

bond (H11A...O53) and an intermolecular hydrogen bond (H11B...O24). This intermolecular hydrogen bond forms the connection between the molecular layers in the crystal. The hydrogen bonds between the carbamoyl H atoms (H25A, H25B) and the adjacent O24 and N3 atoms lie in these layers perpendicular to the *ac* plane.

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Structure of the Methyl Esters of Barbatic and Evernic Acids: Natural *para*-Depside

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Abstract. Methyl 2-hydroxy-4-(2-hydroxy-4-methoxy-3,6-dimethylbenzoyloxy)-3,6-dimethylbenzoate (barbaticin), $C_{20}H_{22}O_7$, $M_r = 374.4$, triclinic, $P\bar{1}$, $a = 4.750$ (1), $b = 7.178$ (1), $c = 27.621$ (2) Å, $\alpha = 82.37$ (1), $\beta = 88.42$ (1), $\gamma = 80.87$ (1)°, $V = 921.6$ Å³, $Z = 2$, D_m (floatation in KI/H₂O) = 1.37, $D_x = 1.349$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.63$ cm⁻¹, $F(000) = 396$, room temperature, $R = 0.049$ for 2119 reflections. Methyl 2-hydroxy-4-(2-hydroxy-4-methoxy-6-methylbenzoyloxy)-3,6-dimethylbenzoate (evernin), $C_{19}H_{20}O_7$, $M_r = 360.4$, monoclinic, $P2_1/c$, $a = 5.100$ (1), $b = 27.323$ (2), $c = 12.816$ (1) Å, $\beta = 98.84$ (1)°, $V = 1764.7$ Å³, $Z = 4$, D_m (floatation in KI/H₂O) = 1.37, $D_x = 1.356$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.0$ cm⁻¹, $F(000) = 760$, room temperature, $R = 0.044$ for 2086 reflections. In both compounds two highly substituted phenyl rings are bridged by an ester group, and are inclined to one another [by 106.1 (1)° in barbaticin and 88.6 (1)° in evernin]. There are two strong intramolecular hydrogen bonds, involving the hydroxyl substituents

and the adjacent ester carbonyl groups, in both compounds.

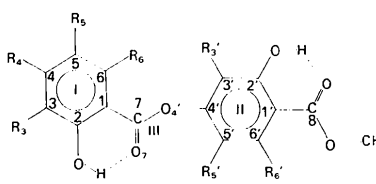
Introduction. Depsides form a large group of secondary metabolites of lichens. Their biosynthesis follows the acetate–polymalonate pathway with the basic structural unit being phenyl benzoate. Their synthesis is difficult owing to the large number and nature of the substituents, often hydroxyl groups, on the two aromatic rings, see Table 1. The majority of known depsides can be divided into two groups; the first are derived from orcinol-type units, the second from β -orcinol-type units. The intermolecular esterification of two or three identical units or analogues, leads to two major classes of depsides; the *para*-depsides and the tridepsides (Culberson, 1969). Barbatic acid is found in the majority of lichens of genera *Usnea* and was first isolated in the last century (Stenhouse & Groves, 1880). Later coccellic acid, from *Cladonia coccifera*, was shown to be identical to barbatic acid (Asahina & Fuzikawa, 1934), which was isolated by the same authors from *Cladonia amourocrea*. A little earlier it had been

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shown that barbatic acid, from *Usnea barbata*, could be converted to its methyl ester by the action of diazomethane in ether. Continued reaction produced a crystalline *o*-monomethyl derivative of methyl barbata whose chemical structure was confirmed by synthesis (Robertson & Stephenson, 1932). However, the work of St Pfau (1928) had shown that the hydrolytic fragmentation or alcoholysis of barbatic acid, and indeed of the majority of natural depsides, gives rhizonic acid and β -orcinecarboxylic acid and their derivatives. They also showed that barbatic acid is the higher homologue of evernic acid, usually formed from one unit of orcinol and one unit of β -orcinol. The isolation and synthesis of the methyl ester of the latter (Tabacchi & Nicollier, 1976; Nicollier, Rebetez, Tabacchi, Gerlach & Thalmann, 1978) and a preliminary crystal structure analysis (Stoekli-Evans & Tabacchi, 1985) have been reported. Here we wish to discuss the crystal structure analysis of the methyl ester of barbatic acid (B = barbatin) and a new analysis of the methyl ester of evernic acid (E = evernin) and compare their structures with those of four other depsides all possessing the same basic structural unit, *i.e.* phenyl benzoate (Adams & Morsi, 1976).

