Crystal data

$C_{11}H_{12}N_2O$
M_r = 188.23
Monoclinic
$I2/a$
a = 12.1685 (19) Å
b = 13.724 (2) Å
c = 13.315 (3) Å
β = 114.792 (9)°
V = 2018.7 (6) Å^3
Z = 8
D_x = 1.239 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 54 reflections
θ = 15–16°
μ = 0.082 mm^{-1}
T = 220.0 (2) K
Lath
0.66 × 0.31 × 0.31 mm
Colourless

Data collection

Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)
ω–θ scans
Absorption correction: none
4252 measured reflections
1789 independent reflections

1428 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 25.03°
$h = -14 \rightarrow 1$
$k = -1 \rightarrow 16$
$l = -14 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.089
S = 1.048
1789 reflections
136 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.6438P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.151 e Å^{-3}
$\Delta\rho_{min}$ = −0.165 e Å^{-3}
Extinction correction: *SHELX*97 (Sheldrick, 1997)
Extinction coefficient: 0.0056 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

H1 and H4 were located from a ΔF map and were refined freely. Other H atoms (also clearly visible in maps) were constrained with a riding model and with U(H) = 1.2 U_{eq}(C).

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SHELX*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELX*97. Molecular graphics: *SHELXTL* (Sheldrick, 1995).

We thank EPSRC for provision of a four-circle diffractometer and Kodak Ltd for a studentship to MCE.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1321). Services for accessing these data are described at the back of the journal.

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N-(6-Amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)methionine

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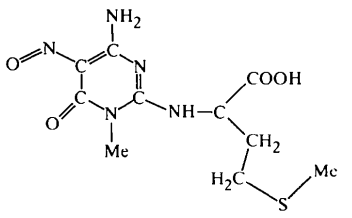
Abstract

The absolute configuration of the title compound, $C_{10}H_{15}N_5O_4S$, has been determined and is in agreement with that of the starting material, L-methionine. Two identical hydrogen-bonded buckled sheets run parallel to the [101] and [$\bar{1}$01] planes. Molecules lying in either of these planes are linked together by a ring structure to form these sheets, in which two chains of molecules run antiparallel to each other along the *b* axis. A further hydrogen-bonded ring structure links the [10$\bar{1}$] and [101] sheets together, resulting in an infinite three-dimensional hydrogen-bonded network.

Comment

Our interest in amino acid/nucleobase adducts is in their use as intermediates in the formation of metal complexes which have potential biological applications. The coordinating ability of the title compound, HL, is demonstrated by the preparation of three solid metal–ligand species, $(ZnL_2\cdot 2H_2O)_n$, $(CdL_2\cdot 3H_2O)_n$ and $(MnL_2\cdot 3H_2O)_n$. In these, the carboxyl group acts as deprotonated (L^-), resulting in a bidentate coordination mode through the carboxylate of the amino-acid moi-

ety and through either O5 of the nitroso group or the chelating 4-oxo and 5-nitroso residue, to form the head-to-tail polymeric species (López-Garzón *et al.*, 1999). The molecule is of interest because of the different ways in which it can bind to a metal and here we present the conformation of the free ligand, H*L*, and its hydrogen bonding.



H*L*

Data collection had to be carried out at 123 K, since an attempted structure determination at room temperature indicated that the methyl C atom attached to the S atom was so highly disordered that no reasonable disordered model could be found. A perspective view of the molecule is shown in Fig. 1. The absolute configuration of the title compound was determined and is in agreement with that of the starting material, L-methionine.

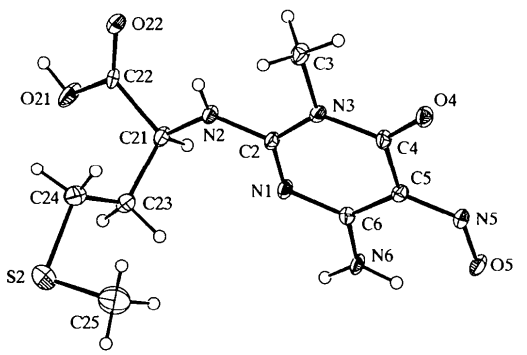


Fig. 1. A view of H*L* with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of an arbitrary radius.

The groups O4—C4—C5—N5 and O21—C22—O22, with O4···N5 and O21···O22 distances of 2.696 (3) and 2.247 (3) Å, respectively, give the ligand potential chelating and/or bidentate coordinating character. In the case of the O4···N5 residue, the lone-pair on the nitroso N atom lies on the same side of the molecule as O4, a conformation favoured because of an intramolecular hydrogen bond between N6 and O5.

