200 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 0.3777P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.285$ e Å^{-3}
$\Delta\rho_{min} = -0.397$ e Å^{-3}

Scattering factors from
International Tables for Crystallography (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.05 (5)

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

O3—C7	1.230 (8)	C1—C7	1.470 (9)
N2—C4	1.349 (8)	C2—C3	1.371 (8)
N2—C15	1.425 (9)	C3—C4	1.385 (9)
N2—C16	1.468 (9)	C4—C5	1.412 (9)
C1—C2	1.388 (8)	C5—C6	1.343 (8)
C1—C6	1.390 (8)		
C4—N2—C15	122.0 (6)	N2—C4—C3	123.2 (6)
C4—N2—C16	120.1 (6)	N2—C4—C5	120.5 (6)
C15—N2—C16	117.6 (6)	C3—C4—C5	116.2 (6)
C2—C1—C6	116.0 (6)	C6—C5—C4	120.6 (6)
C2—C1—C7	124.3 (6)	C5—C6—C1	123.6 (7)
C6—C1—C7	119.7 (5)	O3—C7—C1	121.6 (6)
C3—C2—C1	121.2 (7)	O3—C7—C8	118.4 (6)
C2—C3—C4	122.4 (6)	C1—C7—C8	120.0 (6)
C15—N2—C4—C3	−178.7 (7)	O3—C7—C8—C9	4.4 (11)
C16—N2—C4—C3	−5.1 (10)	C1—C7—C8—C9	−177.0 (7)
C15—N2—C4—C5	3.1 (11)	C7—C8—C9—C10	−63.2 (9)
C16—N2—C4—C5	176.7 (6)	O2—N1—C10—C11	139.7 (7)
C2—C1—C7—O3	176.2 (7)	O1—N1—C10—C11	−40.7 (10)
C6—C1—C7—O3	−5.4 (12)	O2—N1—C10—C9	−38.0 (10)
C2—C1—C7—C8	−2.4 (11)	O1—N1—C10—C9	141.6 (8)
C6—C1—C7—C8	176.0 (7)		

The title structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990). Refinement was performed using *SHELXL*97 (Sheldrick, 1997) using anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for the H atoms. Figures were drawn using *ZORTEP* (Zsolnai, 1994) and material for publication was prepared using *SHELXL*97. All calculations were carried out on a VAXstation 4000VLC computer system.
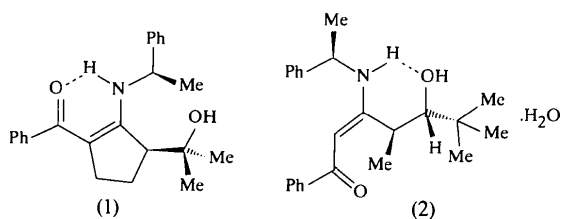
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Enantiopure δ-Hydroxy-β-enamino Ketones

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Abstract

The absolute configurations of 2-(α-methylbenzylamino)-3-(1-hydroxy-1-methylethyl)cyclopent-1-en-1-yl phenyl ketone, $C_{23}H_{27}NO_2$, and 5-hydroxy-4,6,6-trimethyl-3-(α-methylbenzylamino)-1-phenyl-2-hepten-1-one monohydrate, $C_{24}H_{31}NO_2.H_2O$, obtained by a directed enantioselective aldol condensation, have been ascertained to be ($\alpha R,3S$) and ($\alpha R,4S,5S$), respectively. While in the first cyclic δ-hydroxy-β-enamino ketone the enaminic N atom is hydrogen bonded to the carbonyl O atom, in the second acyclic compound, the N atom is hydrogen bonded to the hydroxyl group.

Comment

δ-Hydroxy-β-enamino ketones and related compounds are important structural subunits which are present in many synthetic targets of natural origin and in key intermediates in the construction of a wide variety of heterocyclic compounds. The introduction of an alkyl side chain containing a hydroxyl function of fixed configuration at the γ-position of β-enamino ketones and derivatives represents an important synthetic goal, since the added functionality would increase the synthetic scope of these intermediates. The aldol reaction is one of the more powerful tools for the stereoselective construction of acyclic molecules (Heathcock, 1991; Franklin & Paterson, 1994). Among the most important advantages of using an imine is the ability to introduce a 'stereogenic center' *via* an enantiomerically pure amine, thus enabling diastereoselective control of the C—C bond-forming process (Meyers *et al.*, 1981; Enders *et al.*, 1992; Denmark & Ares, 1988).

