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An anomalous racemate of naringenin at 120 K

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.005 Å
R factor = 0.067
wR factor = 0.155
Data-to-parameter ratio = 15.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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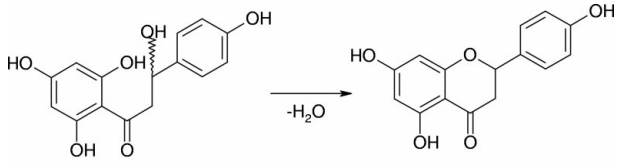
Unlike a previously reported structure for racemic naringenin [systematic name: 2,3-dihydro-5,6-dihydroxy-2-(4-hydroxyphenyl)-4*H*-1-benzopyran-4-one], $C_{15}H_{12}O_5$, both *S* and *R* enantiomers appear to occupy somewhat randomly the four crystallographic sites of the unit cell in an approximate 3:1/1:3 ratio.

Comment

The crystal structure of racemic naringenin has been reported in space group $P2_1/c$ at 295 K with a = 4.965 (3), b = 15.449 (6), c = 16.845 (8) Å and β = 103.86 (8)° (Shin & Lah, 1986). This cell reduces (Spek, 1988) to a = 4.965, b = 15.449, c = 16.381 Å and β = 93.25° in $P2_1/n$. These reduced values are very similar to the cell parameters in the present low-temperature study. The expected small reduction in cell volume from the previous value of 1254 (2) to 1220.5 (14) Å^3 is also observed.



(I) (II)

However, whereas the previous structure was apparently normal, the present study reveals a structure in which both enantiomers are somewhat randomly, not systematically, arranged in the crystal lattice. Hence, characteristics of a solid solution are present. The ratio of the two enantiomers (*S*:*R*) in the asymmetric unit in this crystallographic analysis is 0.775:0.225 (9), which gives an approximate 3:1/1:3 ratio in the centrosymmetric crystal structure overall. As the space group

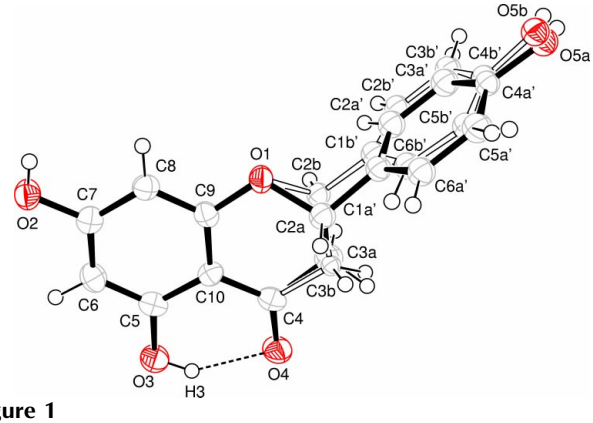


Figure 1
The atomic arrangement in the overlapping enantiomers. The atoms of the *R* enantiomer are linked with open bonds. Displacement ellipsoids are shown at the 50% probability level.

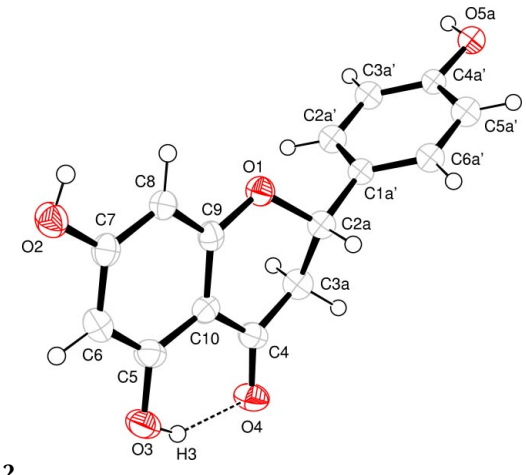


Figure 2
The atomic arrangement in the *S* enantiomer. Displacement ellipsoids are shown at the 50% probability level.

multiplicity is 4, this might suggest an equal number of two types of unit cells. One such cell would contain three (*S*) enantiomers and one (*R*) enantiomer, and its complementary cell would contain three (*R*) enantiomers and one (*S*) enantiomer, such that the overall ratio of *S*:*R* remains as 1:1 in the racemate. Other more elaborate substitution schemes are also possible, but it seems that in every unit cell one or other of the four sites is occupied by the 'wrong' enantiomer. The integrity of the crystal structure is maintained by the close overlap of equivalent atom positions in the two enantiomers, which can easily substitute for each other.

The formation of anomalous racemates (3:1/1:3) of tetramisole has been reported (Töke *et al.*, 1979), and evidence for anomalous racemates (4:1/1:4) of carvone has been presented (Gallis *et al.*, 1999). Accomodation of enantiomers at the same sites in a completely random distribution is also known, *e.g.* crystal structures of the solid solutions formed by racemic 3-carboxyproxyl (Cox *et al.*, 1995) and the hydrate of 8,11-dihydroxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-carbolactam (Kruger *et al.*, 1996). Furthermore, crystallographic studies on solid solutions of tetracosane/hexacosane and icosane/docosane (Gerson & Nyburg, 1994) show that these structures are often associated with high conventional *R* values (0.09 and 0.12, respectively).

