The Stereochemistry of Reduction of the 1- and 16-Carbonyl Group in the Normal and 8,13-Isogibberellins

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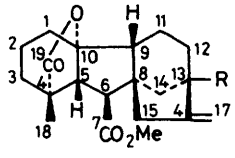
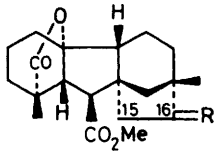
N.m.r. and *X*-ray studies show that reduction of the 16-carbonyl group in the normal and 8,13-isogibberellin series by sodium borohydride affords the 16-*endo*-alcohols; a 1-carbonyl group affords the 1α-alcohol.

The rearrangement reactions of the bicyclo[3.2.1]octane unit of rings C and D of the tetracyclic diterpenoids have been extensively studied.[1] A number of these reactions involve the generation of carbocations by the solvolysis of derivatives of C-15 and C-16 alcohols. The C-16 alcohols are obtained in turn by the reduction of the 16-ketones. In the phyllocladene series the alcohol obtained by hydride reduction was assigned[2] the *endo*-stereochemistry on the basis of attack by the reagent from the less-hindered face of the molecule whilst in the kaurene series[3] this was supplemented by ^{1}H n.m.r. coupling constant measurements although the individual $J_{H,H}$ assignments were not made. The *endo*-stereochemistry assigned to the alcohols is consistent with the stereochemistry of reduction of norbornanone as a model.[4] We have utilized a 16-alcohol in the 8,13-isogibberellin series to generate 13-desoxygibberellins by rearrangement[5] although the stereochemistry of the alcohol itself was not fully defined. Before examining these rearrangements further in the gibberellin series, we have endeavoured to establish the stereochemistry of hydride reduction at C-16 in both the normal and 8,13-isogibberellin series more rigorously.

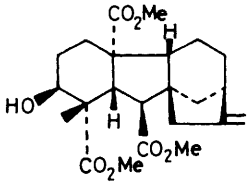
The 8,13-isogibberellin (**3**) was obtained by isomerization of gibberellin A_{20} methyl ester (**1**), prepared from methyl gibberellate,[6] with trifluoroacetic acid in chloroform in the presence of a catalytic amount of sulphuric acid. The C-16 carbonyl group was then reduced with sodium borohydride in methanol to afford the alcohol (**4**).



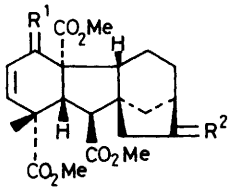
(**1**) R = OH
(**2**) R = H



(**3**) R = O
(**4**) R = ---OH, ▬H
(**5**) R = ---H, ▬Cl



(**6**)



(**7**) R^1 = H_2, R^2 = CH_2
(**8**) R^1 = H_2, R^2 = O
(**9**) R^1 = R^2 = O
(**10**) R^1 = H_2, R^2 = ▬H, ---OH
(**11**) R^1 = H_2, R^2 = ▬H, ---OAc
(**12**) R^1 = R^2 = ▬H, --OH.

The assignment of the stereochemistry to the C-16 alcohol and its derivatives was based on several pieces of evidence. Firstly the selective deuteriation of the '*exo*'-proton (15β-H) and the consequent change in the multiplicity of 16-H facilitated the analysis of the 15-H,16-H coupling constants and their comparison with well-established models in the bicyclo[2.2.1]heptane series.[7] In particular, it is known that the coupling constants decrease in the order $J_{exo,exo} > J_{endo,endo} > J_{exo,endo}$. Secondly, the '*endo*' protons on a bicyclo[2.2.1]heptane can be distinguished from their *exo*-counterparts by the long-range W type coupling which they show to a proton on the methylene bridge.[8]

