Acta Cryst. (1992). C**48**, 1348–1350

A 9,15-Cyclogibberellin Formed from a Bromogibberellin-16-one Derivative

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(*Received* 23 *January* 1992; *accepted* 26 *March* 1992)

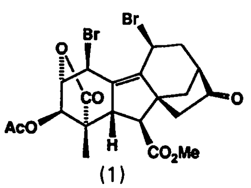
Abstract

ent-3α,11β-Diacetoxy-7α-methoxycarbonyl-16-oxo-7,17,20-trinor-9α,15α-cyclogibberell-1(10)-eno-19,2β-lactone was produced by treating a 1β,11β-dibromogibberellin-16-one with caesium acetate and 18-crown-6 ether. An intramolecular alkylation reaction has led to the formation of a bond between C15 and C9 to afford a cyclopropyl moiety. Bond lengths to C8 and C9 are slightly shorter than in comparable gibberellins.

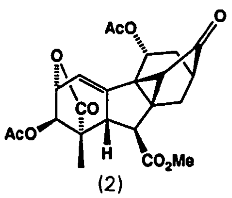
Comment

The 1β,11β-dibromogibberellin-16-one (1) was treated with caesium acetate and 18-crown-6 ether, affording cyclopropyl ketone (2) as the only identifiable product in 86% yield. Details of this conversion and related processes will be published elsewhere.

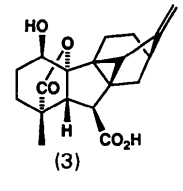
Dibromide (1) is an important intermediate in the preparation (Furber, Mander & Patrick, 1990) of the two rare plant hormones (3) (Nakanishi, Endo, Näf & Johnson, 1971) and (4) (Furber & Mander, 1988) which induce antheridia formation in gametophytes of ferns from the genus *Anemia*.



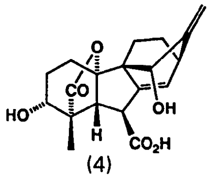
(1)



(2)



(3)



(4)

The pivotal step in these syntheses involved an intramolecular alkylation reaction between the enolate derived from the 16-one function and the Δ^9- ene-1β-bromo moiety with formation of a bond between C15 and C9. It was suspected that another plant hormone isolated from *Anemia phyllitidis* in only nanogram quantities, and isomeric with (4), might be hydroxylated in the *C* ring, so prior to the alkylation process we investigated the replacement of the 11β-bromo substituent with a view to preparing the unidentified substance. The two bromo substituents in (1) are in similar steric environments, but it was expected that the electron-withdrawing lactone substituent at C2 would inhibit S_N2 substitution at C1, allowing selective reaction at C11.

In the event, treatment of (1) with caesium acetate/18-crown-6 ether afforded a product which possessed only one additional acetate group, but which was devoid of bromine. NMR spectra were consistent with structure (2), which was confirmed by the X-ray crystallographic analysis described in this paper. Apparently the caesium acetate under these conditions is a sufficiently strong base to enolize the 16-ketone function and initiate alkylation. It is not clear whether this step is preceded or followed by replacement of the 11-bromo group. Details of the interconversion and subsequent manipulations will be published elsewhere.

A search of the January 1991 version of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed over 40 crystal structure determinations of gibberellin derivatives. None, however, exhibited a C9—C15 bond as observed in (2) and only two had a C1—C10 double bond: 2,7-dihydroxy-10-methoxycarbonyl-1-methyl-8-methylene-4β-gibberell-4-ene-1-carboxylic acid (Kutschabsky, Reck, Adam, Argay & Czugler, 1981) and *ent*-3α,13-dihydroxy-7-methoxycarbonyl-20-norgibberella-1(10),16-diene-19-carboxylic acid (Kutschabsky, Adam & Voigt, 1987).

Bond lengths within (2) are comparable with the corresponding values in matching sections of other gibberellins, with the exception of bonds to C8 and C9 which are slightly shorter than normal, presumably as a consequence of the existence of the C8—C9—C15 cyclopropyl ring. The additional linkage predictably affects the angles and the conformation of the ring C8—C9—C11—C12—C13—C14. This part of the structure resembles the tricyclic skeleton of 3-*exo*,4-*endo*,6-*exo*-tribromo-7-bromomethyl-1,5-dimethyltricyclo[3.2.1.$0^{2,7}$]octan-8-one (Peter-Katalinic, Zsindely, Schmid & Oberhänsli, 1975) and exhibits similar distances, angles and torsion angles.

