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Epiclusianone: a New Natural Product Derivative of Bicyclo[3.3.1]nonane-2,4,9-trione

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Abstract

Epiclusianone [3-benzoyl-4-hydroxy-6,6-dimethyl-1,5,7-tris(3-methyl-2-butenyl)bicyclo[3.3.1]non-3-ene-2,9-dione] is a new isomeric form of the $C_{33}H_{42}O_4$ compound identified by X-ray diffraction analysis. Structure comparison with the known clusianone evidences a case of epimerism in one of the chiral C atoms. A comparison of the melting point and the optical activity of the two isomers shows them to have different values.

Comment

The title compound, (I), was isolated from *Rheedia gardneriana*. NMR, UV, IR and MS characterization indicated a formula of $C_{33}H_{42}O_4$ for the compound, which is consistent with clusianone [(II); McCandlish *et al.*, 1976; Delle Monache *et al.*, 1991; Oliveira *et al.*, 1996]. The values obtained for the melting point and optical rotation of (I) (m.p. 365–366 K and $[\alpha]_D^{25}$ +77°, respectively) were inconsistent with those previously determined for clusianone, (II). In addition, the NMR spectra

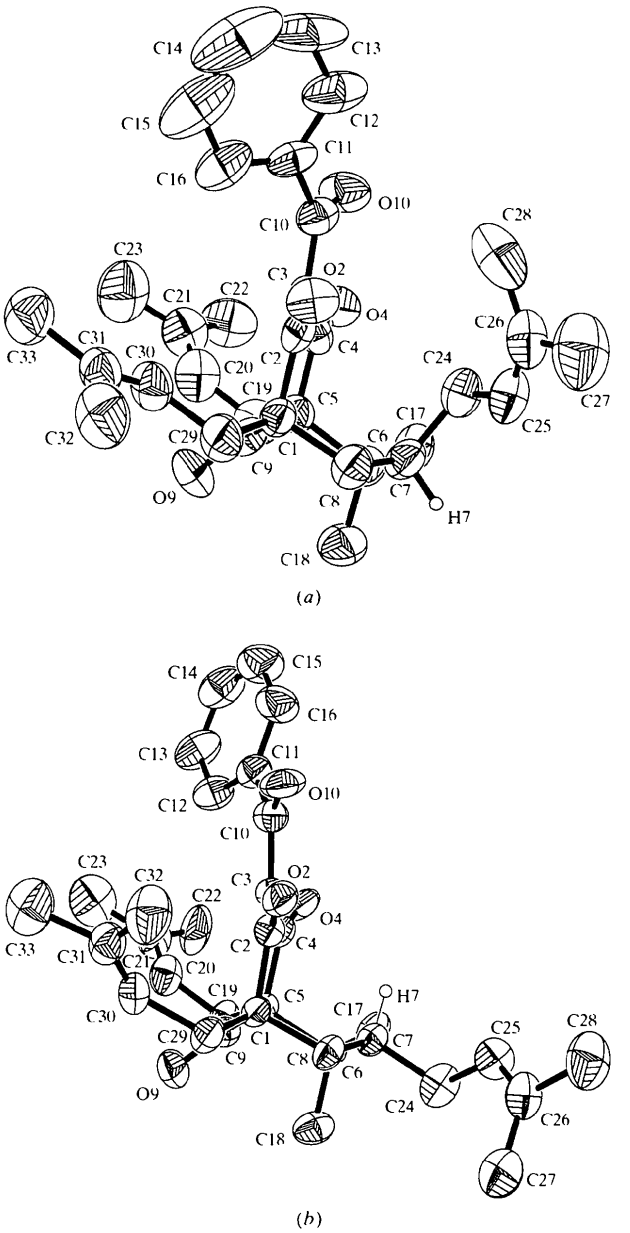


Fig. 1. A view of the molecular structures of (*a*) (I) and (*b*) (II) with 50% probability ellipsoids. The different configurations of the isopentenyl group and the H atom bound to C7 can be seen clearly.

