82. The Crystal Structure of Methyl β-orcinol-carboxylate (= Methyl 2,4-dihydroxy-3,6-dimethylbenzoate)

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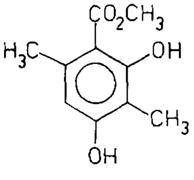
Summary

The mono-arylic compound, methyl β-orcinol-carboxylate (**I**) is one of the principal components of lichens which grow on the oak tree. In the crystal structure of **I** the molecules are H-bonded to form sheets separated by 3.56 (5) Å. The carbonyl O-atom of the ester group and the *ortho*-hydroxyl group form a strong intramolecular H-bond. The IR. spectrum of the solid contains two (O–H)-stretching frequencies which, by comparison with the spectra of the 4-methoxy and the 2-methoxy analogues, can be assigned to one intra- and one intermolecular H-bond.

Introduction. - The chemical composition of extracts of lichen growing on the oak tree, and known as "oakmoss", have been the subject of a number of studies [1]. The extracted materials are essentially depsides [2] which have high molecular weights, are involatile and hence not responsible for the odour of lichen. On hydrolysis or alcoholysis the depsides give mono-arylic compounds; in particular methyl β-orcinol-carboxylate which is highly smelling and believed to be responsible for the typical odour of oakmoss. It is also present in large quantities in the



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lichen itself. The solid state IR. spectrum of the title compound shows two (O–H)-stretching frequencies at 3400 cm^{-1} and 3080 cm^{-1}. By comparison with the IR. spectra of solid methyl 2-hydroxy-4-methoxy-3,6-dimethylbenzoate and solid methyl 2-methoxy-4-hydroxy-3,6-dimethylbenzoate [3], it was possible to assign them to one inter and one intramolecular H-bond, respectively.

Experimental Part. – The title compound was obtained by direct treatment of oakmoss from Yougoslavia (*Evernia prunastic* L. ACH.) [4]. Suitable crystals were grown from an acetonitrile solution. Crystal data: $C_{10}H_{12}O_4$, space group $P2_1/c$, $a = 7.104$ (3), $b = 18.261$ (6), $c = 7.352$ (2) Å, $\beta = 97.23$ (3)°, $V = 946.2$ Å^3, $D_x = 1.37$ Mg/m^3 (KI/H_2O), $Z = 4$, $D_c = 1.376$ Mg/m^3, Mo$K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.7$ cm^{-1}.

A crystal of size 0.3 × 0.4 × 0.4 mm was used for data collection. Preliminary *Weissenberg* and precession photographs indicated the crystal to be monoclinic, space group $P2_1/c$. Accurate cell parameters were obtained by least-squares from the setting of 16 high-order reflections measured on an *Enraf-Nonius CAD-4* diffractometer with graphite monochromated Mo$K\alpha$ radiation. Intensities for 1875 independent reflections with $\theta < 25°$ were measured as ω-scans; 1177 reflections were considered observed ($I > 2\sigma(I)$) and corrected for *Lorentz* and polarization effects. The structure was solved by direct methods using *MULTAN-78* [5]. All other calculations were carried out using the *SHELX-76* system [6]. All H-atoms were located from intermediate difference maps. Weighted anisotropic (isotropic for H-atoms) blocked full-matrix least-squares refinement converged at R = 0.043 for 1177

Table 1. *Final positional parameters* (× 10^4) *and equivalent isotropic thermal parameters* (× 10^4), *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}\, a_i^* a_j^*\, \vec{a}_i \cdot \vec{a}_j$$