We have prepared two δ-hydroxy-β-enamino ketones with good stereoselectivity: 2-(α-methylbenzylamino)-3-(1-hydroxy-1-methylethyl)cyclopent-1-en-1-yl phenyl ketone, (1), and 5-hydroxy-4,6,6-trimethyl-3-(α-methylbenzylamino)-1-phenyl-2-hepten-1-one monohydrate, (2). As they have not been reported previously, it was necessary to determine their absolute configuration un-

equivocally by single-crystal X-ray analysis to understand the asymmetric induction mechanism.

(1)   (2)

The crystal structure of (1) contains one molecule of the δ-hydroxy-β-enamino ketone in the asymmetric unit and the crystal structure of (2) contains one molecule of the δ-hydroxy-β-enamino ketone and one molecule of water in the asymmetric unit. The absolute configurations of the δ-hydroxy-β-enamino ketones have been ascertained as ($\alpha R,3S$) and ($\alpha R,4S,5S$) for (1) and (2), respectively [commercially available (R)-(+)-α-methylbenzylamine was used in the preparation of the compounds]. The geometry of the phenyl rings is in good agreement with the accepted values although the atoms suffer from a high degree of thermal motion. The crystal structures are stabilized by a network of hydrogen bonds involving the enaminic N(1) atom, the carbonyl O(2) atom and the hydroxyl O(1) atom. In (1), the intramolecular N(1)—H(1)$\cdots$O(2) hydrogen-bonding distance is 2.639 (4) Å [H(1)$\cdots$O(2) = 1.81 Å] while the intermolecular O(1)—H(27)$\cdots$O(2^i) hydrogen-bonding distance is 2.743 (3) Å [H(27)$\cdots$O(2^i) = 1.89 Å] [symmetry code: (i) $\frac{1}{2} - x$, $1 - y$, $z - \frac{1}{2}$]. In (2), the intramolecular N(1)—H(1)$\cdots$O(1) hydrogen-bonding distance is 2.753 (5) Å [H(1)$\cdots$O(1) = 2.02 Å] while the intermolecular O(1)$\cdots$O(2^{ii}) hydrogen-bonding distance is 2.701 (5) Å [symmetry code: (ii) $\frac{2}{3} - y$, $-\frac{2}{3} + x - y$,