Experimental. Barbatin (B), from *Usnea barbata* *sp.*, transparent rod-like crystals were obtained from a THF/CH₃CN solution. A crystal of dimensions 0.13 × 0.19 × 0.61 mm was used for data collection using a Stoe-Siemens AED-2 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. 2% intensity variation for four standard reflections measured every hour. Accurate cell parameters from $\pm \omega$ values of 27 reflections and their Friedel pairs in the range $18 < 2\theta < 25^\circ$. 6545 reflections were measured by the $\omega/2\theta$ scan mode with $\theta_{\max} = 25^\circ$, and index limits $h - 5$ to 5 , $k - 8$ to 8 , $l - 32$ to 32 . 3275 unique reflections ($R_{\text{int}} = 0.029$), 2119 [$I > 3\sigma(I)$] were considered observed and used for all further calculations. Structure solved using a combination of *SHELXS86* (Sheldrick, 1986) and *PATSEE* (Egert, 1985). Refinement initially carried out using *SHELX76* (Sheldrick, 1976). Final cycles and all further calculations were with the *NRCVAX* system (Gabe, Le Page, Charland & Lee, 1989). H atoms were located from difference maps and refined isotropically; all bond lengths and angles involving the H atoms were normal within experimental error. Weighted anisotropic full-matrix least-squares refinement for 2119 reflections gave $R = 0.049$, $wR = 0.076$; function minimized $\sum w(|F_o| - |F_c|)^2$, $w^{-1} = \sigma^2(F_o) + 0.0012(F_o^2)$. In the final cycle of refinement the maximum Δ/σ ratio was 0.043. Residual density limits in final difference map were 0.25 and $-0.25 \text{ e } \text{\AA}^{-3}$.

Table 1. Substituents on the two phenyl rings of various depsides



	R ₂	R ₃	R ₄	R ₅	R ₆	R ₂ '	R ₃ '	R ₄ '	R ₅ '	R ₆ '
Barbatin	OH	CH ₃	OCH ₃	H	CH ₃	OH	CH ₃	—	H	CH ₃
Evernin	OH	H	OCH ₃	H	CH ₃	OH	CH ₃	—	H	CH ₃
Atranonin	OH	CHO	OH	H	CH ₃	OH	CH ₃	—	H	CH ₃
Wrightin	OH	Cl	OCH ₃	H	CH ₃	OH	H	—	H	CH ₃
KHHT83	OCH ₃	CH ₃	OH	CH ₃	CH ₃	OCH ₃	CH ₃	—	CH ₃	CH ₃
4- <i>o</i> -Methyl-cryptochloro-phacic acid	OCH ₃	H	OCH ₃	H	C ₆ H ₁₁	OH	—	OH	H	C ₆ H ₁₁
Phenyl benzoate	H	H	H	H	H	H	H	—	H	H

Evernin (E), from *Evernia prunastica* (L.) ACH, transparent blocks from a DMF solution. A crystal of dimensions 0.27 × 0.42 × 0.53 mm was used for data collection using a Stoe-Siemens AED-2 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. 3% intensity variation for three standard reflections measured every hour. Accurate cell parameters from $\pm \omega$ values of 17 reflections and all equivalents in the range $25 < 2\theta < 35^\circ$. 6256 reflections were measured by the ω/θ scan mode with $\theta_{\max} = 25^\circ$, and index limits $h - 6$ to 5 , $k - 32$ to 32 , $l - 0$ to 15 . 3086 unique reflections ($R_{\text{int}} = 0.019$), 2086 [$I > 2.5\sigma(I)$] were considered observed and used for all further calculations. Structure solved by direct methods using the *NRCVAX* system (Gabe *et al.*, 1989), which was also used for all further calculations. H atoms were located from difference maps and refined isotropically; all bond distances and angles involving the H atoms were normal within experimental error. Weighted anisotropic full-matrix least-squares refinement for 2086 reflections gave $R = 0.044$, $wR = 0.066$; 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 Δ/σ ratio was 0.002. Residual density limits in final difference map were +0.15 and $-0.18 \text{ e } \text{\AA}^{-3}$.