The pyrimidine ring itself is essentially planar, with all groups directly linked to it being close to that plane. The largest deviations from the pyrimidine ring mean plane by atoms of the ring itself are −0.011 (2) Å for N1 and 0.011 (2) Å for N3. The base ring mean plane makes an angle of 27.67 (13)° with that of the carboxyl group defined by C21/C22/O21/O22, and an angle of 89.82 (7)° with the mean plane of the atoms C21/C23/C24/S2/C25.

The two amino groups, 6-NH_2 and 2-NH–, show sp^2 character due to delocalization of their lone pairs into the ring. The effect of this is shown by the C—N distances in the N2—C2—N1—C6—N6 fragment, which range between 1.308 (4) and 1.335 (3) Å. The nitroso group has bonds and angles of C5—N5 1.321 (3) and N5—O5 1.309 (3) Å, and C5—N5—O5 116.0 (2)°. The C6—C5—N5—O5 torsion angle is 6.3 (4)°.

Two identical hydrogen-bonded buckled sheets run parallel to the [101] and [$\bar{1}$01] planes. Molecules lying in either of these planes are linked together within the plane by a ring structure, to form sheets in which two rows of molecules run antiparallel to each other along the *b* axis (Fig. 2*a*). A further hydrogen-bonded ring structure links the [10$\bar{1}$] and [101] sheets together, resulting in an infinite three-dimensional hydrogen-bonded network (Fig. 2*b*). The former ring, with 17 members *via* O5, which links

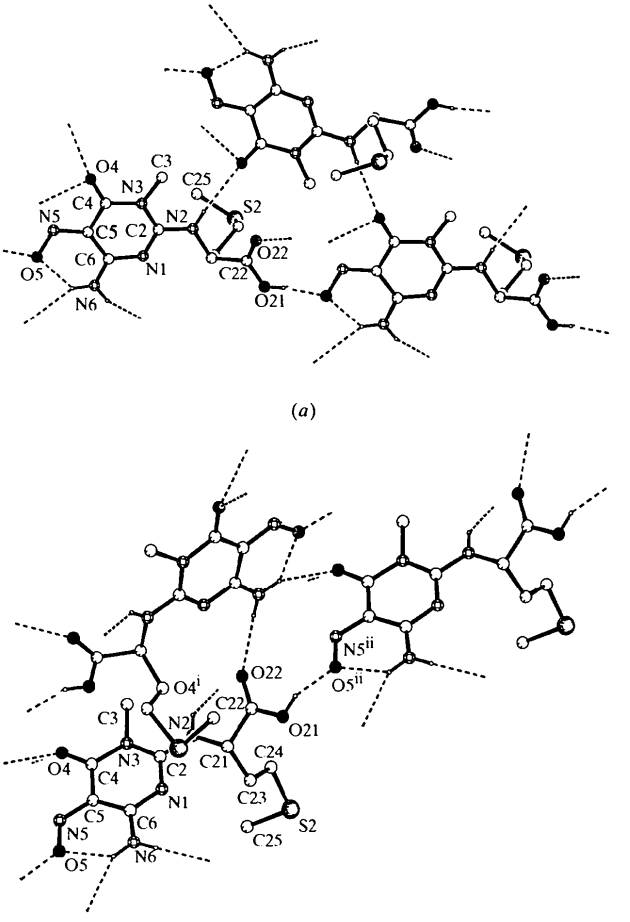


Fig. 2. View (*a*) of the ring structure forming sheets containing antiparallel chains running along the *b* axis and (*b*) down the *c* axis showing the hydrogen-bonded ring structure linking [101] sheets to [10$\bar{1}$] sheets. Symmetry codes are as given in Table 1.

