Monoclinic
$C2/c$
a = 49.87 (2) Å
b = 5.406 (3) Å
c = 8.471 (3) Å
β = 88.66 (3)°
V = 2282.9 (17) Å^3
Z = 8
D_x = 1.351 Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
θ = 11.8–14.8°
μ = 0.099 mm^{-1}
T = 296 K
Plate
0.3 × 0.3 × 0.1 mm
Colourless

Data collection

Rigaku AFC-7*R* diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.960, T_{max} = 0.990
2667 measured reflections
2638 independent reflections

1124 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 27.5°
$h = 0 \rightarrow 64$
$k = 0 \rightarrow 7$
$l = -11 \rightarrow 11$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F
R = 0.052
wR = 0.116
S = 1.10
2638 reflections
154 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o) + 0.00265|F_o|^2]$
$(\Delta/\sigma)_{max}$ = 0.02
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

O1—C6	1.186 (4)	N5—C6	1.397 (4)
O2—C7	1.200 (4)	N5—C8	1.367 (4)
O3—C8	1.204 (4)	N5—C9	1.457 (4)
N4—C6	1.391 (4)	C7—C8	1.539 (5)
N4—C7	1.354 (4)	C9—C10	1.510 (4)
N4—C17	1.461 (4)	C10—C11	1.509 (4)
C6—N4—C7	112.2 (3)	N5—C8—C7	104.5 (3)
C6—N5—C8	111.7 (2)	N5—C9—C10	112.7 (3)
N4—C6—N5	106.5 (3)	C9—C10—C11	111.4 (3)
N4—C7—C8	105.1 (3)		
N5—C9—C10—C11	173.8 (3)	C6—N5—C9—C10	94.1 (4)

In (I), all H atoms were located from difference syntheses. In (II), all H-atom positions were calculated geometrically with U_{iso}(H) = 1.2U_{eq}(parent atom). A riding model was used in their refinement (C—H 0.96 Å).

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software* for (I); *MSC/AFC Diffractometer Control Software* for (II). For both compounds, data reduction: *TEXSAN* (Molecular Structure Corporation, 1998); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1052). Services for accessing these data are described at the back of the journal.

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3,3,6,6-Tetramethyl-9-(3-nitrophenyl)-3,4,5,6,9,10-hexahydroacridine-1,8(2*H*,7*H*)-dione

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Abstract

In the title compound, $C_{23}H_{26}N_2O_4$, the central ring adopts a distorted boat conformation, while the two outer rings are almost in ideal envelope conformations.

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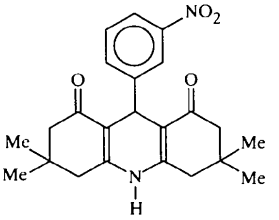
The molecular packing is stabilized by van der Waals interactions and hydrogen bonds.

Comment

Since the discovery of the pharmacological effects of the 1,4-dihydropyridines (1,4-DHPs) as calcium channel blockers (Bossert *et al.*, 1981), a great deal of work has been directed towards the synthesis of novel 1,4-DHPs acting as calcium antagonists (Bossert & Vater, 1989). It is of particular interest to know which conformation produces the optimum result in the 1,4-DHP moiety of the nifedipine type and consequently the relationship between conformation and pharmacological effect (Goldmann & Stoltefuss, 1991). Recent investigations carried out on rigid dihydropyridines have provided information on the active conformation (Goldmann & Stoltefuss, 1991). Thus, 4-aryl-substituted 1,4-DHPs with calcium antagonist properties exist in a boat conformation in which the aryl substituent is in a pseudo-axial position orthogonal to the dihydropyridine plane (Straub *et al.*, 1997). Previous reports have described the synthesis of 1,4-DHPs fused to one (Meyer *et al.*, 1976) or two (Loev *et al.*, 1974) cyclohexanone rings, which present a positive ionotropic effect, promoting instead of blocking the entry of calcium to the intracellular space (calcium agonist effect) (Rose & Dräguer, 1992). Previous work has described the synthesis and conformational study of acridine derivatives related to 1,4-dihydropyridines (Martín *et al.*, 1995). Quantum-chemical calculations were carried out on these molecules using the *AM*1 method with complete geometry optimization and showed that the 1,4-DHP moiety adopts a flattened boat conformation in which the C atoms of the two fused rings are in the same main boat plane, with the C3 and C6 atoms out of this plane. The calculated heats of formation indicate two equally favoured conformations in terms of energy in which the C atoms bearing the methyl groups are out of the molecular plane. The synthesis the title compound, (I), was carried out according to the Hantzsch method by the reaction of dimedone (5,5-dimethyl-1,3-cyclohexanedione) with *m*-nitrobenzaldehyde in the presence of ammonium hydroxide.



