

Table 1. Selected geometric parameters (\AA , $^\circ$)

N1—C2	1.357 (3)	C6—C7	1.372 (4)
N1—C8	1.381 (3)	C7—C8	1.391 (3)
C2—C3	1.375 (3)	C8—C9	1.408 (3)
C3—C10	1.442 (3)	C10—C11	1.329 (3)
C3—C9	1.447 (3)	C11—C12	1.472 (3)
C4—C5	1.382 (4)	C12—O14	1.238 (3)
C4—C9	1.397 (3)	C12—N13	1.336 (3)
C5—C6	1.393 (4)		
C2—N1—C8	108.9 (2)	N1—C8—C9	107.9 (2)
N1—C2—C3	110.6 (2)	C7—C8—C9	123.0 (2)
C2—C3—C10	122.6 (2)	C4—C9—C8	117.9 (2)
C2—C3—C9	106.0 (2)	C4—C9—C3	135.5 (2)
C10—C3—C9	131.2 (2)	C8—C9—C3	106.6 (2)
C5—C4—C9	119.4 (2)	C11—C10—C3	128.9 (3)
C4—C5—C6	121.3 (3)	C10—C11—C12	121.2 (2)
C7—C6—C5	121.1 (3)	O14—C12—N13	121.5 (2)
C6—C7—C8	117.4 (3)	O14—C12—C11	122.8 (2)
N1—C8—C7	129.1 (2)	N13—C12—C11	115.7 (2)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O14 ⁱ	0.90 (3)	2.09 (3)	2.945 (3)	157 (2)
N13—H13A...O14 ⁱⁱ	0.94 (3)	1.95 (3)	2.892 (3)	173 (2)

Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

The data were collected using a 1.0 mm collimator. The structure was solved by direct methods, locating all non-H atoms. All H atoms were located on difference Fourier maps and freely refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1071). Services for accessing these data are described at the back of the journal.

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Taraxerone

MASOOD PARVEZ,^a WASEEM GUL,^a MOHAMMAD YOUSAF,^b M. IQBAL CHOUDHARY,^b ATTA-UR-RAHMAN^b AND M. RIAZ KHAN^b

^aDepartment of Chemistry, The University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4, and ^bHEJ Research Institute of Chemistry, University of Karachi, Karachi-75270, Pakistan. E-mail: parvez@acs.ualgary.ca

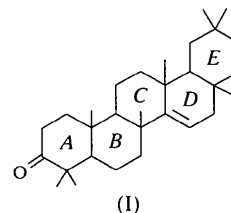
(Received 10 July 1998; accepted 28 September 1998)

Abstract

The crystal structure of taraxerone (*D*-friedoolean-14-en-3-one), $C_{30}H_{48}O$, a pentacyclo-triterpenoid isolated from *Skimmia laureola*, is composed of independent molecules which are separated by normal van der Waals distances. The molecular dimensions are normal, with mean bond distances as follows: Csp^3-Csp^3 1.539 (17), Csp^3-Csp^2 1.519 (19), $C=C$ 1.338 (3) and $C=O$ 1.199 (4) \AA . The structure is composed of five six-membered rings, with two rings in chair, one in twisted boat and two in slightly twisted boat conformations.

Comment

Skimmia laureola, a plant indigenous to the Western Himalayas, is abundant in the Bagh district, Azad Kashmir, Pakistan. It contains a large number of terpenoids, including the title compound, (I). In this article we report the molecular structure of (I), which has been determined unequivocally by the X-ray crystallographic method; (I) has also been reported as one of the constituents of *Myrica rubra* (Sakurai *et al.*, 1987).



(I)

The crystal structure of the title compound contains independent molecules (Fig. 1), which are separated by normal van der Waals distances. The molecular dimensions in (I) are normal, and lie within expected ranges for the corresponding bond distances and angles, with mean bond distances as follows: Csp^3-Csp^3 1.539 (17), Csp^3-Csp^2 1.519 (19), $C=C$ 1.338 (3) and $C=O$ 1.199 (4) \AA .