Neutral complex atom scattering factors included in the *NRCVAX* system were from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final positional and equivalent isotropic thermal parameters are given in Table 2, interatomic distances and bond angles are in Table 3.* The atomic

* Lists of structure factors, anisotropic thermal parameters, H-atom positions, and selected least-squares planes and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54305 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic parameters and B_{iso} values (\AA^2) (e.s.d.'s refer to the last digit printed)

B_{iso} is the mean of the principal axes of the thermal ellipsoid.

	x	y	z	B_{iso}
Barbatin				
C(1)	0.3327 (6)	0.8069 (4)	0.17807 (10)	3.01 (12)
C(2)	0.1286 (6)	0.9003 (4)	0.14263 (10)	3.26 (12)
C(3)	0.0547 (7)	0.8150 (4)	0.10359 (11)	3.59 (13)
C(4)	0.1999 (7)	0.6355 (5)	0.09863 (11)	3.80 (14)
C(5)	0.4021 (8)	0.5404 (5)	0.13233 (12)	4.02 (15)
C(6)	0.4724 (7)	0.6216 (4)	0.17220 (11)	3.37 (13)
C(1')	0.7087 (6)	1.0531 (4)	0.37785 (10)	2.96 (11)
C(2')	0.5461 (6)	0.9038 (4)	0.38221 (10)	3.20 (12)
C(3')	0.4787 (6)	0.8207 (4)	0.34166 (10)	3.05 (11)
C(4')	0.5822 (6)	0.8937 (4)	0.29730 (10)	2.94 (11)
C(5')	0.7462 (6)	1.0371 (4)	0.29155 (11)	3.03 (12)
C(6')	0.8141 (6)	1.1195 (4)	0.33128 (10)	2.77 (11)
C(7)	0.3857 (6)	0.9123 (4)	0.21796 (10)	2.96 (11)
C(8)	0.7555 (7)	1.1341 (5)	0.42279 (11)	3.85 (14)
C(9)	0.9474 (22)	1.3613 (11)	0.46090 (19)	7.5 (3)
C(10)	0.2834 (14)	0.3782 (6)	0.05001 (17)	6.5 (3)
C(11)	-0.1670 (10)	0.9172 (7)	0.06763 (16)	5.18 (20)
C(12)	0.6924 (10)	0.5056 (5)	0.20635 (15)	4.62 (17)
C(13)	0.3039 (8)	0.6611 (5)	0.34751 (15)	3.98 (15)
C(14)	0.9963 (8)	1.2751 (5)	0.32153 (13)	3.35 (14)
O(2)	-0.1013 (5)	1.0794 (3)	0.14570 (9)	4.50 (10)
O(2')	0.4368 (5)	0.8329 (4)	0.42549 (8)	4.59 (11)
O(4')	0.5259 (5)	0.8058 (3)	0.25650 (7)	3.56 (9)
O(7)	0.3037 (5)	1.0817 (3)	0.21844 (8)	3.95 (10)
O(8)	0.6690 (8)	1.0778 (5)	0.46250 (9)	7.35 (18)
O(9)	0.9010 (7)	1.2758 (4)	0.41752 (8)	6.00 (14)
O(10)	0.1289 (6)	0.5601 (3)	0.05856 (8)	5.34 (12)
Evernin				
C(1)	0.4080 (5)	0.88670 (8)	0.12236 (18)	3.65 (10)
C(2)	0.2615 (5)	0.92770 (9)	0.07890 (20)	4.12 (11)
C(3)	0.3328 (6)	0.97504 (10)	0.11038 (22)	4.50 (13)
C(4)	0.5538 (5)	0.98184 (9)	0.18486 (22)	4.41 (12)
C(5)	0.7040 (6)	0.94208 (10)	0.22772 (23)	4.59 (12)
C(6)	0.6376 (5)	0.89481 (9)	0.19849 (19)	3.70 (10)
C(1')	0.1502 (5)	0.65839 (8)	0.07836 (18)	3.61 (9)
C(2')	0.3216 (5)	0.67991 (9)	0.01474 (18)	3.85 (10)
C(3')	0.4139 (5)	0.72827 (9)	0.02922 (19)	4.07 (10)
C(4')	0.3315 (5)	0.75309 (8)	0.11183 (20)	4.06 (10)
C(5')	0.1691 (5)	0.73313 (9)	0.17780 (21)	4.14 (11)
C(6')	0.0732 (5)	0.68592 (9)	0.16307 (18)	3.81 (10)
C(7)	0.3070 (5)	0.83872 (8)	0.08581 (19)	4.00 (11)
C(8)	0.0613 (5)	0.60782 (9)	0.05137 (21)	3.99 (11)
C(9)	-0.2165 (8)	0.54132 (11)	0.0755 (4)	6.18 (18)
C(10)	0.5007 (9)	1.06851 (12)	0.1779 (3)	6.07 (20)
C(12)	0.8168 (6)	0.85481 (11)	0.2480 (3)	4.70 (13)
C(13)	0.5913 (7)	0.75027 (13)	-0.0407 (3)	5.30 (15)
C(14)	-0.1016 (7)	0.66785 (12)	0.23827 (24)	4.81 (14)
O(2)	0.0430 (4)	0.92350 (8)	0.00498 (17)	5.62 (9)
O(2')	0.4100 (4)	0.65535 (7)	-0.06460 (15)	5.15 (9)
O(4')	0.4309 (4)	0.80045 (6)	0.13769 (14)	4.75 (8)
O(7)	0.1206 (4)	0.83164 (6)	0.01556 (16)	5.56 (9)
O(8)	0.1501 (4)	0.58256 (7)	-0.01353 (17)	5.53 (9)
O(9)	-0.1259 (4)	0.59084 (6)	0.10220 (16)	5.25 (9)
O(10)	0.6452 (4)	1.02657 (7)	0.22109 (18)	5.91 (10)