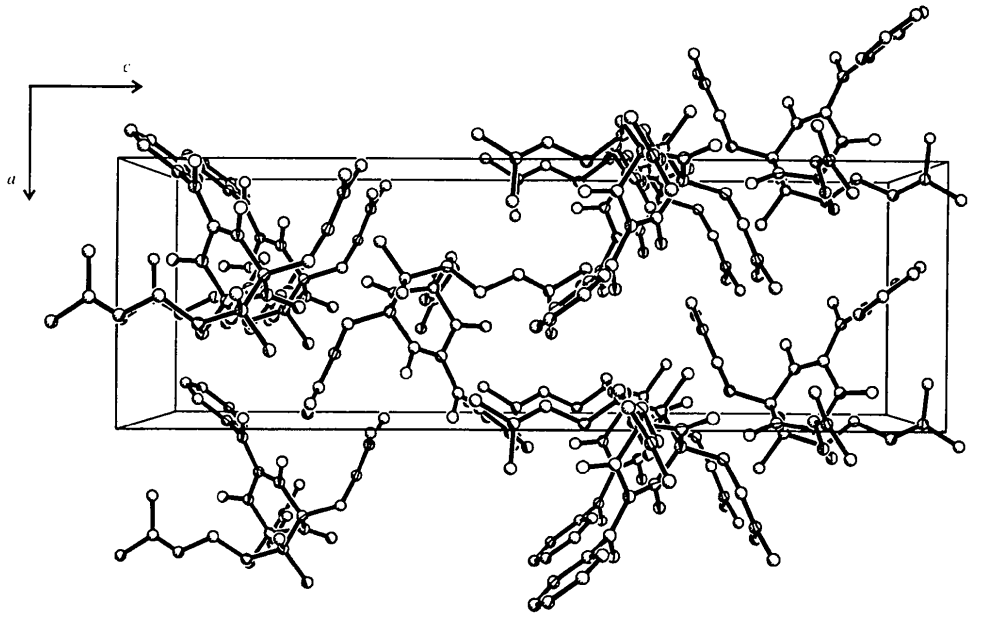
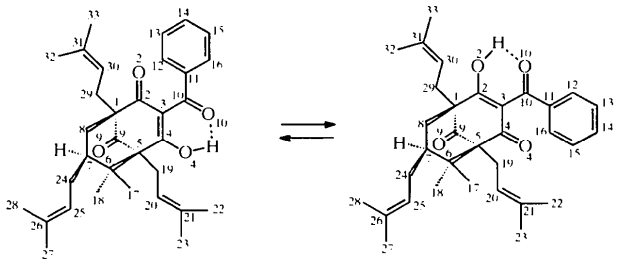


Fig. 2. Packing diagram of epiclusianone, (I).

(^{1}H and ^{13}C) evidenced a tautomeric equilibrium caused by the enolizable character of the 2,4-dione system (see Scheme below); this made an unambiguous interpretation of the spectra difficult. Therefore, X-ray structure determination was undertaken to unambiguously determine the structure of (I).



(I)

X-ray diffraction analysis of (I) elucidated its structure, which when compared with that of (II) shows a configurational difference in the C7 atom. Both structures are shown in Fig. 1. Considering a plane that passes through atoms C1, C5 and C7, it is possible to see that the isopentenyl group (C24—C28) is opposite the H7 atom. In (II), the isopentenyl group is below this plane, *i.e.* in an equatorial position, while in (I), it is above the plane, *i.e.* in an axial position. These two configurations are quite common in Guttiferae family compounds (Gustafson *et al.*, 1992). Another difference is observed in the benzoyl group, which is rotated about 180° around the C3—C10 axis in one structure compared with the other. As a consequence the structure stabilization is probably attained *via* hydrogen bonds; O4—H4O···O10 in (I) and O2—H2O···O10 in (II). The unusually long C5—C6 bond observed in (II) [1.603(4) Å] is also found in (I) [1.610(7) Å] and in both cases is due both to the high degree of substitution and to steric factors (McCandlish *et al.*, 1976, and references therein). The configuration difference at C7 is the main reason for the difference in packing (Fig. 2): the unit-cell volume is 5% larger in (I) than (II) (McCandlish *et al.*, 1976). The epimerization may also be the reason for the significant differences in the melting point and the optical activity values.

Experimental

Fruits of *Rheedia gardneriana* collected at the Universidade Federal de Viçosa (UFV) were subjected to chemical analysis. Epiclusianone, (I), was obtained by purification of hexane extract of the bark taken from a silica-gel chromatographic column. Single crystals were obtained by evaporation from a methanol solution and were used for the X-ray diffraction analysis.