The classical hydrogen bonding given in Table 2 (for the major occupancy only) is similar to that reported previously for this compound.

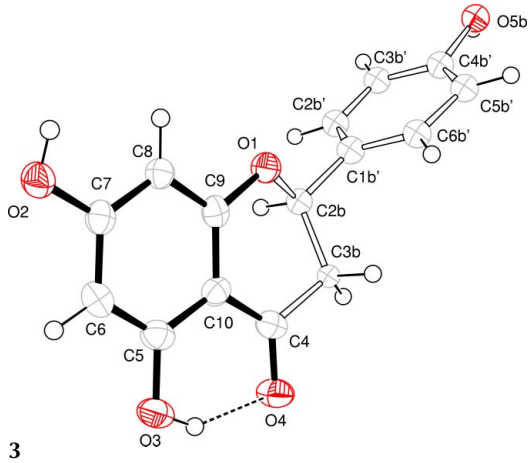


Figure 3
The atomic arrangement in the *R* enantiomer. Displacement ellipsoids are shown at the 50% probability level.

Experimental

The precursor, (I), of the title compound, (II), was extracted from *Euonymus europaeus* L. (Celastraceae), and naringenin was formed by the subsequent elimination of water during recrystallization from ethanol.

Crystal data

$C_{15}H_{12}O_5$
M_r = 272.25
Monoclinic, $P2_1/n$
a = 4.8740 (5) Å
b = 15.2610 (15) Å
c = 16.423 (2) Å
β = 92.375 (5)°
V = 1220.5 (2) Å^3
Z = 4
D_x = 1.482 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 13 970 reflections
θ = 2.9–27.5°
μ = 0.11 mm^{-1}
T = 120 (2) K
Needle, colourless
0.38 × 0.06 × 0.04 mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
T_{min} = 0.959, T_{max} = 0.996
11 748 measured reflections
2701 independent reflections
1099 reflections with $I > 2\sigma(I)$
R_{int} = 0.158
θ_{max} = 27.5°
$h = -6 \rightarrow 6$
$k = -18 \rightarrow 19$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.155
S = 0.93
2701 reflections
170 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C9	1.370 (4)	O5*A*—C4*A*′	1.385 (5)
O1—C2*B*	1.446 (14)	C2*A*—C3*A*	1.515 (7)
O1—C2*A*	1.457 (5)	C2*A*—C1*A*′	1.493 (6)
O2—C7	1.368 (4)	O5*B*—C4*B*′	1.378 (14)
O3—C5	1.343 (4)	C2*B*—C3*B*	1.508 (15)
O4—C4	1.251 (4)	C2*B*—C1*B*′	1.499 (14)
O1—C2*A*—C3*A*	109.9 (4)	C3*B*—C2*B*—O1	112.6 (13)
O1—C2*A*—C1*A*′	108.8 (3)	C3*B*—C2*B*—C1*B*′	115.7 (13)
C3*A*—C2*A*—C1*A*′	114.2 (4)	O1—C2*B*—C1*B*′	107.8 (11)
O1—C2*A*—C3*A*—C4	−53.1 (7)	O1—C2*B*—C3*B*—C4	52 (2)
C1*A*′—C2*A*—C3*A*—C4	−175.6 (5)	C1*B*′—C2*B*—C3*B*—C4	176.3 (14)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O4	0.84	1.89	2.624 (3)	145
O2—H2···O5*A*^{i}	0.84	2.00	2.788 (6)	156
O5*A*—H5*A*···O4^{ii}	0.84	1.88	2.713 (6)	172
O5*B*—H5*B*···O4^{ii}	0.84	2.01	2.651 (18)	133

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}+z$.

In the present analysis, many atoms overlap directly (Fig. 1) and some overlap partially, but atoms at position 2 in the pyrone ring [C2A and H2A (higher occupancy factor) and C2B and H2B (lower occupancy factor)] are clearly resolved. Separate views of the two enantiomers are shown in Figs. 2 and 3. In the two groups of atoms, C2*A*/C3*A*/C1*A*′–C6*A*′/O5*A* and C2*B*/C3*B*/C1*B*′–C6*B*′/O5*B*, the bonds were restrained to be equal, isotropic displacement parameters were used, and common occupancy factors for the group atoms converged at 0.775 (8) and 0.225 (8), respectively. The isotropic displacement parameters of aromatic atoms C1*B*′–C6*B*′ were restrained to refine with a common value which converged at 0.028 Å^2. Other non-H atoms were refined with anisotropic displacement parameters. H atoms were placed in calculated positions and allowed to ride on their attached atoms, with each isotropic displacement parameter set at 1.2U_{eq} of the attached atom.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*,1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *PLATON* (Spek, 2001).

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