(I)

Bond distances and angles of the acridine skeleton are in agreement with those of related acridine derivatives (Bundule *et al.*, 1980; Selladurai *et al.*, 1990; Sivaraman *et al.*, 1996; Brito-Arias *et al.*, 1996). The bond lengths in the pyridine ring range from 1.351 (3) to 1.516 (4) Å and show the respective greater or lesser degree of single- or double-bond character predicted from comparisons with related structures (Selladurai *et al.*, 1989, 1990; Sivaraman *et al.*, 1994, 1996). The ketone bond lengths, C1=O1 and C8=O8, of 1.243 (3) and 1.228 (4) Å, respectively, are in agreement with values observed for related structures (Dideberg *et al.*, 1973). Both outer six-membered rings of the acridine moiety adopt almost ideal envelope conformations, with puckering parameters (Cremer & Pople, 1975) Q = 0.448 (3) Å, θ = 127.4 (4)° and ψ = 290.5 (5)° for the C1,C2–C9a ring, and Q = 0.463 (3) Å, θ = 122.8 (4)° and ψ = 249 (5)° for the C5,C6–C10a ring. The central pyridine ring (N1,C4a–C10a) adopts a distorted boat conformation, with puckering parameters Q = 0.219 (3) Å, θ = 105.5 (8)° and ψ = 363.8 (7)°. The phenyl ring is nearly perpendicular to the acridine moiety, with the dihedral angle between their respective least-squares planes being 89.8 (1)°. The mean Csp^2—Csp^2 bond length within this ring is 1.382 (3) Å. The N1 atom of the pyridine ring participates in an intermolecular hydrogen bond with a neighbouring carbonyl O1 atom.

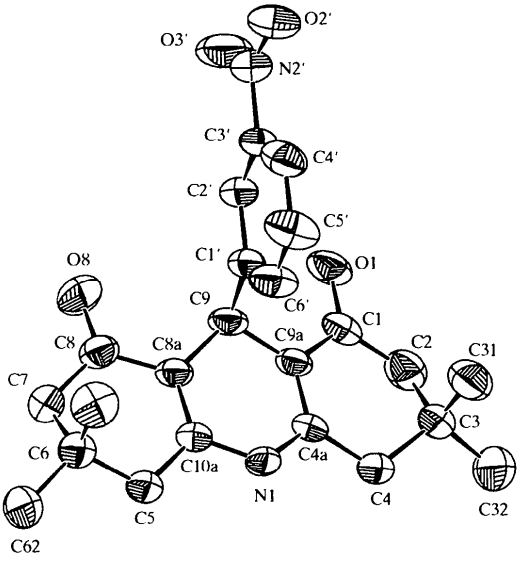


Fig. 1. Plot showing the atomic numbering scheme of the title compound. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms and H atoms have been omitted for clarity.

Experimental

Ammonium hydroxide solution (32%) was added to a mixture of dimedone (7 mmol) and *m*-nitrobenzaldehyde (3.5 mmol) in ethanol (10 ml). The reaction mixture was refluxed for 1 h and then poured into ice water. The solid that precipitated was collected by filtration and recrystallized from ethanol (yield 85%).

Crystal data

$C_{23}H_{26}N_2O_4$
M_r = 394.46
Monoclinic
$P2_1/n$
a = 11.8787 (8) Å
b = 15.483 (1) Å
c = 12.3467 (8) Å
β = 108.21 (1)°
V = 2157.0 (3) Å^3
Z = 4
D_x = 1.2147 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 44 reflections
θ = 11.48–27.74°
μ = 0.6763 mm^{-1}
T = 293 (2) K
Prism
0.47 × 0.47 × 0.10 mm
Light yellow

Data collection

Siemens $P4$ four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.672, T_{max} = 0.935
4668 measured reflections
3787 independent reflections

2524 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 69.13°
$h = -1 \rightarrow 14$
$k = -1 \rightarrow 18$
$l = -14 \rightarrow 14$
3 standard reflections every 100 reflections
intensity decay: <1.0%

Refinement

Refinement on F^2
$R(F)$ = 0.059
$wR(F^2)$ = 0.186
S = 1.108
3787 reflections
267 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.072P)^2 + 1.1366P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.220 e Å^{-3}
$\Delta\rho_{min}$ = −0.206 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997*a*)
Extinction coefficient: 0.0056 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1═C1	1.243 (3)	N1—C4a	1.374 (3)
O2′═N2′	1.221 (4)	N1—C10a	1.380 (3)
O3′═N2′	1.211 (5)	N2′—C3′	1.477 (4)
O8═C8	1.228 (4)		
C4a—N1—C10a	121.6 (2)	N2′—C3′—C2′	118.0 (3)
O2′═N2′═O3′	123.1 (3)	N1—C4a—C9a	120.1 (2)
O2′═N2′—C3′	118.1 (3)	N1—C4a—C4	115.7 (2)
O3′═N2′—C3′	118.7 (3)	O8—C8═C8a	120.6 (3)
O1═C1—C2	121.4 (2)	O8—C8═C7	121.5 (2)
O1═C1—C9a	120.5 (2)	N1—C10a—C5	115.6 (2)
N2′—C3′—C4′	118.5 (3)	N1—C10a—C8a	120.5 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H···O1^i	0.86	1.99	2.835 (3)	166

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

The title structure was solved by direct methods and Fourier synthesis. Non-H atoms were refined anisotropically by full-matrix least-squares techniques. H atoms were calculated geometrically and included in the refinement, but were restrained to ride on their parent atoms. The isotropic displacement parameters of the H atoms were fixed at $1.3U_{eq}$ of the parent atoms.

