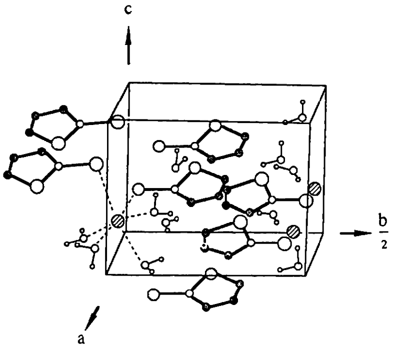

Fig. 3. *PLUTO* (Motherwell & Clegg, 1978) illustration of octahedral sodium 1,2,3,4-thiatriazole-5-thiolate dihydrate.

MNDO calculations indicated strict planarity for the anion, in contrast to slight but definite distortions from planarity found from the best least-squares plane: S2 0·0092, S1 −0·0040, C1 −0·0084, N3 −0·0090, N2 0·0080, N1 0·0042 Å, all displacements being three or more times greater than the estimated standard deviation. The pattern of the deviations is consistent with a slight bowing of the molecule.

The coordination of the sodium ion in this complex is very similar to that observed in $NaCN.2H_2O$ (Van Rij & Britton, 1978) and $NaCl.2H_2O$ (Klewe & Pedersen, 1974). In this case the coordination octahedron consists of four water molecules and two S atoms as illustrated in Fig. 3.

The 5-benzoylthio-1,2,3,4-thiatriazole molecule is close to planar with the dihedral angle between the best least-squares plane of the phenyl and thiatriazole rings being 0·9 (1·6)° and no torsion angle in the molecule being further than 1° from planarity. For the thiatriazole ring no atom deviates by more than 0·0024 Å from the best least-squares plane, most displacements being of the order of experimental error.

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Structure of 7-Methoxy-8-(morpholinocarbonylmethyl)coumarin

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Abstract. $C_{16}H_{17}NO_5$, $M_r = 303·3$, monoclinic, $P2_1/c$, $a = 10·191$ (3), $b = 13·792$ (3), $c = 11·469$ (4) Å, $\beta = 112·14$ (2)°, $V = 1493·2$ (8) Å^3, $Z = 4$, $D_x = 1·349$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·062$ mm^{-1}, $F(000) = 640$, room temperature, $R = 0·061$ for 1383 observed reflections. The structure of

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7-methoxy-8-(morpholinocarbonylmethyl)coumarin is very similar to that of 7-methoxy-8-(3-methyl-2-butenyl)coumarin, and confirms that oxidation of the latter changes only the terminal part of 3-methyl-2-butenyl substituent. The morpholine substituent is in a chair conformation and the coumarinacetyl moiety is oriented equatorially to it.

Introduction. Coumarin derivatives occurring in plants have different biological activities (Cisowski, 1983, 1984). Some synthetic modifications of natural coumarins are of pharmacological importance, like aesculamin, intencordin or folescutol. Osthol [7-methoxy-8-(3-methyl-2-butenyl)coumarin], extracted from *Peucedanum ostruthium* L. Koch, is a suitable substrate for the partial synthesis of some ostholic acid amides; in this paper we present the crystal structure of the morpholide of ostholic acid.

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}
O(1)	0·1132 (3)	0·1750 (2)	0·7093 (3)	0·063 (1)
C(2)	0·2479 (6)	0·1971 (3)	0·7137 (5)	0·066 (2)
O(2)	0·3322 (4)	0·2228 (3)	0·8146 (4)	0·083 (2)
C(3)	0·2717 (6)	0·1882 (4)	0·5976 (5)	0·078 (2)
C(4)	0·1715 (6)	0·1599 (3)	0·4920 (5)	0·071 (2)
C(5)	−0·0814 (6)	0·1084 (3)	0·3792 (4)	0·060 (2)
C(6)	−0·2145 (5)	0·0920 (3)	0·3798 (4)	0·060 (2)
C(7)	−0·2361 (5)	0·1044 (3)	0·4923 (4)	0·055 (2)
C(8)	−0·1256 (5)	0·1307 (3)	0·6047 (4)	0·052 (2)
C(9)	0·0054 (5)	0·1461 (3)	0·5988 (4)	0·054 (2)
C(10)	0·0319 (5)	0·1374 (3)	0·4880 (4)	0·055 (2)
O(11)	−0·3653 (3)	0·0937 (2)	0·5012 (3)	0·069 (1)
C(12)	−0·4855 (5)	0·0759 (4)	0·3874 (5)	0·080 (2)
C(13)	−0·1525 (5)	0·1438 (3)	0·7255 (4)	0·058 (2)
C(14)	−0·1646 (4)	0·0472 (3)	0·7860 (4)	0·053 (2)
O(15)	−0·1405 (4)	−0·0296 (2)	0·7453 (3)	0·074 (1)
N(16)	−0·2027 (5)	0·0504 (3)	0·8853 (3)	0·079 (2)
C(17)	−0·2084 (6)	−0·0391 (4)	0·9520 (5)	0·096 (3)
C(18)	−0·3230 (8)	−0·0363 (4)	0·9945 (6)	0·116 (3)
O(19)	−0·3223 (4)	0·0477 (3)	1·0682 (3)	0·094 (2)
C(20)	−0·3223 (7)	0·1335 (4)	1·0001 (6)	0·106 (3)
C(21)	−0·2069 (7)	0·1375 (4)	0·9579 (6)	0·114 (3)