Fig. 1 was prepared and most calculations performed with the *Xtal*2.4 and *Xtal*3.0 packages (Hall & Stewart,

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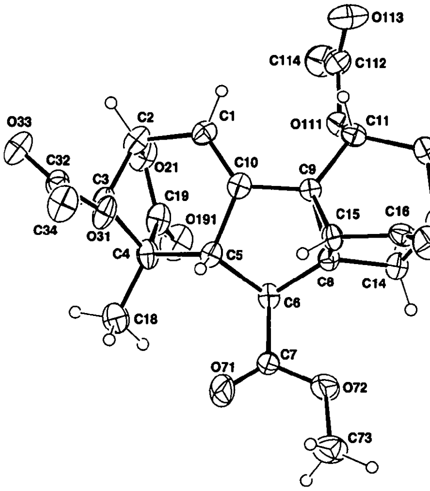

Fig. 1. View of $C_{23}H_{24}O_9$ showing the labelling of the non-H atoms. Thermal ellipsoids are shown at 30% probability levels, except for H atoms which are drawn as small circles of arbitrary radius. The minor site of disordered O71, and the H atoms on C34 and C114 are not shown.

1988, 1990). The Crystallographic Information File used for the submission of this paper was generated with the use of *Xtal*3.0.

Experimental

Crystal data

$C_{23}H_{24}O_9$
$M_r = 444.44$
Orthorhombic
$P2_12_12_1$
$a = 7.825$ (1) Å
$b = 14.254$ (1) Å
$c = 18.910$ (2) Å
Cell parameters from 25 reflections
$\theta = 18$-$20°$

$V = 2109.2$ (4) Å^3
$Z = 4$
$D_x = 1.400$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
$\mu = 1.0$ cm^{-1}
$T = 293$ K
0.28 × 0.25 × 0.20 mm
Colourless

Data collection

Philips PW1100/20 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1923 measured reflections
1923 independent reflections
1386 observed reflections
$[I_{\rm net} > 3.00\sigma(I_{\rm net})]$

$\theta_{\rm max} = 24.05°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 90 min
intensity variation: 0%

Refinement

Refinement on F
Final $R = 0.040$
$wR = 0.048$
$S = 1.419$
1386 reflections
296 parameters
H atoms at calculated positions, disordered on C34 and C114 (see below)
$w = 1/[\sigma^2(F)+0.0006F^2]$

$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.212$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.179$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: Philips PW1100/20 software 1976. Cell refinement: Philips PW1100/20 software 1976. Data reduction: *PWREDU* (McLaughlin, 1983), *Xtal ADDREF SORTRF* (Hall & Stewart, 1988, 1990) . Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985) . Program(s) used to refine structure: *Xtal CRYLSQ* (Hall & Stewart, 1988, 1990) . Molecular graphics: *Xtal* (Hall & Stewart, 1988, 1990) . Software used to prepare material for publication: *Xtal BONDLA CIFIO* (Hall & Stewart, 1988, 1990) .

