Tabacchi & Nicollier, 1977), and was obtained by chemical transformation of (1). First the hydroxyl substituent *para* to the



carboxylate group was protected by benzylation. The hydroxyl group in the *ortho* position was then methylated using  $\text{CH}_3\text{I}$  in the presence of  $\text{K}_2\text{CO}_3$  and finally the protecting group was removed by hydrolysis (Gunzinger, 1985). Transparent block-like crystals were obtained by slow evaporation of a toluene/2-propanol ( $\approx 1/1$ ) solution. A crystal of dimensions  $0.38 \times 0.30 \times 0.27$  mm was used for data collection using a Stoe AED2 four-circle diffractometer with graphite-monochromated  $\text{Mo } K\alpha$  radiation.  $<2\%$  intensity variation for 5 standard reflections measured every hour. Accurate cell parameters from  $\pm\omega$  values of 20 reflections and

their equivalents in the range  $25 < 2\theta < 35^\circ$ . 2691 reflections were measured by the  $\omega/2\theta$  scan mode with  $\theta_{\text{max}} = 27.5^\circ$ , and index limits  $h - 10$  to  $10$ ,  $k - 10$  to  $10$ ,  $l 0$  to  $11$ . 1361 unique reflections,  $R_{\text{int}} = 0.026$ ; 1161 [ $I > 2.0\sigma(I)$ ] were considered observed and used for all further calculations. Systematic absences  $0k0$  when  $k$  odd. Space group  $P2_1$  or  $P2_1/m$ . The  $E$  statistics indicated a noncentrosymmetric arrangement and this was confirmed by the successful refinement. Structure solved using *SHELXS86* (Sheldrick, 1986). Refinement and all further calculations were carried out using the *NRCVAX* system (Gabe, Le Page, Charland & Lee, 1989). In order to fix the origin in space group  $P2_1$  the  $y$  coordinate of atom O(1) was held fixed. H atoms located from difference maps and refined isotropically. No attempt was made to determine the absolute structure of the crystal of (2) chosen. Weighted full-matrix least-squares refinement for 1107 reflections gave  $R = 0.040$  and  $wR = 0.052$ ; function minimized  $\sum w(|F_o| - |F_c|)^2$ ,  $w^{-1} = \sigma^2(F_o) + 0.001(F_o^2)$ . In the final cycle of refinement the maximum shift/ $\sigma$  ratio was 0.160. Residual density limits in final difference map  $+0.14$  and  $-0.18$  e Å<sup>-3</sup>. Neutral complex-atom scattering factors in *NRCVAX* from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final positional† and equivalent isotropic thermal parameters are given in Table 1 and interatomic distances and angles in Table 2. The numbering scheme is illustrated in Fig. 1.

**Related literature.** In the title compound (2) the orientation of the carboxylate group and the adjacent methoxy group with respect to the phenyl ring is very similar to that found in (*R,R,R*)-methyl 2,3-dimethoxy-4-hydroxy-5-iodo-6-methylbenzoate (Nicolau, Ebata, Stylianides, Groneberg & Carrol, 1988). The intermolecular hydrogen bonding involv-

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54809 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0508]

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Table 1. Atomic parameters  $x$ ,  $y$ ,  $z$  and  $B_{\text{iso}}$  values

|       | E.s.d.'s refer to the last digit printed. |            |            |                                  |
|-------|---|------------|------------|----------------------------------|
|       | $x$                                       | $y$        | $z$        | $B_{\text{iso}}^*(\text{\AA}^2)$ |
| O(1)  | 0.6623 (3)                                | 0.4171     | 0.6727 (2) | 4.92 (9)                         |
| O(2)  | 0.4723 (3)                                | 0.2218 (4) | 0.7017 (2) | 4.74 (8)                         |
| O(3)  | 0.5325 (2)                                | 0.3685 (4) | 1.0185 (2) | 3.96 (8)                         |
| O(4)  | 1.0236 (3)                                | 0.0825 (4) | 1.3094 (2) | 4.92 (9)                         |
| C(1)  | 0.7289 (3)                                | 0.2359 (4) | 0.8916 (3) | 3.10 (8)                         |
| C(2)  | 0.6787 (3)                                | 0.2708 (4) | 1.0283 (3) | 3.11 (9)                         |
| C(3)  | 0.7780 (3)                                | 0.2234 (4) | 1.1701 (3) | 3.37 (9)                         |
| C(4)  | 0.9281 (3)                                | 0.1314 (5) | 1.1701 (3) | 3.46 (9)                         |
| C(5)  | 0.9786 (3)                                | 0.0949 (5) | 1.0348 (3) | 3.45 (9)                         |
| C(6)  | 0.8819 (3)                                | 0.1485 (4) | 0.8931 (3) | 3.30 (9)                         |
| C(7)  | 0.6204 (3)                                | 0.3034 (5) | 0.7447 (3) | 3.33 (9)                         |
| C(8)  | 0.3530 (5)                                | 0.2827 (7) | 0.5661 (4) | 5.63 (16)                        |
| C(9)  | 0.9394 (5)                                | 0.1055 (6) | 0.7479 (4) | 5.16 (14)                        |
| C(10) | 0.7305 (5)                                | 0.2734 (6) | 1.3182 (4) | 4.83 (14)                        |
| C(11) | 0.3825 (4)                                | 0.2798 (6) | 1.0400 (5) | 5.13 (15)                        |

\*  $B_{\text{iso}}$  is the mean of the principal axes of the thermal ellipsoid.