three molecules, contains the atoms O4—C4—C5—N5—O5···H21—O21—C22—C21—N2—H2···O4—C4—N3—C2—N2—H2 and forms sheets of molecules, one of which is parallel to the [101] plane and the other to the [$\bar{1}$01] plane. The hydrogen bonds involved in this ring structure (Figs. 2*a* and 2*b*) are N2···O4^{i} 3.145 (3) Å [symmetry code: (i) $1-x$, $y+\frac{1}{2}$, $\frac{1}{2}-z$], a screw-related N2···O4 bond linking molecules at (i) and (ii) [symmetry code: (ii) x, $1+y$, z] and the O21···O5^{ii} hydrogen bond [2.473 (2) Å], which lies along the outer edges of the sheet but runs in opposite directions parallel to the *b* axis: essentially, the two rows of molecules are 'zipped' together to form the sheet. The [10$\bar{1}$] and [101] sheets are then interlinked by the latter hydrogen-bonded ring structure through bonds N6···O22^{iii} 2.932 (3) Å [symmetry code: (iii) $x-\frac{1}{2}$, $\frac{1}{2}-y$, $-z$], N6···O4^{iv} 3.327 (3) Å [symmetry code: (iv) $x-\frac{1}{2}$, $-y-\frac{1}{2}$, $-z$] and finally the O21^{iii}···O5^{iv} three-centred bond which links the three molecules together to form a 13-membered ring *via* O5. This ring comprises atoms N6—H6*B*···O4—C4—C5—N5—O5···H21—O21—C22—O22···H6*A*—(N6). The hydrogen bonds in the structure are given in Table 1. The basic graph-set analysis (Bernstein, 1995) of the chains associated with the H atoms are H21*A* $R_1^2(4)[C_1^2(11, O5)]$, H6*A* $C_1^1(9)$, H6*B* $C_1^1(6)$ and H2 $C_1^1(6)$. A description of the ring structures described above and other possible chains can be derived from these basic sets.

Experimental

The title compound was prepared by adding a suspension of 6-amino-3,4-dihydro-3-methyl-2-methoxy-5-nitroso-4-oxopyrimidine (5.00 g, 27.17 mmol) in acetonitrile (100 ml) to a suspension of L-methionine (4.43 g, 29.69 mmol) in 0.50 *M* aqueous KOH (60 ml, 30.00 mmol). The mixture was stirred at 343 K for 1 h. The wine-red solution was cooled and the pH was adjusted to 3.0 by dropwise addition of glacial acetic acid to neutralize and induce crystallization. After 6 h at room temperature, the orange crystalline solid was collected by filtration and washed successively with water, ethanol and diethyl ether to yield the title compound (6.14 g, 20.40 mmol, 75% yield). Analysis calculated: C 37.85, H 4.76, N 22.07, S 10.10%; found: C 37.91, H 4.72, N 21.98, S 10.19%.

Crystal data

$C_{10}H_{15}N_5O_4S$
M_r = 301.33
Orthorhombic
$P2_12_12_1$
a = 9.0165 (4) Å
b = 11.3057 (3) Å
c = 13.4155 (6) Å
V = 1367.55 (9) Å^3
Z = 4
D_x = 1.464 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from all reflections
θ = 2.35–26.27°
μ = 0.260 mm^{-1}
T = 150 (2) K
Needle
0.25 × 0.15 × 0.10 mm
Orange

Data collection

KappaCCD area-detector diffractometer
$\varphi + \omega$ scans
Absorption correction: none
10 372 measured reflections
1609 independent reflections (plus 1169 Friedel-related reflections)
2331 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 26.27°
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 16$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.128
S = 1.208
2778 reflections
184 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0679P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.07 (13)

Table 1. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O4^{i}	0.86	2.39	3.145 (3)	147
O21—H21A···O5^{ii}	0.82	1.70	2.473 (2)	157
N6—H6A···O22^{iii}	0.86	2.11	2.932 (3)	159
N6—H6B···O5	0.86	1.99	2.613 (3)	128
N6—H6B···O4^{iv}	0.86	2.57	3.327 (3)	148

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

Data collection: *COLLECT* (Nonius, 1998). Cell refinement: *COLLECT*. Data reduction: *COLLECT* and *DATRD2* in *NRCVAX*94 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*. Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*97. Molecular graphics: *PLATON* (Spek, 1998) and *PLUTON* (Spek, 1995). Software used to prepare material for publication: *NRCVAX*94, *SHELXL*97 (Sheldrick, 1997) and *PREP*8 (Ferguson, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1287). Services for accessing these data are described at the back of the journal.

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Triterpenoide. XVI.† 2-Formylderivate des Oleanonsäure-methylesters und *Allo*-betulons

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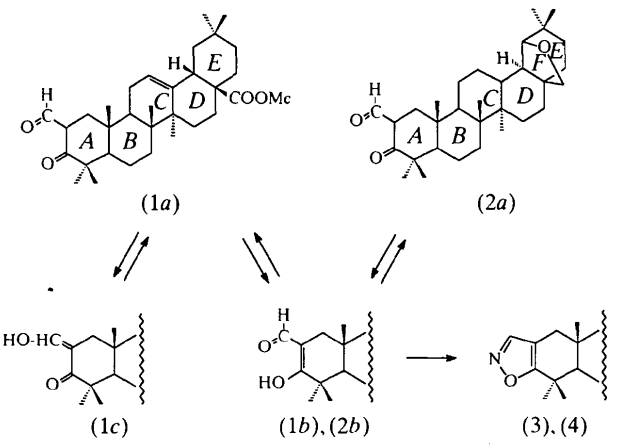
Abstract