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.7426 (6)	0.4592 (3)	0.7173 (3)	0.045 (3)
C2	0.7551 (7)	0.4957 (4)	0.7910 (3)	0.052 (3)
C3	0.6475 (7)	0.4415 (3)	0.8435 (3)	0.048 (3)
C4	0.4669 (7)	0.4630 (3)	0.8143 (2)	0.045 (3)
C5	0.4495 (5)	0.4028 (3)	0.7461 (2)	0.036 (2)
C6	0.2874 (6)	0.4134 (3)	0.6996 (2)	0.037 (3)
C7	0.1510 (6)	0.3429 (4)	0.7196 (2)	0.044 (3)
C8	0.3513 (6)	0.3972 (3)	0.6244 (2)	0.036 (2)
C9	0.5434 (6)	0.4008 (3)	0.6223 (2)	0.035 (2)
C10	0.5981 (6)	0.4205 (3)	0.6959 (2)	0.039 (3)
C11	0.6285 (6)	0.4480 (3)	0.5609 (2)	0.042 (3)
C12	0.5438 (7)	0.4244 (3)	0.4895 (2)	0.051 (3)
C13	0.3732 (7)	0.3742 (3)	0.5011 (2)	0.048 (3)
C14	0.2633 (6)	0.4251 (3)	0.5563 (2)	0.043 (3)
C15	0.4531 (6)	0.3072 (3)	0.6115 (2)	0.040 (2)
C16	0.4184 (6)	0.2830 (3)	0.5368 (2)	0.046 (3)
C18	0.3270 (7)	0.4524 (4)	0.8675 (3)	0.060 (3)
C19	0.4942 (7)	0.5654 (3)	0.7951 (3)	0.050 (3)
O21	0.6633 (5)	0.5868 (2)	0.7916 (2)	0.059 (2)
O31	0.6752 (5)	0.3418 (2)	0.8433 (2)	0.053 (2)
C32	0.8046 (7)	0.3089 (4)	0.8823 (2)	0.049 (3)
O33	0.9018 (5)	0.3573 (3)	0.9138 (2)	0.068 (2)
C34	0.8058 (8)	0.2033 (4)	0.8803 (3)	0.068 (4)
O71†	0.137 (1)	0.3018 (9)	0.7751 (3)	0.097 (6)
O71*B*‡	0.074 (3)	0.364 (2)	0.772 (1)	0.066 (9)
O72	0.0584 (6)	0.3157 (3)	0.6667 (2)	0.082 (3)
C73	−0.0690 (8)	0.2448 (4)	0.6789 (3)	0.080 (4)
O111	0.6122 (4)	0.5479 (2)	0.5748 (2)	0.046 (2)
C112	0.7478 (7)	0.6028 (4)	0.5592 (3)	0.052 (3)
O113	0.8759 (5)	0.5743 (3)	0.5329 (2)	0.078 (3)
C114	0.7106 (8)	0.7021 (4)	0.5782 (3)	0.072 (4)
O161	0.4204 (5)	0.2059 (2)	0.5110 (2)	0.064 (2)
O191	0.3877 (5)	0.6248 (2)	0.7850 (2)	0.070 (2)

† Occupancy 0.78(2).

‡ Occupancy 0.22(2). Isotropic *U*.

Table 2. *Geometric parameters* (Å, °)

C1—C2	1.491 (7)	C9—C10	1.483 (6)
C1—C10	1.322 (7)	C9—C11	1.498 (6)
C2—C3	1.513 (7)	C9—C15	1.524 (6)
C2—O21	1.484 (6)	C11—C12	1.542 (7)
C3—C4	1.548 (7)	C11—O111	1.455 (5)
C3—O31	1.438 (5)	C12—C13	1.531 (7)
C4—C5	1.554 (6)	C13—C14	1.535 (7)
C4—C18	1.495 (7)	C13—C16	1.507 (7)
C4—C19	1.520 (6)	C15—C16	1.479 (6)
C5—C6	1.551 (6)	C16—O161	1.202 (6)
C5—C10	1.522 (6)	C19—O21	1.359 (7)
C6—C7	1.514 (7)	C19—O191	1.203 (6)
C6—C8	1.526 (6)	O31—C32	1.338 (6)