	x/a	*y/b*	*z/c*	U_{eq}(Å^2)
C(1)	11540 (3)	2842 (1)	1863 (2)	379 (6)
C(2)	12091 (3)	2098 (1)	2077 (3)	415 (6)
C(3)	10856 (3)	1517 (1)	1596 (3)	429 (6)
C(4)	9001 (3)	1700 (1)	920 (3)	427 (6)
C(5)	8410 (3)	2426 (1)	737 (3)	424 (6)
C(6)	9624 (3)	2999 (1)	1163 (2)	394 (6)
O(2)	13885 (2)	1898 (1)	2758 (2)	574 (5)
O(4)	7765 (2)	1143 (1)	452 (2)	596 (5)
C(7)	11505 (4)	738 (1)	1796 (4)	594 (8)
C(8)	8802 (3)	3759 (1)	887 (0)	523 (10)
C(9)	12985 (3)	3400 (1)	2364 (3)	437 (6)
O(9)	14598 (2)	3264 (1)	3106 (2)	618 (6)
O(10)	12479 (2)	4082 (1)	1945 (2)	560 (5)
C(10)	13897 (4)	4642 (1)	2320 (4)	689 (9)
	x/a	*y/b*	*z/c*	U_{iso}
H(2)	14422 (32)	2286 (13)	2969 (30)	683 (61)
H(4)	6726 (51)	1316 (20)	54 (47)	1189 (106)
H(5)	7104 (26)	2542 (11)	405 (25)	479 (50)
H(7.1)	10579 (73)	394 (27)	1824 (61)	1758 (155)
H(7.2)	12073 (48)	608 (17)	2980 (46)	1086 (100)
H(7.3)	12443 (69)	577 (24)	1100 (68)	1541 (163)
H(8.1)	7499 (35)	3723 (14)	521 (32)	699 (66)
H(8.2)	8960 (38)	4022 (13)	2066 (34)	710 (70)
H(8.3)	9385 (36)	4041 (14)	– 112 (33)	638 (71)
H(10.1)	13279 (46)	5072 (17)	2069 (41)	1093 (96)
H(10.2)	15009 (47)	4564 (21)	1649 (47)	1075 (113)
H(10.3)	14393 (52)	4617 (20)	3606 (49)	1265 (106)

Table 2. *Bond distances* (Å) *and angles* (°)

C(1)–C(2)	1.416 (3)	C(4)–C(5)	1.393 (3)
C(1)–C(6)	1.423 (2)	C(4)–O(4)	1.360 (2)
C(1)–C(9)	1.460 (3)	C(5)–C(6)	1.367 (3)
C(2)–C(3)	1.395 (3)	C(6)–C(8)	1.509 (3)
C(2)–O(2)	1.359 (2)	C(9)–O(9)	1.230 (2)
C(3)–C(4)	1.389 (3)	C(9)–O(10)	1.322 (2)
C(3)–C(7)	1.496 (3)	C(10)–O(10)	1.437 (3)
C(6)–C(1)–C(2)	118.2 (2)	O(4)–C(4)–C(3)	117.6 (2)
C(9)–C(1)–C(2)	117.7 (2)	O(4)–C(4)–C(5)	120.7 (2)
C(9)–C(1)–C(6)	124.1 (2)	C(6)–C(5)–C(4)	122.2 (2)
C(3)–C(2)–C(1)	123.2 (2)	C(5)–C(6)–C(1)	118.4 (2)
O(2)–C(2)–C(1)	122.2 (2)	C(8)–C(6)–C(1)	124.8 (2)
O(2)–C(2)–C(3)	114.7 (2)	C(8)–C(6)–C(5)	116.8 (2)
C(4)–C(3)–C(2)	116.5 (2)	O(9)–C(9)–C(1)	123.8 (2)
C(7)–C(3)–C(2)	121.5 (2)	O(10)–C(9)–C(1)	115.9 (2)
C(7)–C(3)–C(4)	122.0 (2)	O(10)–C(9)–O(9)	120.3 (2)
C(5)–C(4)–C(3)	121.7 (2)	C(10)–O(10)–C(9)	117.5 (2)