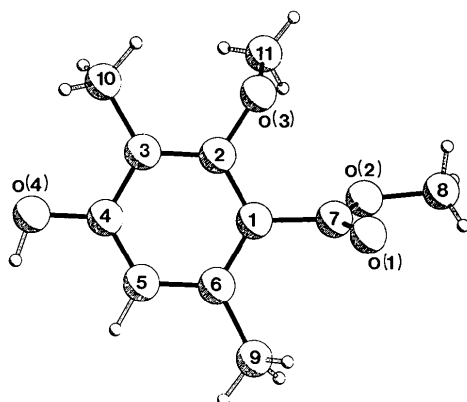


Fig. 1. PLUTO (Motherwell & Clegg, 1978) plot of (2) showing the numbering scheme.

ing the 4-hydroxy substituent and the carboxylate carbonyl group (see Table 2) is also similar to that found in the above-mentioned compound (Nicolaou *et al.*, 1988), and to that found in acetylcholine  $\beta$ -resorcyate (Jensen, 1975) and (1) (Brehm, Stoeckli-Evans, Tabacchi & Bürgi, 1983).

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## Structure of 6,7,8,9,10,11-Hexafluoro-2,4-diphenyl-3H-naphtho[2,1-*b*]azepine

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**Abstract.**  $\text{C}_{26}\text{H}_{13}\text{F}_6\text{N}$ ,  $M_r = 453.39$ , triclinic,  $P\bar{1}$ ,  $a = 13.59$  (1),  $b = 10.62$  (1),  $c = 7.59$  (1)  $\text{\AA}$ ,  $\alpha = 110.0$  (1),  $\beta = 106.2$  (1),  $\gamma = 91.4$  (1) $^\circ$ ,  $V = 979.74$   $\text{\AA}^3$ ,  $Z = 2$ ,

Table 2. Final distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

|                 |           |                    |           |
|-----------------|-----------|--------------------|-----------|
| O(1)—C(7)       | 1.197 (4) | C(1)—C(7)          | 1.500 (4) |
| O(2)—C(7)       | 1.322 (3) | C(2)—C(3)          | 1.387 (4) |
| O(2)—C(8)       | 1.445 (4) | C(3)—C(4)          | 1.397 (4) |
| O(3)—C(2)       | 1.382 (3) | C(3)—C(10)         | 1.507 (4) |
| O(3)—C(11)      | 1.432 (4) | C(4)—C(5)          | 1.385 (4) |
| O(4)—C(4)       | 1.361 (3) | C(5)—C(6)          | 1.393 (4) |
| C(1)—C(2)       | 1.393 (4) | C(6)—C(9)          | 1.506 (4) |
| C(1)—C(6)       | 1.396 (4) | O(4)—H(O4)         | 0.91 (6)  |
| O(4)···O(1')    | 2.790 (3) | O(1')···H(O4)      | 1.92 (6)  |
| C(7)—O(2)—C(8)  | 117.0 (3) | O(4)—C(4)—C(3)     | 116.8 (3) |
| C(2)—O(3)—C(11) | 115.2 (3) | O(4)—C(4)—C(5)     | 121.8 (3) |
| C(2)—C(1)—C(6)  | 120.5 (2) | C(3)—C(4)—C(5)     | 121.4 (2) |
| C(2)—C(1)—C(7)  | 118.3 (2) | C(4)—C(5)—C(6)     | 121.4 (3) |
| C(6)—C(1)—C(7)  | 121.0 (2) | C(1)—C(6)—C(5)     | 117.6 (2) |
| O(3)—C(2)—C(1)  | 117.1 (2) | C(1)—C(6)—C(9)     | 122.3 (2) |
| O(3)—C(2)—C(3)  | 120.6 (2) | C(5)—C(6)—C(9)     | 120.1 (3) |
| C(1)—C(2)—C(3)  | 122.0 (2) | O(1)—C(7)—O(2)     | 123.3 (3) |
| C(2)—C(3)—C(4)  | 117.0 (2) | O(1)—C(7)—C(1)     | 124.5 (2) |
| C(2)—C(3)—C(10) | 121.9 (3) | O(2)—C(7)—C(1)     | 112.3 (3) |
| C(4)—C(3)—C(10) | 121.1 (3) | O(4)—H(O4)···O(1') | 159 (5)   |

Symmetry operation: (i)  $2 - x, -0.5 + y, 2 - z$ .

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