The formylation products of 3-oxo-18β-olean-12-en-28-oic acid methyl ester (oleanonic acid methyl ester) and 19β,28-epoxy-18α-oleanan-3-on (*allo*-betulon) by the method of Govardhan, Reddy, Ramaiah & Rao [*J. Indian Chem. Soc.* (1983), pp. 858–860] have the structure of the corresponding methyl 2-formyl-3-hydroxy-18β-olean-2,12-dien-28-oate [$C_{32}H_{48}O_4$, (1*b*)] and 19β,28-epoxy-3-hydroxy-18α-olean-2-ene-2-carbaldehyde [$C_{31}H_{48}O_3$, (2*b*)]. These enols are stabilized by short intramolecular O2—H2*A*···O1 hydrogen bonds between the O atoms of the C3-hydroxy and C31-carbonyl groups and conjugation systems of C3=C2—C31=O1. The enol structure is in agreement with our earlier observation that compounds (1*b*) and (2*b*) on treatment with hydroxylamine hydrochloride are not converted into [3,2-*c*]- but [2,3-*d*]isoxazoles [Gzella, Linkowska, Zaprutko & Wrzeciono (1999). *Acta Cryst.* C**55**, 1031–1034]. Rings *A* and *C* in (1*b*) have a distorted sofa form. The ring *A* in (2*b*) has an intermediate conformation between a sofa and half-chair. Ring *C* in (2*b*) and rings *B*, *D* and *E* in (1*b*) and (2*b*) take the chair conformation. Rings *D*/*E* are *cis*-fused in (1*b*) and *trans*-fused in (2*b*). The axial O3 and C28 atoms in (2*b*) are β oriented and form together with the C17, C18 and C19 atoms the five-membered ring *F*, which has an envelope conformation.

Kommentar

Bei der Umsetzung von 3-Ketotriterpenderivaten mit Ethylformiat und Dimethylformamid (Govardhan *et al.*, 1983) bzw. Isopentylformiat (Ruzicka *et al.*, 1934) in Gegenwart von Natriummethylat bzw. Natriumethylat entstehen die entsprechenden 2-Formylderivate. Auf Grund spektroskopischer Untersuchungen (UV, IR, ^{1}H NMR) haben Govardhan *et al.* (1983) gezeigt, daß es sich bei dem so dargestellten 2-Formylderivat des 3-Oxo-18β-olean-12-en-28-säure-methylesters (Oleanonsäure-methylesters) um konstitutionsisomere Verbindungen (1*a*)/(1*c*) handelt. In dieser Mitteilung wird über die Röntgenstrukturanalyse der Formylierungsprodukte des erwähnten Methylesters und des 19β,28-Epoxy-18α-oleanan-3-ons (*Allo*-betulons) berichtet und gezeigt, daß diese Verbindungen im Kristall in der Enolform (1*b*) und (2*b*) vorliegen.



Die Ergebnisse der Röntgenstrukturanalyse der Verbindungen (1*b*) und (2*b*) sind in den Abb. 1 und 2, und in den Tabellen 1–5 zusammengefaßt.

Die Enolformen (1*b*) und (2*b*) sind durch kurze intramolekulare Wasserstoffbrückenbindungen O2—H2*A*···O1 (Tabellen 2 und 4, Abb. 1 und 2) stabilisiert. Die Enolformen (1*b*) und (2*b*) sind zusätzlich durch die Ausbildung des konjugierten Systems C3=C2—C31=O1 stabilisiert. Bei (1*b*) sind die Bindungen C2=C3 [1,372 (2) Å] und C31=O1 [1,258 (2) Å] um etwa 14 bzw. 16 Standardabweichungen länger als die normalen Doppelbindungslängenwerte [C=C(—CO): 1,340 (1); (Csp^2—)C=O: 1,222 (1) Å] (Allen *et al.*, 1987), die Bindungslänge C2—C31 [1,408 (2) Å] um etwa 25 Standardabweichungen kürzer im Vergleich mit der normalen Einfachbindung [(C=)C—C(=O): 1,465 (1) Å] (Allen *et al.*, 1987). Es ist auch bemerkenswert, daß sich die Bindungslängen C3—O2 und C31=O1 nur um 0,060 (3) Å voneinander unterscheiden

† Teil XV: Zaprutko (1999).