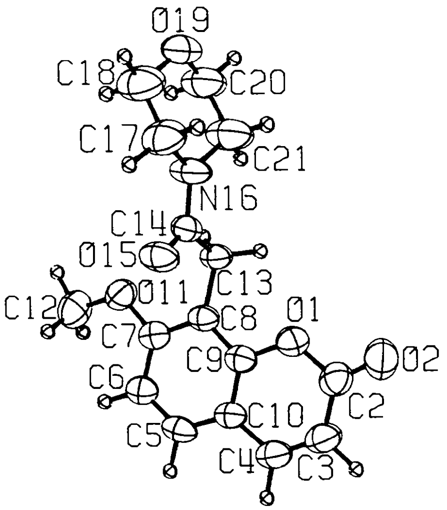

Fig. 1. A view of the molecule with atomic numbering.

Experimental. Poor-quality single crystals were grown from methyl alcohol by slow evaporation; crystal system and approximate cell dimensions were determined from oscillation and Weissenberg photographs; accurate cell parameters refined from setting angles of 15 reflections with $9{\cdot}0 \leq 2\theta \leq 23{\cdot}9°$; crystal specimen $0{\cdot}65 \times 0{\cdot}15 \times 0{\cdot}50$ mm; Syntex $P2_1$ four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, θ–2θ scan mode, background and intensity of reflections determined by peak profile analysis (Lehmann & Larsen, 1974; Jaskólski, 1982); max. $(\sin\theta/\lambda) = 0{\cdot}595$ Å^{-1}, $0 \leq h \leq 13$, $0 \leq k \leq 16$, $-14 \leq l \leq 14$, two standard reflections after every 100 reflections showed no systematic intensity change (< 4 %). 2386 unique reflections measured, 1383 with $I \geq 2\sigma(I)$. Lp correction but no absorption correction. Structure solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); the best set of phases resulted in the location of seven atoms. The other 15 non-H atoms were found by a *MULTAN*-oriented procedure. Structure refined by full-matrix least squares with *SHELX*76 (Sheldrick, 1976), 203 parameters [including three rotational parameters for the C(12) methyl group], function minimized $\sum w(|F_o| - |F_c|)^2$, $w^{-1} = \sigma^2(F_o) + 0{\cdot}0002F_o^2$, $\sigma(F_o)$ based on counting statistics. Non-H atoms refined anisotropically, all H atoms located from geometry and assigned fixed isotropic temperature factors of 0·01 times the U_{iso} of their carriers. Empirical isotropic extinction parameter x, $F_c' = F_c(1 - xF_c^2/\sin\theta)$ (Sheldrick, 1976), converged at $3{\cdot}8\ (9) \times 10^{-7}$. One reflection, 150, with high F_c/F_o ratio possibly due to extinction, was removed. Final $R = 0{\cdot}061$, $wR = 0{\cdot}076$, $S = 3{\cdot}05$, $(\Delta/\sigma)_{max} = 0{\cdot}083$ in final cycle; $-0{\cdot}23 < \Delta\rho < 0{\cdot}43$ e Å^{-3}, atomic scattering factors as in *SHELX*76. Other computer programs used were *PLUTO*78 (Motherwell & Clegg, 1978), *ORTEP* (Johnson, 1976) and *PARST* (Nardelli, 1983).

Discussion. Final positional parameters and U_{eq} values for non-H atoms are given in Table 1.* Fig. 1 shows a perspective view of the molecule; bond lengths and angles are listed in Table 2.