$\frac{1}{3} + z$]. The water oxygen atom O(3) is involved in three hydrogen bonds [distance 2.82 (2) Å] to equivalent O(3) sites related by a threefold axis.
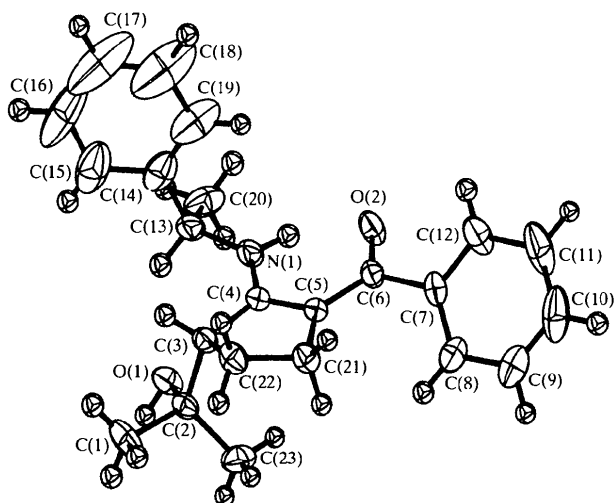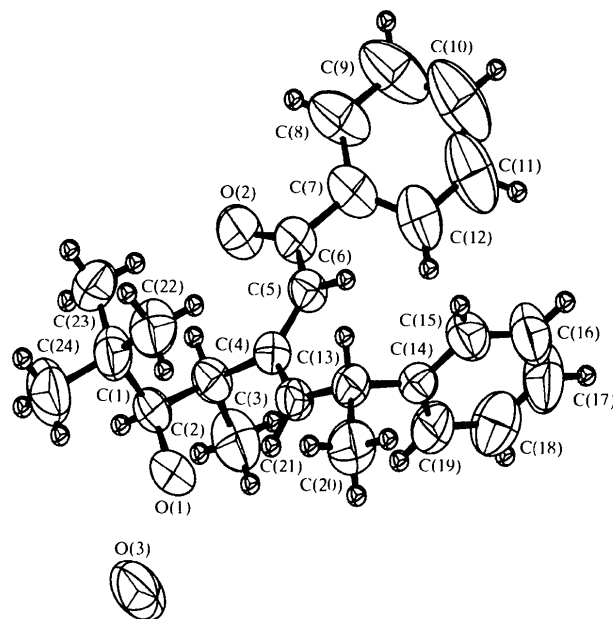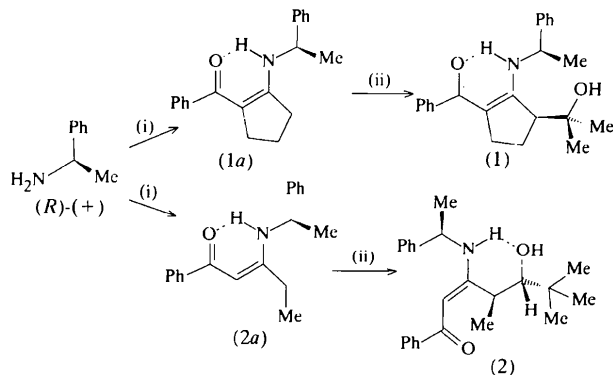

Fig. 2. Molecular structure of compound (2) with the atomic labeling scheme and drawn with displacement ellipsoids at the 30% probability level.

Experimental

The δ-hydroxy-β-enamino ketones (1) and (2) were prepared by treatment of enamino ketone (1a) or (2a) [obtained by condensation of α-methylbenzylamine with either 2-benzoyl-cyclopentanone for (1a) or 5-phenyl-3,5-pentadione for (2a)] in tetrahydrofuran with 3 eq methyllithium in the presence of 3 eq hexamethylphosphoramide and heated from 273 to 303 K for 30 min (Bartoli et al., 1992, 1993). These lithium dianions of (1a) and (2a) were then treated with 2.5 eq of acetone or pivaldehyde, respectively, at 173 K for 30 min. After quenching (H₂O/tetrahydrofuran, 223 K), chromatographic purification gave the enantiopure δ-hydroxy-β-enamino ketone (1) or (2) (Camalli et al., 1997).

Fig. 1. Molecular structure of compound (1) with the atomic labeling scheme and drawn with displacement ellipsoids at the 30% probability level.

Compound (1)

Crystal data

$C_{23}H_{27}NO_2$
$M_r = 349.47$
Orthorhombic
$P2_12_12_1$
$a = 10.802\,(3)$ Å
$b = 12.896\,(8)$ Å
$c = 14.936\,(6)$ Å
$V = 2080\,(2)$ Å^3
$Z = 4$
$D_x = 1.116$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 3–12°$
$\mu = 0.070$ mm^{-1}
$T = 296$ K
Prism
$0.5 \times 0.4 \times 0.3$ mm
Colorless

Data collection

Huber/CS diffractometer
$\theta/2\theta$ scans
Absorption correction:
   ψ scan (North et al., 1968)
$T_{min} = 0.84$, $T_{max} = 1.00$
3768 measured reflections
3391 independent reflections
1465 reflections with
   $I > 3\sigma(I)$

$R_{int} = 0.084$
$\theta_{max} = 30°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 20$
3 standard reflections
   every 97 reflections
   intensity decay: 4%

Refinement

Refinement on F
$R = 0.058$
$wR = 0.086$
$S = 1.178$
3390 reflections
235 parameters
H atoms rigid to parent C atom
$w = 1/[0.00025 + 0.05105F + 0.00085F^2]$

