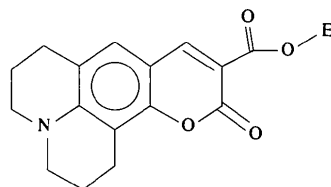


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features of the fused piperidine ring system. A displacement ellipsoid plot of the molecule with atomic numbering scheme is given in Fig. 1.



(I)

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Coumarin 314

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Abstract

Coumarin 314, ethyl 2,3,6,7-tetrahydro-11-oxo-1*H*,5*H*,-11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizine-10-carboxylate, C₁₈H₁₉NO₄, crystallizes in a monoclinic crystal system. One of the piperidine rings is in a sofa conformation while the other adopts a conformation between a half chair and a sofa. The coumarin moiety is planar; the molecules are stacked in layers parallel to (20 $\bar{2}$). The crystal packing is governed by van der Waals forces.

Comment

The title compound, (I), is a rigidized aminocoumarin derivative and is used as a laser dye. Its photophysical properties have been studied extensively by Sahyun & Sharma (1992), and Reynolds & Drexhage (1975). The crystal structure determination of this compound was performed in order to examine the conformational

Bond lengths and angles in the coumarin ring system of the title structure display normal values and are in agreement with those observed in coumarin 480, which is also a rigidized coumarin molecule with a methyl group at C4 (Chinnakali, Sivakumar & Natarajan, 1990). Another analogue, coumarin 337, with a cyano (C≡N) group at C3 (Chinnakali, Selladurai, Sivakumar, Subramanian & Natarjan, 1990) shows disorder in the quinolizine ring system; therefore, the structural features of the present molecule are compared with coumarin 480. The coumarin ring system is planar with a maximum deviation of 0.022 (2) Å for C3. All these coumarin compounds are used in laser-dye studies.

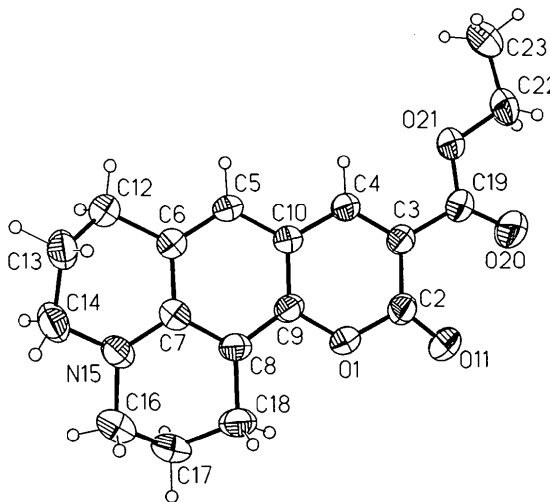


Fig. 1. Structure of coumarin 314 with the atomic numbering scheme showing 50% probability displacement ellipsoids.

The significant feature in these rigidized coumarins is the single bond C—C distances and endocyclic valence angles in the piperidine ring system. In general the C_{sp³}—C_{sp³} bond lengths are less than the ideal values. In our case, the C—C bond lengths range from 1.500 (3) to 1.522 (3) Å with an average value of 1.510 Å, whereas coumarin 480 shows much shorter values, C13—C14 is the shortest [1.451 (11) Å], the maximum is C6—C12 [1.508 (7) Å] and the average value is 1.487 Å.

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The average value of the endocyclic bond angles at C_{sp^3} atoms is 110.4° for the present case and 112.8° for coumarin 480.

In the quinolizine ring system, one of the piperidine rings (C7—C6—C12—C13—C14—N15) has a conformation between a sofa and a half chair. This is evident from the asymmetry parameters $\Delta C_s(C7) = 0.095(1)$ and $\Delta C_2(C7—N15) = 0.052(1)$. The other piperidine ring, consisting of C7—C8—C18—C17—C16—N15, adopts a sofa conformation [asymmetry parameter $\Delta C_s(C7) = 0.027(1)$] (Nardelli, 1983a). In the case of coumarin 480, both piperidine rings adopt half-chair conformations.

Also, in the ethoxycarbonyl side chain, the C—C single-bond distances are shorter than the usual values. The shorter C19=O20 bond [$1.188(2) \text{ \AA}$] is as expected for a conjugated C=O bond (Low & Wilson, 1984; Skrzat & Roszak, 1986). This shortening may also be influenced by the relatively high thermal motion of O20; such cases are common among C=O lengths in acetoxy groups (Ravikumar, Rajan, Sivakumar & Natarajan, 1989). The ethoxycarbonyl group is nearly planar and is slightly twisted from the coumarin ring. The dihedral angle between the planes of the ethoxycarbonyl group and the coumarin moiety is $12.29(7)^\circ$.