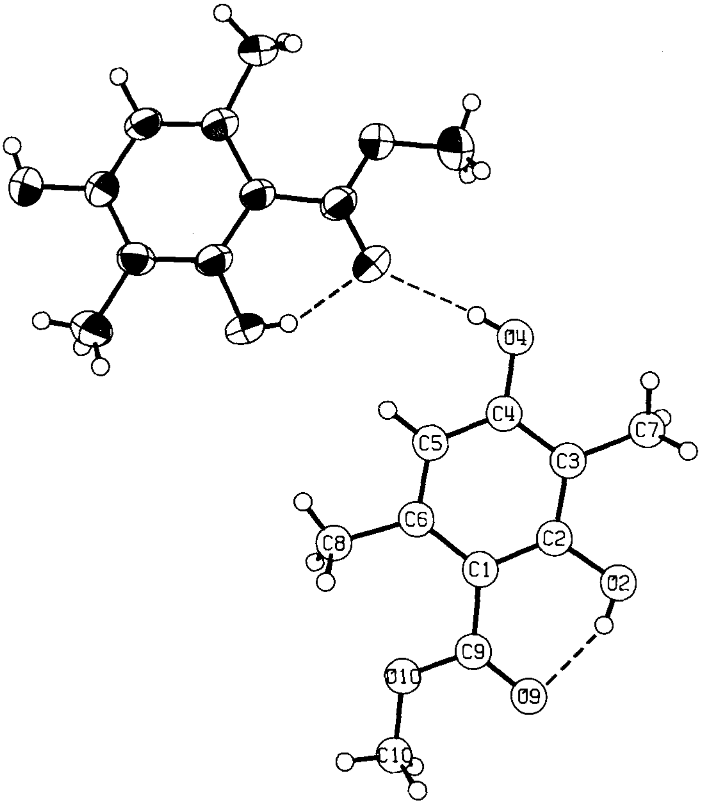

Figure. *View of the c-glide plane related molecules* (*1+x*, $\frac{1}{2}-y$, $\frac{1}{2}+z$), *showing the atomic numbering and vibrational ellipsoids* (50% probability level) reflections; $R_w = 0.052$ ($R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$; $R_w = \Sigma \| F_o| - |F_c\| \; w^{1/2} / \Sigma |F_o| \; w^{1/2}$. $w = 1/(\sigma^2(F_o) + 0.00572(F_o)^2)$). In the final cycle of refinement the average parameter shift was less than 0.5 e.s.d. A final difference map showed no significant residual electron density.

The IR. spectra of solid methyl 2,4-dihydroxy-3,6-dimethylbenzoate, solid methyl 2-hydroxy-4-methoxy-3,6-dimethylbenzoate and solid methyl 2-methoxy-4-hydroxy-3,6-dimethylbenzoate were measured in the form of KBr disks at 0.5% concentration.

Discussion. – Final positional and thermal parameters are given in *Table 1*. Bond distances and angles and their standard deviations are given in *Table 2*. The numbering scheme used is apparent from the *Figure* (*cf.* [7]). Molecules related by the c-glide plane form a H-bonded sheet-like structure. The inter-planar distance is 3.56 (5) Å. Distance O(4) to O(9′) is 2.870 (2) Å, distance H(4) to O(9′) is 2.09 (3) Å and angle O(4)–H(4)...O(9′) is 157.5 (5.0)°. There is a strong intramolecular H-bond between hydroxyl O(2) and the carbonyl O-atom O(9). Distance O(2) to O(9) is 2.552 (3) Å, distance H(2) to O(9) is 1.79 (2) Å and angle O(2)–H(2)...O(9) is 155.5 (4.8)°. There are no intermolecular distances less than 3.2 Å between non-hydrogen atoms.

Atoms C(1), C(9), O(9) and O(10) of the carboxylate group are co-planar. The methyl C-atom, C(10), is displaced by 0.07 Å from this plane, which is inclined by 7.5 (5)° to the best plane through the phenyl group. Torsion angles O(10)–C(9)–C(1)–C(2) and O(10)–C(9)–C(1)–C(6) are 172.3 (5)° and −7.2 (5)°, respectively. The phenyl group appears to be divided into two halves; a highly substituted half in which atoms are displaced by much as 0.03 Å from the best plane and a less substituted, more planar half. This difference is probably due to the non-bonded interactions in the more substituted half of the molecule.

As expected in the solid state IR. spectrum there are two (O–H)-stretching frequencies at 3400 cm^{-1} and 3080 cm^{-1}. The spectrum of the 4-methoxy analogue shows only one such frequency at 3080 cm^{-1}, and the spectrum of the 2-methoxy analogue shows only one such frequency at 3320 cm^{-1}. Hence the band at 3400 cm^{-1} can be assigned to the intermolecular H-bond (O...O distance 2.87 Å), and that at 3080 cm^{-1} to the intramolecular H-bond (O...O distance 2.55 Å), in agreement with the general correlation observed by Nakamoto et al. [8].

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