There is considerable evidence that the *exo*-hydrogen atom adjacent to a carbonyl group on a bicyclo[2.2.1]heptane is exchanged much more readily than its *endo*-epimer.[9] Consequently we reasoned that the 15β-H in (**3**) could be selectively exchanged. Treatment of (**3**) with sodium deuteroxide for 3 h at room temperature gave a monodeuterio-ketone. The stereochemistry of the deuteriation was established from the changes in the ^{1}H n.m.r. spectrum (determined at 360 MHz). The relevant assignments which were confirmed by spin decoupling experiments, are given in Figure 1. In the deuteriated ketone (**3**) the 15-*exo*-proton resonance (δ 2.10) disappeared whilst the 15α-H signal (δ 2.99, *J* 3.9 and 18.8 Hz) collapsed to a doublet (*J* 3.9 Hz). In the C-16 alcohol (**4**), the C*H*(OH) resonance (δ 3.87) appeared as a double-doublet (*J* 4 and 10.5 Hz) whilst in the deuteriated analogue this signal was a doublet (*J* 4 Hz). Thus the *exo,exo* coupling was missing implying that the hydroxy group had the *endo*-configuration. In accord with the *exo*-configuration of the 16β-H, it showed only vicinal and no long-range coupling. Extensive spin-decoupling experiments led to the assignment of the proton resonances and coupling pattern as shown in Figure 2.

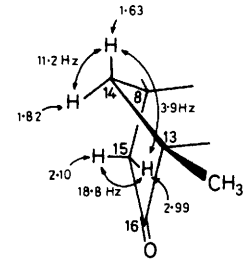


Figure 1. Proton assignments in the ketone (**3**)

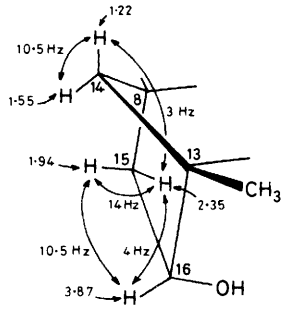


Figure 2. Proton assignments in the alcohol (**4**)

In the course of the 'double-inversion' route to 13-desoxygibberellins, treatment of the alcohol (**4**) with phosphorus pentachloride gave[5] a mixture of gibberellin A_9 methyl ester (**2**), its endocyclic Δ^{15}-isomer, and a chloro compound, $C_{20}H_{27}ClO_4$, m.p. 180—181 °C which was tentatively assigned structure (**5**). This has now been re-examined. The alcohol reacted slowly over 7 h with triphenylphosphine–carbon tetrachloride to afford the same 16-chloro derivative in which the CHCl resonance at δ 3.86 appeared as a quartet of doublets (*J* 1.5, 3.5, and 7.5 Hz). Spin-decoupling experiments led to the analysis of the coupling patterns shown in Figure 3.

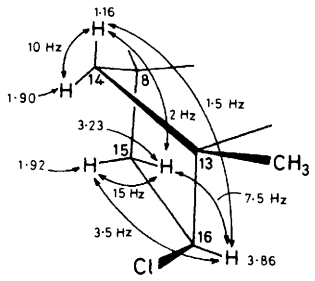


Figure 3. Proton assignments in the chloro compound (**5**)

The C-16 proton was assigned the *endo*-configuration since, in contrast to the alcohol (**4**), it shows a long-range coupling to 14-H whilst the *endo,endo* coupling (7.5 Hz) is, as anticipated, less than the *exo,exo* coupling in the alcohol. The full structure and stereochemistry, including the C-9 configuration, was confirmed by *X*-ray analysis (Figure 4). This also showed that no skeletal rearrangement had taken place.

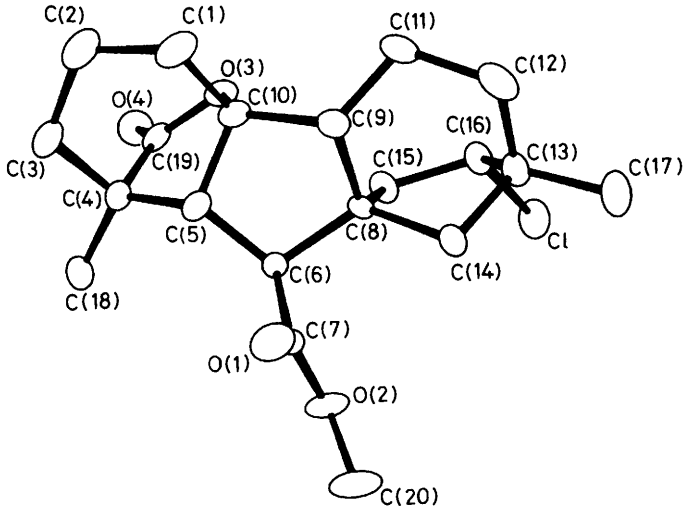


Figure 4. Molecular structure of the chloro compound (**5**)