C7—O71	1.207 (9)	C32—O33	1.186 (6)
C7—O71*B*	1.20 (2)	C32—C34	1.505 (7)
C7—O72	1.293 (6)	O72—C73	1.439 (8)
C8—C9	1.505 (6)	O111—C112	1.351 (6)
C8—C14	1.515 (6)	C112—O113	1.190 (7)
C8—C15	1.530 (6)	C112—C114	1.489 (8)
C2—C1—C10	119.3 (4)	C10—C9—C15	115.2 (3)
C1—C2—C3	113.4 (4)	C11—C9—C15	119.6 (4)
C1—C2—O21	106.2 (4)	C1—C10—C5	122.1 (4)
C3—C2—O21	99.9 (4)	C1—C10—C9	127.8 (4)
C2—C3—C4	100.0 (4)	C5—C10—C9	109.5 (4)
C2—C3—O31	114.8 (4)	C9—C11—C12	113.0 (4)
C4—C3—O31	109.4 (4)	C9—C11—O111	105.1 (3)
C3—C4—C5	105.5 (4)	C12—C11—O111	109.6 (4)
C3—C4—C18	114.1 (4)	C11—C12—C13	110.5 (4)
C3—C4—C19	98.4 (4)	C12—C13—C14	111.4 (4)
C5—C4—C18	116.0 (4)	C12—C13—C16	105.3 (4)
C5—C4—C19	110.2 (4)	C14—C13—C16	103.7 (4)
C18—C4—C19	111.1 (4)	C8—C14—C13	101.4 (4)
C4—C5—C6	119.2 (4)	C8—C15—C9	59.0 (3)
C4—C5—C10	111.0 (4)	C8—C15—C16	104.7 (4)
C6—C5—C10	104.8 (3)	C9—C15—C16	114.7 (4)
C5—C6—C7	111.8 (4)	C13—C16—C15	105.6 (4)
C5—C6—C8	104.2 (3)	C13—C16—O161	127.6 (4)
C7—C6—C8	111.3 (4)	C15—C16—O161	126.7 (4)
C6—C7—O71	126.9 (6)	C4—C19—O21	111.3 (4)
C6—C7—O72	113.7 (4)	C4—C19—O191	128.1 (5)
O71—C7—O72	118.5 (7)	O21—C19—O191	120.6 (4)
C6—C8—C9	110.3 (4)	C2—O21—C19	106.0 (3)
C6—C8—C14	127.2 (4)	C3—O31—C32	117.3 (4)
C6—C8—C15	116.6 (3)	O31—C32—O33	123.9 (5)
C9—C8—C14	115.0 (4)	O31—C32—C34	110.0 (4)
C9—C8—C15	60.3 (3)	O33—C32—C34	126.1 (5)
C14—C8—C15	108.7 (3)	C7—O72—C73	118.3 (4)
C8—C9—C10	105.7 (4)	C11—O111—C112	117.3 (4)
C8—C9—C11	118.6 (4)	O111—C112—O113	123.8 (5)
C8—C9—C15	60.7 (3)	O111—C112—C114	110.1 (5)
C10—C9—C11	121.0 (4)	O113—C112—C114	126.1 (5)

Intensity data were collected with θ-scan widths of $(0.8 + 0.346\tan\theta)^\circ$, a θ-scan rate of 2° min^{-1} and background counts of 7 s at each end of every scan. H atoms, with the exception of those on C34 and C114, were observed in a $\Delta\rho$ synthesis. H atoms were placed at geometrically determined positions (those on C34 and C114 were assumed to be disordered over the two orientations giving rise to staggered conformations with respect to the β atoms) and held fixed during the least-squares refinement, but were periodically recalculated. All non-methyl H atoms were given a common U parameter which was refined, and methyl H atoms were treated likewise. The absolute configuration was assigned to conform with the known chirality of the compound's precursors. Refinement was by full-matrix least-squares methods.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55050 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1000]

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Acta Cryst. (1992). C**48**, 1350–1352

Structure of $Ni(H_2O)_6(NH_4)_2(PO_3F)_2$

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(*Received* 20 *January* 1992; *accepted* 9 *March* 1992)

Abstract

The structure of diammonium hexaaquanickel bis(monofluorophosphate) consists of $Ni(H_2O)_6^{2+}$ and NH_4^+ cations and PO_3F^{2-} anions held together by hydrogen bonds involving all H atoms except one belonging to the ammonium cation. The Ni atoms are octahedrally coordinated by the six water molecules.

Comment

The present work forms part of a structural study of monofluorophosphates. The corresponding alkali-metal salts have been widely studied (Durand, Cot & Galigné, 1974, 1978; Galigné, Durand & Cot, 1974; Durand, Granier, Cot & Galigné, 1975; Payen, Durand, Cot & Galigné, 1979). However, the fluorophosphates of divalent transition metals have received less attention. Only the structures of