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* Lists of structure factors, anisotropic thermal parameters, torsion angles, H-atom parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53537 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

O(1)—C(2)	1·388 (6)	C(8)—C(13)	1·522 (7)
O(1)—C(9)	1·387 (6)	C(9)—C(10)	1·400 (7)
C(2)—O(2)	1·206 (7)	O(11)—C(12)	1·435 (7)
C(2)—C(3)	1·446 (9)	C(13)—C(14)	1·528 (6)
C(3)—C(4)	1·315 (8)	C(14)—O(15)	1·219 (6)
C(4)—C(10)	1·440 (7)	C(14)—N(16)	1·335 (6)
C(5)—C(6)	1·378 (7)	N(16)—C(17)	1·466 (7)
C(5)—C(10)	1·401 (7)	N(16)—C(21)	1·472 (7)
C(6)—C(7)	1·399 (7)	C(17)—C(18)	1·424 (10)
C(7)—C(8)	1·402 (7)	C(18)—O(19)	1·433 (8)
C(7)—O(11)	1·367 (6)	O(19)—C(20)	1·417 (8)
C(8)—C(9)	1·378 (7)	C(20)—C(21)	1·432 (10)

C(2)—O(1)—C(9)	121·9 (4)	C(4)—C(10)—C(5)	124·2 (4)
O(1)—C(2)—O(2)	115·9 (4)	C(4)—C(10)—C(9)	118·6 (4)
O(1)—C(2)—C(3)	117·0 (4)	C(5)—C(10)—C(9)	117·2 (4)
O(2)—C(2)—C(3)	127·1 (5)	C(7)—O(11)—C(12)	117·8 (4)
C(2)—C(3)—C(4)	122·1 (5)	C(8)—C(13)—C(14)	112·5 (3)
C(3)—C(4)—C(10)	120·6 (5)	C(13)—C(14)—O(15)	121·4 (3)
C(6)—C(5)—C(10)	121·6 (4)	C(13)—C(14)—N(16)	117·2 (3)
C(5)—C(6)—C(7)	118·8 (4)	O(15)—C(14)—N(16)	121·4 (4)
C(6)—C(7)—C(8)	121·9 (4)	C(14)—N(16)—C(17)	120·0 (4)
C(6)—C(7)—O(11)	123·1 (4)	C(14)—N(16)—C(21)	126·1 (4)
C(8)—C(7)—O(11)	115·0 (4)	C(17)—N(16)—C(21)	112·1 (4)
C(7)—C(8)—C(9)	116·9 (4)	N(16)—C(17)—C(18)	110·8 (5)
C(7)—C(8)—C(13)	120·6 (4)	C(17)—C(18)—O(19)	113·7 (5)
C(9)—C(8)—C(13)	122·5 (4)	C(18)—O(19)—C(20)	110·5 (4)
O(1)—C(9)—C(8)	116·6 (4)	O(19)—C(20)—C(21)	112·9 (5)
O(1)—C(9)—C(10)	119·8 (4)	N(16)—C(21)—C(20)	111·3 (5)
C(8)—C(9)—C(10)	123·5 (4)		

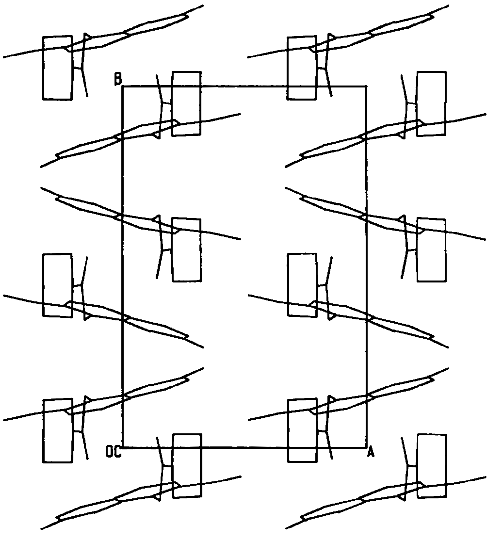

Fig. 2. The molecular packing as seen along the *c* axis.

The coumarin ring system of 7-methoxy-8-(morpholinocarbonylmethyl)coumarin is planar and does not differ from other coumarin derivatives (Borowiak & Wolska, 1989; Chinnakali, Sivakumar & Natarajan, 1989; Ueno, 1985; Ueno & Saito, 1977; Messager & Delugeard, 1974; Gaultier & Hauw, 1965). As a consequence of the large *ortho* substituent, the methoxy group and the benzene ring are not coplanar, O(11) being 0·070 (3) and C(12) 0·216 (5) Å out of the plane. The orientation of the acetylmorpholine substituent is defined by the torsion angle C(7)—C(8)—C(13)—C(14), which is 77·1 (4)°. The same orientation has been found in osthol [torsion angle 88·7 (2)°; Borowiak & Wolska, 1989].