The stereochemistry of reduction at C-16 in the normal gibberellin series was examined with compounds derived from gibberellin A_{13} trimethyl ester (**6**).[10] Treatment of gibberellin A_{13} trimethyl ester with triphenylphosphine–carbon tetrachloride and pyridine under reflux gave Δ^2-dehydrogibberellin A_{25} trimethyl ester (**7**)[11] which was oxidized with t-butyl chromate to give a separable mixture of the 17-nor-16-ketone (**8**) and the 17-nor-1,16-diketone (**9**).[12] Reduction of the ketone (**8**) with sodium borohydride cleanly furnished a mono-ol (**10**).

The assignment of the stereochemistry was based on the magnitudes of the 15-H,16-H and 13-H,16-H coupling constants, the analysis of which was facilitated by deuteriation at C-15. Treatment of the 16-ketone (**8**) with sodium deuterioxide in dioxane for 15 h at room temperature gave a deuteriated ketone which lacked the ^{1}H n.m.r. signals at δ 2.19 (dd, *J* 3 and 16.4 Hz) and δ 1.81 (doublet, *J* 16.4 Hz). The former, showing the long-range coupling was assigned to the 15β-H and the latter to the 15α-H. Reduction then afforded a [15-$^2H_2$]alcohol. Both the deuteriated and undeuteriated alcohols were converted into their acetates which gave clearer spectra. Comparison of the highfield (360 MHz) spectra of these acetates (**11**) together with a series of spin-decoupling experiments enabled a full assignment of the ring A and D resonances to be made. The ^{2}H n.m.r. spectrum of the deuteriated sample had signals at δ 1.35 and 1.84 which were assigned to 15-H. These signals were missing from its ^{1}H n.m.r. spectrum. The C*H*OAc signal in the deuteriated sample appeared as a doublet, δ 5.0 (*J* 6.7 Hz). Bearing in mind the long-range couplings between the bridge proton and an *endo*-proton of a bicyclo[2.2.1]heptane and the magnitudes of the coupling constants between the *exo*- and *endo*-protons, this led to the assignment given in Figure 5 in which the acetoxy group has the *endo*-configuration. The stereochemistry of the parent alcohol was confirmed by an *X*-ray analysis (see Figure 6).

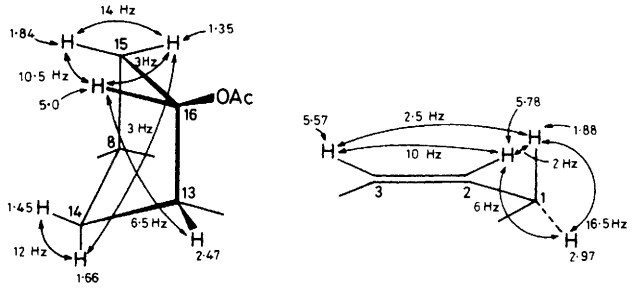


Figure 5. Proton assignments in the acetate (**11**)

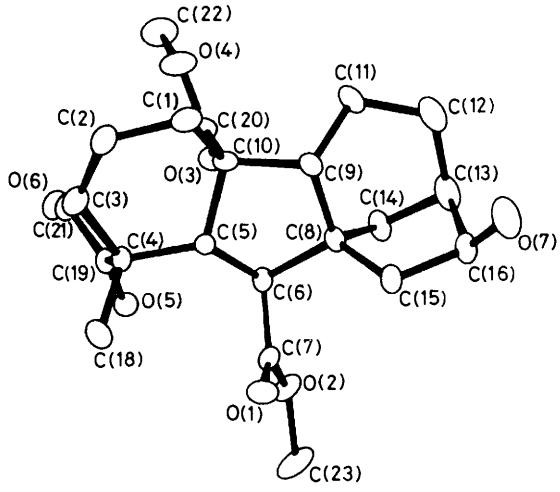


Figure 6. Molecular structure of the alcohol (**10**)