Table 3. Bond distances (\AA) and angles ($^\circ$)

	Barbatin	Evernin
C(1)—C(2)	1.421 (4)	1.412 (3)
C(1)—C(6)	1.416 (4)	1.422 (3)
C(1)—C(7)	1.465 (4)	1.459 (3)
C(2)—C(3)	1.388 (4)	1.387 (4)
C(2)—O(2)	1.361 (4)	1.352 (3)
C(3)—C(4)	1.383 (5)	1.373 (4)
C(3)—C(11)	1.501 (5)	
C(4)—C(5)	1.388 (5)	1.392 (4)
C(4)—O(10)	1.367 (4)	1.364 (3)
C(5)—C(6)	1.385 (4)	1.373 (4)
C(6)—C(12)	1.499 (5)	1.501 (4)
C(1')—C(2')	1.408 (4)	1.412 (3)
C(1')—C(6')	1.418 (4)	1.425 (3)
C(1')—C(8)	1.475 (4)	1.479 (3)
C(2')—C(3')	1.404 (4)	1.405 (3)
C(2')—O(2')	1.359 (3)	1.352 (3)
C(3')—C(4')	1.377 (4)	1.376 (4)
C(3')—C(13)	1.508 (4)	1.494 (4)
C(4')—C(5')	1.377 (4)	1.383 (4)
C(4')—O(4')	1.413 (3)	1.411 (3)
C(5')—C(6')	1.382 (4)	1.382 (3)
C(6')—C(14)	1.512 (4)	1.494 (4)
C(7)—O(4')	1.350 (4)	1.344 (3)
C(7)—O(7)	1.218 (4)	1.220 (3)
C(8)—O(8)	1.202 (4)	1.220 (3)
C(8)—O(9)	1.308 (4)	1.320 (3)
C(9)—O(9)	1.454 (5)	1.453 (3)
C(10)—O(10)	1.438 (5)	1.427 (4)
O(2)—H(O2)	0.91 (5)	0.97 (4)
O(2')—H(O2')	0.98 (8)	1.07 (4)
O(7)...H(O2)	1.76 (5)	1.63 (4)
O(8)...H(O2')	1.61 (8)	1.51 (4)
C(2)—C(1)—C(6)	118.4 (3)	118.5 (2)
C(2)—C(1)—C(7)	116.9 (2)	116.6 (2)
C(6)—C(1)—C(7)	124.8 (3)	125.0 (2)
C(1)—C(2)—C(3)	122.6 (3)	121.7 (2)
C(1)—C(2)—O(2)	121.4 (3)	122.6 (2)
C(3)—C(2)—O(2)	116.0 (3)	115.7 (2)
C(2)—C(3)—C(4)	117.1 (3)	118.6 (2)
C(2)—C(3)—C(11)	120.9 (3)	
C(4)—C(3)—C(11)	121.9 (3)	
C(3)—C(4)—C(5)	121.8 (3)	120.8 (2)
C(3)—C(4)—O(10)	115.2 (3)	124.0 (2)
C(5)—C(4)—O(10)	123.1 (3)	115.2 (2)
C(4)—C(5)—C(6)	121.7 (3)	121.9 (3)
C(1)—C(6)—C(5)	118.3 (3)	118.5 (2)
C(1)—C(6)—C(12)	124.6 (3)	124.1 (2)
C(5)—C(6)—C(12)	117.1 (3)	117.5 (2)
C(2)—C(1')—C(6')	119.3 (2)	119.2 (2)
C(2)—C(1')—C(8)	117.1 (3)	116.7 (2)
C(6')—C(1')—C(8)	123.6 (2)	124.1 (2)
C(1')—C(2')—C(3')	122.1 (3)	122.7 (2)
C(1')—C(2')—O(2')	122.8 (3)	122.4 (2)