The C(8)—C(13)—C(14)—O(15)—N(16) fragment is flat and almost perpendicular to the coumarin system with O(15) directed towards the benzene ring; the O(11)···O(15) distance is 3·338 (5) Å. The morpholine ring adopts a chair conformation and the coumarinacetyl group is oriented equatorially to it; the torsion angles C(13)—C(14)—N(16)—C(21) and C(13)—C(14)—N(16)—C(17) are − 13·0 (5) and − 176·5 (5)°, respectively. The similarity of the structures of osthol and the present compound shows that the oxidation of osthol with Cr_2O_3 (Cisowski & Rzadkowska-Bodalska, 1979; and references cited therein) changes only the terminal part of the 3-methyl-2-butenyl substituent.

The acetylmorpholine substituent presumably hinders the stacking of the molecules in the crystal, as found in flat coumarin derivatives (*e.g.* Gaultier & Hauw, 1965; Stemple & Watson, 1972; Ueno & Saito, 1977; Bravic & Bideau, 1978; Bideau, Bravic & Desvergne, 1979; Dall'Acqua, Benetollo & Bombieri, 1981). Instead, two parallel and partly overlapping coumarin moieties are connected by an inversion center (Fig. 2). The distance between their planes is 3·59 (1) Å.

No short intermolecular contacts are observed.

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Structure of 6,7-Dimethoxy-9-phenyl-1,4-phenanthrenequinone

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Abstract. $C_{22}H_{16}O_4$, $M_r = 344{\cdot}366$, triclinic, $P\bar{1}$, $a = 10{\cdot}490\,(1)$, $b = 11{\cdot}907\,(1)$, $c = 14{\cdot}902\,(1)$ Å, $\alpha = 98{\cdot}91\,(1)$, $\beta = 97{\cdot}83\,(1)$, $\gamma = 110{\cdot}36\,(1)°$, $V = 1687{\cdot}3\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}356$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 7{\cdot}19$ cm^{-1}, $F(000) = 720$, $T = 295$ K, $R = 0{\cdot}048$ for 4587 observed unique reflections. The carbon skeletons of the rings are planar with maximum deviations of 0·033 (4) and −0·033 (4) Å for the quinonoid rings of the discrete molecules *A* and *B*. The carbonyl oxygens O(1*A*), O(1*B*) and O(4*A*), O(4*B*) deviate 0·109 (3), 0·038 (3) and 0·127 (3), 0·153 (3) Å, respectively, from the quinonoid rings. The maximum inclinations of adjacent ring planes are 1·8° in molecule *A* and 3·8° in molecule *B*. The methoxy groups at C(6) and C(7) in molecule *A* and at C(6) in molecule *B* are almost coplanar with the attached ring systems, the methoxy group at O(7*B*) twisting out of the adjacent ring by −0·118 (4) Å. The aromatic skeletons of the independent molecules are inclined at 14 (1)° to each other. The phenyl rings turn away from the phenanthrene moieties by 52·7 (5) and 56·1 (5)°. The molecules in the crystal are packed together by weak intermolecular C—H···O interactions and van der Waals forces.

Introduction. In the course of the identification of the constituents of commercial timbers the title compound was prepared as a by-product during the synthesis of latinone [Fig. 1, compound (I)]. The phenanthrenequinone latinone from *Dalbergia latifolia* Roxb. (East Indian rosewood) and melatinone [Fig. 1, compound (II)] from the African blackwood *Dalbergia melanoxylon* Guill. & Perr have been isolated by O'Criodain, O'Sullivan, Meegan & Donnelly (1981). These tropical wood species are known for their sensitizing properties (Hausen, 1984), and phenanthrenequinones with no substitution at C(2) and/or C(3), like the title compound or latinone, are suspected as the possible contact allergens. The present X-ray structure analysis has been carried out in order to compare the molecular shape and dimensions with other allergenic substituted phenanthrenequinones (Schmalle, Jarchow, Hausen, Schulz, Krohn & Loock, 1986, 1987; Bartsch, Schmalle, Jarchow, Hausen & Schulz, 1986; Krohn, Loock, Kiesele, Hausen & Schmalle, 1991).

Experimental. The crystal structure of the title compound was determined by X-ray diffraction using a CAD-4 diffractometer with graphite-mono-

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