$(\Delta/\sigma)_{max} = 0.05$
$\Delta\rho_{max} = 0.2$ e Å^{-3}
$\Delta\rho_{min} = -0.2$ e Å^{-3}
Extinction correction: none
Scattering factors from
   International Tables for
   X-ray Crystallography
   (1974)

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

O(1)—C(2)	1.431 (3)	N(1)—C(4)	1.344 (4)
O(2)—C(6)	1.274 (4)	N(1)—C(13)	1.471 (5)
C(13)—N(1)—C(4)	128.7 (3)	C(23)—C(2)—C(1)	111.8 (3)
C(1)—C(2)—O(1)	107.4 (2)	C(23)—C(2)—C(3)	113.8 (3)
C(3)—C(2)—O(1)	105.8 (2)	C(5)—C(6)—O(2)	121.4 (3)
C(3)—C(2)—C(1)	109.0 (3)	C(7)—C(6)—O(2)	116.7 (2)
C(23)—C(2)—O(1)	108.7 (3)	C(7)—C(6)—C(5)	121.9 (2)

Compound (2)

Crystal data

$C_{24}H_{31}NO_2.H_2O$
$M_r = 383.52$
Trigonal
$R3$
$a = 27.132\,(5)$ Å
$c = 8.290\,(4)$ Å
$V = 5285\,(3)$ Å^3
$Z = 9$
$D_x = 1.084$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 15 reflections
$\theta = 20–26°$
$\mu = 0.526$ mm^{-1}
$T = 296$ K
Prism
$0.6 \times 0.4 \times 0.4$ mm
Colorless

Data collection

Rigaku AFC-5 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2114 measured reflections
1843 independent reflections
1699 reflections with
   $I > 2\sigma(I)$
$R_{int} = 0.056$

$\theta_{max} = 62°$
$h = 0 \rightarrow 31$
$k = -26 \rightarrow 0$
$l = -9 \rightarrow 9$
3 standard reflections
   every 97 reflections
   intensity decay: none

Refinement

Refinement on F
$R = 0.055$
$wR = 0.074$
$S = 0.997$
1843 reflections
252 parameters
H atoms rigid to parent atom
$w = 1/[20.7883 + 0.0125F + 0.0026F^2]$

$(\Delta/\sigma)_{max} = 0.05$
$\Delta\rho_{max} = 0.2$ e Å^{-3}
$\Delta\rho_{min} = -0.2$ e Å^{-3}
Extinction correction: none
Scattering factors from
   International Tables for
   X-ray Crystallography
   (1974)

Table 2. Selected geometric parameters (Å, °) for (2)

O(1)—C(2)	1.426 (8)	N(1)—C(4)	1.344 (8)
O(2)—C(6)	1.257 (7)	N(1)—C(13)	1.456 (6)
C(13)—N(1)—C(4)	125.6 (4)	C(5)—C(6)—O(2)	125.3 (5)
C(1)—C(2)—O(1)	110.1 (6)	C(7)—C(6)—O(2)	118.3 (6)
C(3)—C(2)—O(1)	111.3 (4)	C(7)—C(6)—C(5)	116.4 (4)
C(3)—C(2)—C(1)	117.4 (5)		

For (1), a goodness of fit of 1.178 was obtained from an optimization procedure included in the CAOS program system (Camalli & Spagna, 1994). The positions of the H atoms bonded to C atoms were calculated (C—H = 0.96 Å). The H atoms bonded to O and N atoms were localized from the final difference Fourier syntheses and refined with isotropic displacement parameters fixed to the corresponding values of the parent atom. For (2), the H atoms were placed in calculated positions (N—H, C—H = 0.96 Å). One H atom bonded to an O atom was not found in the final difference Fourier map and thus was not included.

Data collection: CS (Colapietro et al., 1992) for (1); MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1988) for (2). Cell refinement: CS for (1); MSC/AFC Diffractometer Control Software for (2). Data reduction: DARX (Barba & Pifferi, 1994) for (1); TEXSAN PROCESS (Molecular Structure Corporation, 1985) for (2). Program(s) used to solve structures: SIR92 (Altomare et al., 1994) for (1); SIR97 (Altomare et al., 1998) for (2). Program(s) used to refine structures: CAOS (Camalli & Spagna, 1994) for (1); SIR97 for (2). For both compounds, molecular graphics: CAOS.