The structure is composed of five six-membered rings. Rings A and B have chair conformation, with puckering

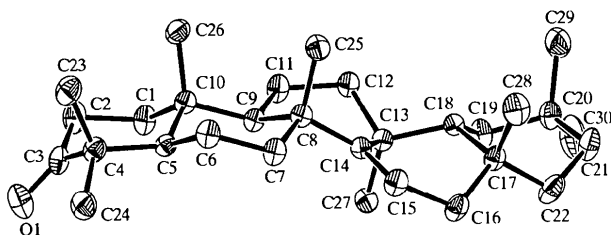


Fig. 1. ORTEP (Johnson, 1976) drawing of a molecule of (I), with the atomic numbering scheme. Displacement ellipsoids are plotted at the 30% probability level; H atoms have been omitted for clarity.

parameters (Cremer & Pople, 1975) $Q = 0.537(3)$ and $0.585(3)$ Å, $\theta = 6.7(3)$ and $8.8(3)^\circ$ and $\varphi = 12(3)$ and $358.7(17)^\circ$, respectively. Ring C adopts a twisted boat conformation, with puckering parameters $Q = 0.705(2)$ Å, $\theta = 86.9(2)^\circ$ and $\varphi = 21.9(2)^\circ$. Rings D and E are in slightly twisted boat conformations, with puckering parameters $Q = 0.625(3)$ and $0.719(3)$ Å, $\theta = 92.1(3)$ and $88.4(2)^\circ$, and $\varphi = 9.0(2)$ and $296.5(2)^\circ$, respectively.

Crystal structures bearing the basic skeleton of (I) which have already been reported include baurenyl acetate (Tinant *et al.*, 1982), swertanone (Chakravarty *et al.*, 1989), *p*-bromobenzyl-3-acetylmaprounate (McPhail *et al.*, 1989), 26-nor-*D*:*A*-friedoolean-14-en-3 β -yl-*p*-bromobenzoate (Matsunaga *et al.*, 1993) and isoursenyl acetate (Nielsen *et al.*, 1994).

Experimental

The air dried aerial parts of *Skimmia laureola* (20 kg) collected from the Bagh district, Azad Kashmir, Pakistan, were ground and extracted with ethanol (50 l). The ethanolic extract was evaporated under reduced pressure to a gum, which was defatted with petroleum ether (313–333 K). The petroleum ether fraction (200.4 g) was chromatographed on a silica gel column and eluted with *n*-hexane/chloroform (95:5 *v/v*). Repeated crystallization of the first few fractions from *n*-hexane/methanol (50:50 *v/v*) afforded colourless plates (450.1 mg) of taraxerone. Crystals suitable for X-ray crystallographic study were grown from acetone at room temperature by slow evaporation.

Crystal data

C₃₀H₄₈O
 $M_r = 424.68$
 Triclinic
 $P1$
 $a = 6.229(2)$ Å
 $b = 7.3544(7)$ Å
 $c = 15.137(3)$ Å
 $\alpha = 90.80(1)^\circ$
 $\beta = 97.34(2)^\circ$
 $\gamma = 113.63(1)^\circ$
 $V = 628.5(2)$ Å³
 $Z = 1$
 $D_x = 1.122$ Mg m⁻³
 D_m not measured

Cu $K\alpha$ radiation
 $\lambda = 1.54178$ Å
 Cell parameters from 25 reflections
 $\theta = 20$ – 30°
 $\mu = 0.483$ mm⁻¹
 $T = 293(1)$ K
 Prismatic
 $0.40 \times 0.27 \times 0.20$ mm
 Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 4453 measured reflections
 4453 independent reflections
 4108 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 68^\circ$
 $h = -6 \rightarrow 7$
 $k = -8 \rightarrow 8$
 $l = -18 \rightarrow 18$
 3 standard reflections
 every 200 reflections
 intensity decay: 2.1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.148$
 $S = 1.060$
 4453 reflections
 281 parameters
 H atoms riding
 $w = 1/[\sigma^2(F_o^2) + (0.096P)^2 + 0.112P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.252$ e Å⁻³
 $\Delta\rho_{\min} = -0.212$ e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)
 Absolute structure: Flack (1983)
 Flack parameter = 0.2 (5)

Based on a statistical analysis of intensity distribution, packing considerations, and successful solution and refinement of the structure, the space group was determined to be $P1$ (No. 1). Friedel opposites (2287) were collected and were not merged. The H atoms were allowed in the refinement at geometrically idealized positions, with C—H at 0.95 Å. The absolute configuration of taraxerone could not be established in this analysis. However, refinement of the inverted structure yielded a Flack parameter of 0.8 (5) and was, therefore, disregarded.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1044). Services for accessing these data are described at the back of the journal.