Crystal data

$C_{33}H_{42}O_4$
M_r = 502.7
Orthorhombic
$P2_12_12_1$
a = 8.777 (2) Å
b = 12.557 (2) Å
c = 27.324 (5) Å
V = 3011.6 (11) Å^3
Z = 4
D_x = 1.109 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 27 reflections
θ = 10.93–12.43°
μ = 0.071 mm^{-1}
T = 298 K
Prism
0.20 × 0.16 × 0.16 mm
Light yellow

Data collection

Siemens P4 diffractometer	$\theta_{max} = 27.67°$
$\theta/2\theta$ scans	$h = -11 \rightarrow 11$
Absorption correction: none	$k = 0 \rightarrow 16$
6375 measured reflections	$l = 0 \rightarrow 35$
6055 independent reflections	3 standard reflections
2535 reflections with $F \geq 4\sigma(F)$	every 247 reflections
	intensity decay: none
$R_{int} = 0.06$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.007$
$R = 0.065$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
$wR = 0.059$	$\Delta\rho_{min} = -0.23$ e Å^{-3}
$S = 1.54$	Extinction correction: none
2495 reflections	Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV, Table 2.2*B*)
334 parameters	
H-atom parameters constrained	
$w=1/[\sigma(F)]$	

Table 1. *Selected geometric parameters (Å, °)*

O2—C2	1.208 (6)	C3—C4	1.380 (6)
O4—C4	1.299 (6)	C3—C10	1.449 (6)
O9—C9	1.209 (7)	C5—C6	1.610 (7)
O10—C10	1.268 (6)	C6—C7	1.557 (8)
C1—C8	1.562 (6)	C7—C24	1.540 (7)
C1—C9	1.496 (7)	C25—C26	1.302 (9)
C2—C3	1.460 (6)	C26—C27	1.499 (10)
C2—C1—C8	108.6 (4)	C9—C5—C19	111.3 (4)
C2—C1—C9	111.9 (4)	C5—C6—C7	111.5 (4)
C8—C1—C9	105.6 (4)	C6—C7—C8	112.1 (4)
C2—C1—C29	109.3 (4)	C6—C7—C24	117.4 (4)
C1—C2—C3	117.4 (4)	C1—C9—C5	114.2 (4)
C2—C3—C4	118.6 (4)	C3—C10—C11	123.2 (4)
C3—C4—C5	124.6 (4)	C7—C24—C25	112.7 (4)
C4—C5—C9	107.2 (4)	C25—C26—C27	125.5 (6)
C6—C5—C19	113.9 (4)		

The structure was solved by direct methods and analysis of the difference Fourier map. H atoms were placed in calculated positions and considered as riding atoms in the structure-factor calculations. The absolute structure could not be reliably determined [the calculated Flack (1983) parameter was 0 (3)] due to the fact that there is no atom heavier than the O atom.

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1009). Services for accessing these data are described at the back of the journal.

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β-1-*N*-Ureido-D-glucopyranose

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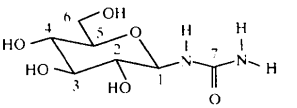
Abstract

β-1-*N*-Ureido-D-glucopyranose, $C_7H_{14}N_2O_6$, adopts a $^4C_1(D)$ conformation. The nearly planar urea moiety is in a *Z-anti* conformation.

Comment

β-1-*N*-Ureido-D-glucopyranose, (1), is conceptually amongst the simplest N-linked aldohexoses with a rigid group at the N atom. Analysis of a cocrystal of glucose and urea revealed strong hydrogen bonding between the two substrates (Snyder & Rosenstein, 1971). In this structure, rows of glucose molecules form layers in the channels formed by the urea. We envisioned that (1) could form a channel structure through an array of strong intermolecular hydrogen bonds. In the structure determined, the β-1-*N*-ureido-D-glucopyranose packs tightly, excluding water from the crystal lattice. Strong intermolecular hydrogen bonding is observed, but there is no evidence of channel formation.



(1)

The title compound was synthesized by the condensation of urea and glucose under acidic conditions (Schoori, 1903). The molecules crystallize in the ortho-