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Triterpenoide. XIII.† Über weitere neue Triterpenlactone

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Abstract

The two new triterpene lactones, 11α-hydroxy-28-methoxy-28-oxo-2,3-dinor-18β-olean-12-en-1,4-olide hydrate [$C_{29}H_{44}O_5 \cdot H_2O$, (5)] and 28-methoxy-28-oxo-1,2-dinor-$10\alpha,18\beta$-oleano-9,12-dien-3,10β-olide [$C_{29}H_{42}O_4$, (6)], were obtained according to the method of Zaprutko [*Pol. J. Chem.* (1995), **69**, 1003–1012]. In both compounds, the lactone bridge connects atoms C4 and C10. In (5), the carbonyl group of the lactone bridge is formed by C1 and O1, and in (6), by C3 and O2. In (5), the methyl group at C10 has a β and in (6) an α

† Teil XII: Zaprutko (1997).

configuration. The *A* and *B* rings are *trans*-fused in (5), and *cis*-fused in (6). The bond lengths in ring *C* indicate double bonds between C12—C13 in (5) and C9—C11 and C12—C13 in (6). The hydroxyl group at C11 in (5) is α oriented. Ring *B* in (5) has a chair conformation and in (6) a distorted half-chair conformation. Ring *C* in (5) has a sofa conformation and in (6) a slightly distorted half-chair conformation. Rings *D* and *E* have a chair conformation in both compounds and are *cis*-fused. The asymmetric unit of (5) contains one water molecule, disordered over two positions, making two alternative hydrogen bonds.

Kommentar

Die Einwirkung von einem 7,5-fachen Überschuß von Natriumdichromat in siedendem Eisessig auf Oleanolsäuremethylester (1) führt zu einem Gemisch von zumindest zwei Verbindungen. Bei der Strukturaufklärung des Hauptproduktes dieser Reaktion hat Zaprutko (1995) die Lactonstrukturen (2) und (3) in Betracht gezogen. Spektroskopische Untersuchungen (IR, MS, ¹H, ¹³C, ²D NMR) deuteten auf die Struktur (2) hin (Zaprutko, 1995). Inzwischen zeigte es sich aber, daß diese Verbindung mit einem der vier Oxidationsprodukte von 3β-Hydroxy-11-oxo-18α-olean-12-en-28-säuremethylester identisch ist und somit die röntgenographisch aufgeklärte Struktur (4) besitzt (Gzella *et al.*, 1997).
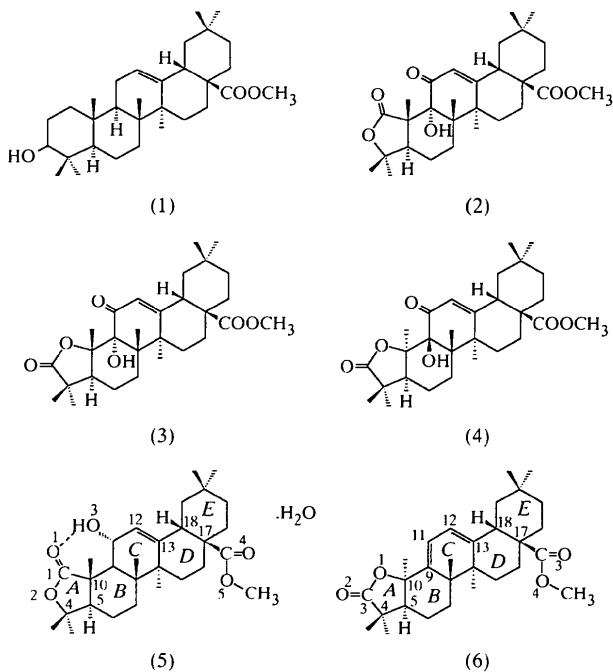
Das zweite Oxidationsprodukt von (1) konnte bis dahin nicht isoliert werden. Reduziert man das rohe Oxidationsgemisch von (1) mit Zink in Eisessig nach dem von Zaprutko (1995) beschriebenen Verfahren,