The packing of the molecules viewed down the *b* axis shows (Fig. 2) that the molecules are stacked in layers parallel to $(20\bar{2})$ planes with an interlayer spacing of 3.624 \AA . An interesting feature observed among the packing modes of the rigidized aminocoumarins is that the molecules are stacked in parallel planes with an interlayer distance of around 3.6 \AA , 3.673 \AA for coumarin 480 [layers parallel to the (201) plane], 3.612 \AA for coumarin 337 [layers parallel to the (200) plane] and all the three coumarins crystallize in the monoclinic crystal system.

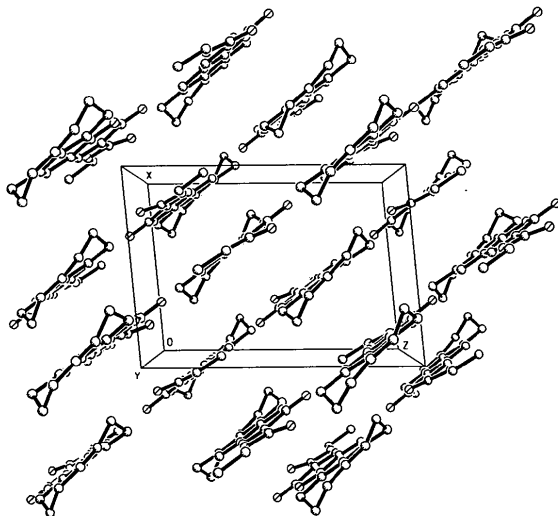


Fig. 2. Packing of the molecules viewed down the *b* axis.

Experimental

The compound was purchased from Aldrich and recrystallized from a mixture of chloroform and ethanol by slow evaporation.

Crystal data

$C_{18}H_{19}NO_4$
 $M_r = 313.34$
 Monoclinic
 $P2_1/n$
 $a = 8.532(1) \text{ \AA}$
 $b = 14.946(1) \text{ \AA}$
 $c = 12.022(1) \text{ \AA}$
 $\beta = 95.24(1)^\circ$
 $V = 1526.6(2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.363 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 8-25^\circ$
 $\mu = 0.097 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Transparent block
 $0.6 \times 0.4 \times 0.3 \text{ mm}$
 Yellow

Data collection

Siemens P4 four-circle diffractometer
 $\theta-2\theta$ scans
 Absorption correction: none
 4461 measured reflections
 3443 independent reflections
 2098 observed reflections
 $[I > 2\sigma(I)]$

$R_{int} = 0.0164$
 $\theta_{max} = 27.50^\circ$
 $h = -1 \rightarrow 11$
 $k = -1 \rightarrow 19$
 $l = -15 \rightarrow 15$
 3 standard reflections monitored every 100 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0432$
 $wR(F^2) = 0.1228$
 $S = 1.198$
 3443 reflections
 285 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0755P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.406 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.313 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL93 (Sheldrick, 1994)
 Extinction coefficient: 0.0085 (15)
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O1	-0.2312 (1)	0.1083 (1)	0.0191 (1)	0.0468 (3)
C2	-0.2392 (2)	0.2009 (1)	0.0053 (1)	0.0435 (4)
C3	-0.1502 (2)	0.2540 (1)	0.0902 (1)	0.0391 (3)
C4	-0.0671 (2)	0.2127 (1)	0.1785 (1)	0.0377 (3)
C5	0.0235 (2)	0.0727 (1)	0.2784 (1)	0.0413 (4)
C6	0.0250 (2)	-0.0186 (1)	0.2837 (1)	0.0434 (4)
C7	-0.0593 (2)	-0.0694 (1)	0.1962 (1)	0.0406 (4)
C8	-0.1466 (2)	-0.0252 (1)	0.1074 (1)	0.0400 (4)
C9	-0.1454 (2)	0.0670 (1)	0.1070 (1)	0.0379 (4)
C10	-0.0616 (2)	0.1190 (1)	0.1902 (1)	0.0380 (3)
O11	-0.3204 (2)	0.2260 (1)	-0.0756 (1)	0.0646 (4)
C12	0.1137 (3)	-0.0692 (1)	0.3777 (2)	0.0577 (5)
C13	0.1837 (2)	-0.1533 (1)	0.3314 (2)	0.0598 (5)
C14	0.0537 (2)	-0.2109 (1)	0.2774 (2)	0.0562 (5)
N15	-0.0550 (2)	-0.1606 (1)	0.2002 (1)	0.0495 (4)
C16	-0.1526 (2)	-0.2159 (1)	0.1208 (2)	0.0543 (5)
C17	-0.2936 (2)	-0.1661 (1)	0.0693 (2)	0.0529 (5)