C(3')—C(2')—O(2')	115.1 (3)	115.0 (2)
C(2')—C(3')—C(4')	115.9 (2)	115.4 (2)
C(2')—C(3')—C(13)	120.9 (3)	121.4 (3)
C(4')—C(3')—C(13)	123.2 (3)	123.2 (2)
C(3')—C(4')—C(5')	123.8 (3)	123.9 (2)
C(3')—C(4')—O(4')	116.4 (2)	119.5 (2)
C(5')—C(4')—O(4')	119.7 (3)	116.4 (2)
C(4')—C(5')—C(6')	120.7 (3)	121.1 (2)
C(1')—C(6')—C(5')	118.2 (2)	117.6 (2)
C(1')—C(6')—C(14)	124.8 (3)	125.4 (2)
C(5')—C(6')—C(14)	117.0 (3)	117.0 (2)
C(1)—C(7)—O(4')	115.0 (2)	115.1 (1)
C(1)—C(7)—O(7)	124.3 (3)	125.2 (2)
O(4')—C(7)—O(7)	120.7 (3)	119.7 (2)
C(1')—C(8)—O(8)	124.1 (3)	123.8 (2)
C(1')—C(8)—O(9)	115.9 (3)	115.6 (2)
O(8)—C(8)—O(9)	120.0 (3)	120.7 (2)
C(4')—O(4')—C(7)	119.3 (2)	118.3 (2)
C(8)—O(9)—C(9)	117.5 (3)	116.0 (2)
C(4)—O(10)—C(10)	117.8 (3)	117.3 (3)
O(2)—H(O2)—O(7)	157 (5)	153 (4)
O(2')—H(O2')—O(8)	158 (8)	156 (3)

numbering scheme used is illustrated in Figs. 1 and 2.

Discussion. The atoms of the molecular skeleton of barbatin (*B*) and evernin (*E*) are contained in three planes defined by the two aromatic rings I [atoms C(1) to C(6)] and II [atoms C(1') to C(6')] and the carboxylate group III [atoms C(7), O(7) and O(4')]. In both compounds two strong intramolecular hydrogen bonds (see Table 3) involving the hydroxyl substituents and the adjacent ester carbonyl groups create two pseudo rings which are almost planar. There are no short intermolecular contacts in the crystal structures of either compound. The only structural differences between the two compounds concern the angles involving atom C(4), which

reflects the different orientation of the methoxy substituent in the two compounds, and atom C(4'), which reflects the different orientation of ring II with respect to the plane of the bridging carboxylate group. For details see Table 4 and Figs. 1 and 2.