The ring A proton resonances were assigned as follows. Irradiation at δ 5.78 removed a 10 Hz coupling from the other olefinic double doublet (*J* 2.5 and 10 Hz) at δ 5.57 and collapsed a double doublet (*J* 6 and 16.5 Hz) at δ 2.97 to a doublet (*J* 16.5 Hz) and converted a multiplet at δ 1.88 into a double doublet (*J* 2.5 and 16.5 Hz). Irradiation at δ 1.88 collapsed the double doublet at δ 2.97 to a doublet (*J* 6 Hz) and removed small couplings (2 and 2.5 Hz) from the olefinic signals at δ 5.77 and 5.57 respectively. In allylic systems as the dihedral angle between the allylic and olefinic protons approaches 90° the vicinal coupling constants tend to zero whilst the allylic coupling constant to the distant proton is at a maximum.[12] This leads to the assignments shown in Figure 5 in which the lower field pseudoequatorial 1α-H proton is deshielded by the adjacent methoxycarbonyl group.

This analysis enabled the stereochemistry of reduction of the C-1 carbonyl group to be defined. Reduction of the unsaturated ketone (**9**) with sodium borohydride gave a diol (**12**). The CHOH resonances appeared as an overlapping octet, δ 4.28 (*J* 3.5, 6.5, and 10 Hz) assigned to 16-H, and broad singlet at δ 4.12. Irradiation at δ 4.12 removed a 2 Hz coupling from the olefinic signal at δ 5.62 and a 1 Hz coupling from δ 5.84. The 6 Hz coupling between 1α-H and 2-H apparent in the parent hydrocarbon, was not present and hence the hydroxy group was replacing this proton. Furthermore, the 5β-H proton resonance in the dehydrogibberellin A_{25} methyl ester (**7**), its 17-nor-16-ketone (**8**) and the alcohol (**12**) appeared at δ 2.45, 2.41, and 2.43 respectively, *i.e.* there was no significant deshielding on introduction of the hydroxy group which might be attributed to a 1,3-diaxial interaction. Hence reduction has taken place as anticipated, from the β-face of ring A.

Experimental

The ^1H and ^2H n.m.r. spectra were determined on a Bruker WH 360 spectrometer for solutions in chloroform.

Rearrangement of Gibberellin A_{20} *Methyl Ester* (**1**).—Gibberellin A_{20} methyl ester (500 mg) in chloroform (5 ml) was treated with trifluoroacetic acid (1.0 ml) in the presence of concentrated sulphuric acid (0.1 ml) at room temperature. The reaction was monitored by ^1H n.m.r. spectroscopy. After 15 min, the mixture was diluted with chloroform (30 ml) and poured into water (50 ml). The chloroform layer was washed with water, aqueous sodium hydrogen carbonate, and water and then dried. The solvent was evaporated to give *ent*-10β-hydroxy-13-methyl-17,20-bisnor-8,13-isogibberellane-7,19-dioic acid 19,10β-lactone 7-methyl ester (**3**) (480 mg) which crystallized as needles, m.p. 177—179 °C (prisms, lit.,[12] m.p. 190—191 °C), $[\alpha]_D^{28}$ +53° (lit.,[12] $[\alpha]_D^{19}$ +50°) (Found: C, 69.3; H, 7.8 Calc. for $C_{20}H_{26}O_5$: C, 69.3; H, 7.5%), $\nu_{max.}$ 1 770 and 1 740 cm^{-1}; δ 1.04 (3 H, s, 13-Me), 1.16 (3 H, s, 18-H), 2.56 (1 H, d, *J* 6.5 Hz, 5-H), 2.70 (1 H, d, *J* 6.5 Hz, 6-H), and 3.74 (3 H, s, OMe).

Deuteriation of (**3**).—The above ketone (**3**) (300 mg) in dioxane (3 ml) was treated with a 3M-solution of sodium [^2H]-hydroxide (5 ml) for 3 h. The mixture was acidified and the product extracted with ethyl acetate. The extract was washed with water, dried, and the solvent evaporated to afford ent-[15α-$^2H_1$]-10β-*hydroxy*-13-*methyl*-16-*oxo*-17,20-*bisnor*-8,13-*isogibberellane*-7,19-*dioic acid* 19,10β-*lactone* (250 mg) which crystallized as fine needles, m.p. 235—236 °C (Found: C, 68.6; H, 7.1. $C_{19}H_{23}{}^2H_1O_5$ requires C, 68.5; H, 6.9%), $\nu_{max.}$ 1 770, 1 740, and 1 710 cm^{-1}; δ 1.05 (3 H, s, 13-Me), 1.20 (3 H, s, 18-H), 2.55 (1 H, d, *J* 6.5 Hz 5-H), and 2.70 (1 H, d, *J* 6.5 Hz, 6-H). Methylation with diazomethane gave the [^2H]-keto-ester (**3**), m.p. 178—179 °C (*M*$^+$, *m/z* 347).