Data collection: *XSCANS* (Siemens, 1996). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*). Molecular graphics: *DIAMOND* (Bergerhoff, 1996). Software used to prepare material for publication: *PLATON* (Spek, 1990), *PARST* (Nardelli, 1983, 1995) and *PARSTCIF* (Nardelli, 1991).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1388). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 599–601

Methyl 4β-bromo-7α-cathyloxy-3-oxo-5β-cholanoate

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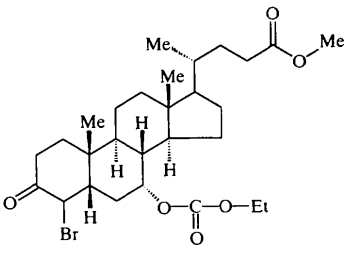
Abstract

In the title compound, methyl 4β-bromo-7α-ethoxycarbonyloxy-3-oxo-5β-cholanoate, $C_{28}H_{43}BrO_6$, the Br—C4 bond is oriented equatorially and (−)-antiperiplanar with respect to the C5—C10 bond. The six-membered rings (*A*, *B* and *C*) have the usual chair conformations, while the five-membered ring (*D*) adopts a distorted 13β,14α-half-chair conformation. The *A*/*B* ring junction is *cis*, and the *B*/*C* and *C*/*D* ring junctions are both *trans*.

Comment

Reduction of bromoketones and elimination reactions involving the halohydrines obtained allows the introduction of double bonds in specific positions of a molecule (Cristol & Rademacher, 1959). This procedure has been used to obtain analogues of brassinosteroids with a 3,4-diol moiety in the *A* ring from 3α,7α-dihydroxy-5β-cholanoic acid (chenodeoxycholic acid) (data not published). We report here the crystal structure of methyl 4β-bromine-7α-cathyloxy-3-oxo-5β-cholanoate, (I), the starting material used in the synthesis of analogues of brassinosteroids.



(I)

The absolute configuration, determined from the refinement of the Flack (1983) parameter in the X-ray analysis, confirmed that predicted beforehand from the synthesis route. The Br—C4 bond is oriented equatorially and (−)-antiperiplanar with respect to the C5—C10 bond. The presence of the Br atom does not disturb the chair conformation in ring *A* of the steroidal nucleus. Ring *A* has a symmetrical chair conformation, with all asymmetry parameters below 8.8 (5)° (Duax *et al.*, 1976). Rotational symmetry is dominant; a pseudo-C_2 axis intercepts the C1—C2 bond [asymmetry parameters: ΔC_2(C1—C2) = 2.5 (5), ΔC_S(C1) = 3.2 (4) and ΔC_S(C3) = 8.0 (4)°]. The modulus of the ring *A* torsion angles is in the range 46.59 (5)–57.76 (6)°. Rings *B* and *C* have the expected chair conformations (Pfeiffer *et al.*, 1985). The five-membered ring (*D*) adopts a distorted 13β,14α-half-chair conformation (Altona *et al.*, 1968). The *A*/*B* ring junction is *cis*, and the *B*/*C* and *C*/*D* ring junctions are both *trans*. The packing of the molecules is assumed to be dictated by van der Waals interactions, and by intramolecular and intermolecular C—H···O hydrogen bonds (Taylor & Kennard, 1982).

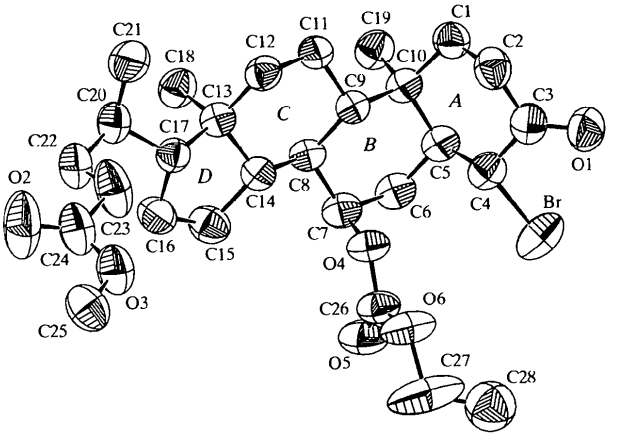


Fig. 1. Plot showing the atomic numbering scheme of the title compound. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms and H atoms have been omitted for clarity.

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