Planes I and II are inclined to one another by $106.1(1)^\circ$ in *B* and $88.6(1)^\circ$ in *E*. Plane III ($-\text{COO}-$) is inclined to planes I and II by $14.8(1)$ and $120.4(1)^\circ$ in *B* and $7.6(2)$ and $82.3(1)^\circ$ in *E*. In Table 4 the same dihedral angles for three further *para*-depsides (atranonin, wrightin and KHHT83) and a *meta*-depside (4-*o*-methylcryptochlorophaeic acid) are compared. The last two compounds have been found to be inhibitors of prostoglandin biosynthesis. The same values are also compared for phenyl benzoate (Adams & Morsi, 1976).

The structural characteristics of the carboxylic ester group have been analysed previously (Schweizer & Dunitz, 1982). There it was found that for the majority of aryl esters the plane of the aromatic ring is inclined by $75(\pm 15)^\circ$ to that of the carboxylate group. In esters of the type $\text{Ar}-\text{COOX}$, the aromatic ring was found to lie close [$5(\pm 5)^\circ$] to the plane of the carboxylate group. In evernin and atranonin the phenyl rings are almost perpendicular to one another, whereas in barbatin, as mentioned, they are inclined by 106.1° . Table 4 shows that the conformation of these two compounds is very similar and different from that in barbatin. This is notable when comparing the dihedral angle between planes II and III, and surprising considering that phenyl ring II is the same β -orcinol-type unit in all three compounds. In wrightin where plane II is an orcinol-type unit, planes I, II and III are almost parallel. The absence of a methyl substituent on atom C(3') brings proton H(3') to within 2.14 \AA of the carbonyl O atom, O(7), in the ester bridge. This is considerably shorter than

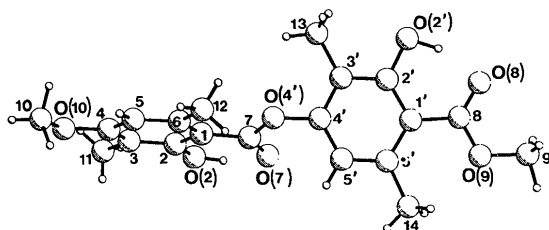


Fig. 1. A PLUTO (Motherwell & Clegg, 1978) view of barbatin (*B*) showing the atom-numbering scheme.

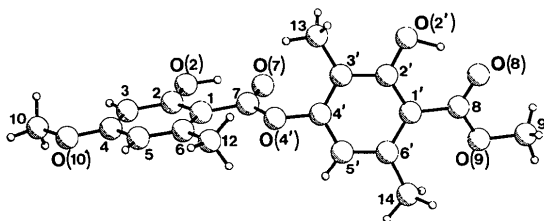


Fig. 2. A PLUTO (Motherwell & Clegg, 1978) view of evernin (*E*) showing the atom-numbering scheme.

Table 4. Dihedral angles ($^\circ$) between the planes of the phenyl rings (I, II) and the plane of the $-\text{COO}-$ group (III)

	I, II	I, III	II, III
Barbatin*	106.1	14.8	120.4
Evernin†	88.6	7.6	82.3
Atraronin‡§	96.2	6.8	90.5
Wrightin§¶	0.6	170.9	171.4
KHHT83 (no coordinates)**	6.2	~90	~90
4- <i>o</i> -Methylcryptochlorophaeic acid§††	24.7	61.8	86.4
Phenyl benzoate§	55.7	9.8	65.1

* Planes I and II are planar to within $0.008(2)$ and $0.006(1) \text{ \AA}$, respectively.

† Planes I and II are planar to within $0.004(1)$ and $0.007(1) \text{ \AA}$, respectively.

‡ Brassy, Bachet, Bodo & Molho (1982).

§ Coordinates and dihedral angles from the Cambridge Structural Database (1991, version 4.2).

¶ Maass & Hanson (1986).

** Methyl 4-(4-hydroxyl-2,3,5-trimethyl-6-methoxybenzoyloxy)-2-methoxy-3,5,6-trimethylbenzoate (Kitahara *et al.*, 1983).