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Flemiculosin, a novel chalcone

KINKINI BHATTACHARYYA,^a SUNIL KUMAR MAZUMDAR,^a
GABRIELE BOCELLI,^b ANDREA CANTONI,^b ANIL B. RAY,^c
PARTHA NEOGI^c AND GAURI MAZUMDAR^d

^aDepartment of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India, ^bDiffrattometrica del CNR, Viale delle Scienze, Palazzo Chimico I-43100, Parma, Italy, ^cDepartment of Medicinal Chemistry, Banaras Hindu University, Varanasi 221 005, India, and ^dB. Barooah College, Guahati 781 007, India. E-mail: mskb@mahendra.iacs.res.in

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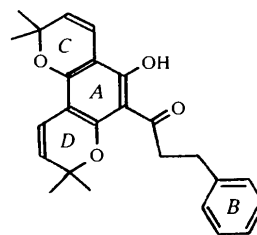
Abstract

The title compound, 6-cinnamoyl-5-hydroxy-2,2,8,8-tetramethyl-2*H*,8*H*-pyrano[2,3-*f*]chromene, C₂₅H₂₄O₄, is an angular benzodipyran system. It contains a central tricyclic core and a peripheral aromatic ring. The central ring of the tricyclic core is fully substituted while the pyran rings on either side are each unsubstituted at two sites. The central fully substituted ring is planar within 0.014 Å. One pyran ring is planar to within 0.041 Å, but the second pyran ring is only planar to within 0.156 Å; this may be attributed to an intramolecular C—H...O contact of 2.30 Å. The structure is stabilized by intramolecular O—H...O hydrogen bonds.

Comment

The genus *Flemingia* is notable for including a variety of flavanoids, particularly stromenochalcones; a number of *Flemingia* species have been examined chemically (Adityachaudhury *et al.*, 1970; Adityachaudhury & Gupta, 1970; Bhatt, 1975). Flemiculosin, (I), a novel chalcone with an angular benzodipyran system, has been studied chemically, and NMR and spectroscopic studies have been carried out by Khattri *et al.* (1984). We report

here the X-ray structure determination of flemiculosin undertaken to provide more details of the structure.



(I)

The title compound has been isolated from the leaves of *Flemingia fruticulosa* wall. (Leguminosae). Flemiculosin is unique among chalcones being the first member of the flavanoid class of compounds to have a benzodipyran unit. It is a 2'-hydroxychalcone in which ring B is unsubstituted and ring A is completely substituted as part of the benzodipyran system. The oxygen substitution pattern of ring A is also biogenetically consistent as prenyl substituents in flavonoids and other related carbo-aromatic compounds are mostly found between two oxygen substituents. The benzodipyran system is not planar: ring A makes angles of 1.94 (7) and 6.36 (6)° with rings C and D, respectively. In the cinnamoyl moiety, the least-squares plane through atoms C6—C11—C12—C13 makes an angle of 20.4 (2)° with the benzene ring, B. This plane is not coplanar with ring A, as shown by the torsion angles C5—C6—C11—C12 [167.4 (2)] and C4'—C6—C11—C12 [−14.6 (3)°]. In the same moiety, O25 lies 0.340 (2) Å above the C6—C11—C12—C13 plane. O24 is nearly coplanar with ring A. The central double bond (C12=C13) has a *trans* configuration and the length of the C11=C25 bond is similar to that seen in related chalcones such as the two nitro- α -methoxy-*trans*-chalcones described

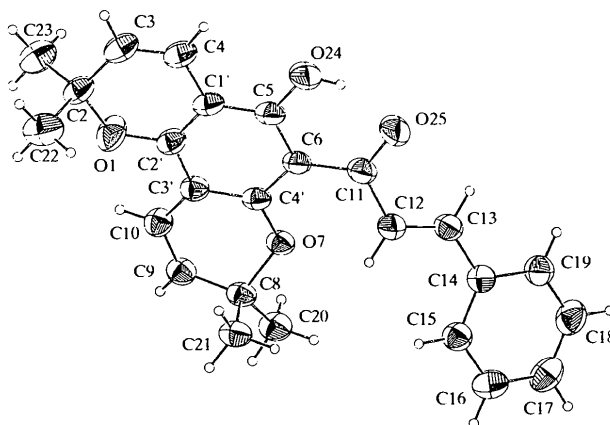


Fig. 1. Structure of the title compound showing 30% probability displacement ellipsoids and atom numbering. H atoms are shown with an arbitrary radius.