C18	-0.2428 (2)	-0.0784 (1)	0.0190 (2)	0.0518 (4)
C19	-0.1489 (2)	0.3518 (1)	0.0759 (1)	0.0490 (4)
O20	-0.1926 (3)	0.3904 (1)	-0.0076 (2)	0.1249 (9)
O21	-0.0859 (1)	0.3945 (1)	0.1654 (1)	0.0526 (3)
C22	-0.0802 (3)	0.4914 (1)	0.1615 (2)	0.0610 (5)
C23	0.0134 (3)	0.5231 (1)	0.2643 (2)	0.0641 (5)

Table 2. Selected geometric parameters (Å, °)

O1—C9	1.376 (2)	C8—C9	1.378 (2)
O1—C2	1.394 (2)	C8—C18	1.509 (2)
C2—O11	1.202 (2)	C9—C10	1.408 (2)
C2—C3	1.451 (2)	C12—C13	1.519 (3)
C3—C4	1.369 (2)	C13—C14	1.503 (3)
C3—C19	1.472 (2)	C14—N15	1.459 (2)
C4—C10	1.408 (2)	N15—C16	1.463 (2)
C5—C6	1.366 (2)	C16—C17	1.500 (3)
C5—C10	1.411 (2)	C17—C18	1.522 (3)
C6—C7	1.436 (2)	C19—O20	1.188 (2)
C6—C12	1.505 (2)	C19—O21	1.322 (2)
C7—N15	1.365 (2)	O21—C22	1.450 (2)
C7—C8	1.410 (2)	C22—C23	1.487 (3)
C9—O1—C2	123.6 (1)	C14—N15—C16	114.5 (1)
O11—C2—O1	115.1 (1)	N15—C16—C17	112.1 (2)
O11—C2—C3	128.6 (2)	C16—C17—C18	110.2 (2)
O1—C2—C3	116.3 (1)	C8—C18—C17	109.3 (1)
C6—C12—C13	109.2 (2)	O20—C19—O21	121.7 (2)
C14—C13—C12	109.4 (2)	O20—C19—C3	125.1 (2)
N15—C14—C13	112.4 (1)	O21—C19—C3	113.0 (1)
C7—N15—C14	123.4 (1)	C19—O21—C22	117.9 (1)
C7—N15—C16	122.0 (1)	O21—C22—C23	108.0 (2)
C12—C6—C7—N15	-0.8 (2)	C8—C7—N15—C16	-6.8 (2)
N15—C7—C8—C18	3.2 (2)	C13—C14—N15—C7	-13.7 (3)
C7—C6—C12—C13	36.3 (2)	C7—N15—C16—C17	-22.2 (2)
C6—C12—C13—C14	-59.9 (2)	N15—C16—C17—C18	53.1 (2)
C12—C13—C14—N15	49.3 (2)	C7—C8—C18—C17	28.0 (2)
C6—C7—N15—C14	-11.7 (3)	C16—C17—C18—C8	-55.0 (2)

The structure was solved in the space group $P2_1$ and refined in $P2_1/n$. All the H atoms were located from difference Fourier maps and refined isotropically. *PARST* (Nardelli, 1983b) was used for geometrical calculations and *SHELXTL/PC* (Sheldrick, 1990) for molecular graphics.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: KH1015). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 958–960

3-Hydroxyimino-5 α ,13 α ,14 β ,17 α -lanosta-8,24-dien-20-oic Acid

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Abstract

Rings *B* and *C* in the title compound, C₃₀H₄₇NO₃, have a common double bond and adopt an envelope shape, whereas ring *D* assumes a half-chair conformation. Crystal packing is established by intermolecular hydrogen bonds forming infinite helices of the molecules.

Comment

'Elemi' acids isolated from *Manila elemi* resins may exist in either 3-hydroxy or 3-oxo forms. Ruzicka and co-workers (Ruzicka & Häusermann, 1942; Ruzicka, Rey & Spillmann, 1942; Ruzicka, Rey, Spillmann & Baumgartner, 1943) systematically elucidated the relationships between the tetracyclic triterpenes (*e.g.* squalene, lanosterol) and, among others, derived the chemical structures of α -elemolic and β -elemonic acids. These natural products may be used as raw materials for the semisynthesis of some biologically active steroids. The crystal structure of the title compound, (I), *i.e.* the oxime of β -elemonic acid, is reported in this paper.