†† Shibuya *et al.* (1983).

the sum of the van der Waals radii for O and H (2.60 \AA). Such a planar arrangement in an aryl ester, to our knowledge, has never been observed previously.

In the *meta*-depside 4-*o*-methylcryptochlorophaeic acid, the two phenyl rings are inclined by an angle of 25° due to the presence of an inter-ring hydrogen bond. The 4'-*o*-methyl derivative, which does not have this inter-ring hydrogen bond to ensure the relative planarity of the molecule, has been shown to be much less active with respect to the inhibition of prostoglandin biosynthesis (Shibuya, Ebizuka, Noguchi, Iitaka & Sankawa, 1983). In the fourth *para*-depside KHHT83, steric hinderance due to the methyl and methoxy *ortho* and *meta* substituents in the region of the bridging ester group, results in the two phenyl rings being almost parallel. The authors (Shibuya *et al.*, 1983; Kitahara, Haruyama, Hata & Takahashi, 1983) suggest that the inhibition of prostoglandin biosynthesis is due to the parallel orientation of the two phenyl rings. If this is the case, wrightin is almost certainly active too.

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Structure of Pannarin: a Natural Depsidone

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Abstract. 2-Chloro-3-hydroxy-8-methoxy-1,6,9-trimethyl-11-oxo-11*H*-dibenzo[*b,e*][1,4]dioxepin-4-carbaldehyde, $C_{18}H_{15}ClO_6$, $M_r = 362.8$, monoclinic, $P2_1/c$, $a = 4.301$ (1), $b = 22.832$ (3), $c = 16.531$ (2) Å, $\beta = 95.09$ (1)°, $V = 1616.9$ Å³, $Z = 4$, D_m (floatation in KI/H₂O) = 1.44, $D_x = 1.490$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 2.6$ cm⁻¹, $F(000) = 752$, room temperature, $R = 0.052$ for 1763 reflections. The central dioxepin-11-one ring exists in a boat conformation. It is fused on either side to highly substituted phenyl rings which are inclined to one another at 123.6 (1)°. Hence the molecule appears to be folded about an axis passing through the ether oxygen in the central seven-membered heterocycle.

Introduction. Pannarin is a natural depsidone isolated essentially from lichen genera *Pannaria* (*fulvescens*, *lurida*, *pityrea* and *rubiginosa*). Depsidones are characterized by the presence of a seven-membered oxygen heterocycle fused on either side to highly substituted phenyl rings. More than twenty examples have been isolated from lichens (Culberston, 1969). The correct chemical structure of pannarin was given by Jackman, Sargent & Elix (1975). In the same year Huneck & Lamb published the structure of argopsin, a depsidone extracted from the lichen *Argopsis friesiana*, which could also be obtained by the chlorination of pannarin. Another

depsidone, vicanicin, has been correlated with argopsin by a Clemmensen reduction (Bodo & Molho, 1974). The crystal structure analysis of the iodoacetate derivative of vicanicin (Dyer, Baillie, Balthis & Bertrand, 1964) was already proof of the structure of argopsin and indirectly of that of pannarin. Hence it could be shown that pannarin possesses the basic structure of a depsidone and that the two phenyl rings were of the β -orcinol type.

Experimental. Transparent rod-like crystals were obtained from a THF/heptane solution. A crystal of dimensions 0.23 × 0.23 × 0.42 mm was used for data collection using a Stoe-Siemens AED-2 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. 3% intensity variation for three standard reflections measured every hour. Accurate cell parameters from $\pm \omega$ values of 44 reflections in the range $15 < 2\theta < 25^\circ$. 2974 reflections were measured by the $\omega/2\theta$ scan mode with $\theta_{\max} = 25^\circ$, and index limits $h -5$ to 5 , $k 0$ to 2 , $l 0$ to 19 . 2874 unique reflections, $R_{\text{int}} = 0.037$, 1763 [$I > 2\sigma(I)$] were considered observed and used for all further calculations. Structure solved by direct methods using *SHELXS86* (Sheldrick, 1986). Refinement and all further calculations were carried out using the *NRCVAX* system (Gabe, Le Page, Charland & Lee, 1989). H atoms located from difference maps and refined isotropically. Weighted full-matrix least-squares refinement for 1763 reflections gave $R =$

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