Reduction of the Keto-ester (**3**).—The keto-ester (**3**) (300 mg) in methanol (20 ml) was treated with sodium borohydride (200 mg) for 30 min at 0 °C. The solution was acidified with dilute hydrochloric acid, the methanol evaporated, and the product recovered in ethyl acetate. The solvent was evaporated to give *ent*-10β,16β-dihydroxy-13-methyl-17,20-bisnor-8,13-isogibberellane-7,19-dioic acid 19,10β-lactone 7-methyl ester (**4**) (210 mg) which crystallized as plates, m.p. 116—118 °C (lit.,[5] 118—119 °C) (Found: C, 69.5; H, 8.1. Calc. for $C_{20}H_{28}O_5$: C, 68.9; H, 8.0%), $\nu_{max.}$ 3 525, 1 775, and 1 715 cm^{-1}; δ 0.98 (3 H, s, 13-Me), 1.13 (3 H, s, 18-H), 2.44 and 2.56 (each 1 H, d, *J* 6.6 Hz, 5- and 6-H), 3.71 (3 H, s, OMe), and 3.87 (dd, *J* 4 and 10.5 Hz). The *acetate*, prepared with acetic anhydride in pyridine, crystallized as cubes, m.p. 120—122 °C (Found; C, 67.8; H, 7.6. $C_{22}H_{30}O_6$ requires C, 67.7; H, 7.7%), $\nu_{max.}$ 1 780 and 1 745 cm^{-1}; δ 0.98 (3 H, s, 13-Me), 1.13 (3 H, s, 18-H), 2.04 (OAc), 2.45 and 2.57 (each 1 H, d, *J* 6.5 Hz, 5- and 6-H), 3.71 (3 H, s, OMe), and 4.76 (1 H, dd, *J* 4.4 and 10.9 Hz, 16-H).

Preparation of the Chloro Compound (**5**).—The above alcohol (**4**) (200 mg) in pyridine (5 ml) and carbon tetrachloride (25 ml) containing triphenylphosphine (400 mg) were heated under reflux for 7 h. The solvents were evaporated and the residue chromatographed on silica. Elution with 15% ethyl acetate–light petroleum gave *ent*-16α-chloro-10β-hydroxy-13-methyl-17,20-bisnor-8,13-isogibberellane-7,19-dioic acid 19,10β-lactone 7-methyl ester (**5**) (185 mg) which crystallized as cubes, m.p. 179—181 °C (lit.,[5] 180—181 °C) (Found: C, 65.8; H, 7.24. Calc. for $C_{20}H_{27}ClO_4$: C, 65.6; H, 7.37%), $\nu_{max.}$ 1 780 and 1 730 cm^{-1}; δ 1.12 and 1.15 (each 3 H, s, 13-Me and 18-H), 1.92 (1 H, dd, *J* 3.5 and 15 Hz, 15-H), 2.47 and 2.61 (each 1 H, d, *J* 6.6 Hz, 5- and 6-H), 3.23 (1 H, octet, *J* 2, 7.5 and 15 Hz, 15-H), and 3.86 (1 H, octet, *J* 1.5, 3.5 and 7.5 Hz, 16-H).

Preparation of Δ^2-*Dehydrogibberellin* A_{25} *Trimethyl Ester* (**7**).—Gibberellin A_{13} trimethyl ester (1.5 g) in pyridine (10 ml) and carbon tetrachloride (50 ml) containing triphenylphosphine (3 g) was heated under reflux for 2.5 h. The solvents were evaporated and the residue was chromatographed on silica. Elution with 10% ethyl acetate–light petroleum gave *ent*-gibberella-2,16-diene-7,19,20-trioic acid 7,19,20-trimethyl ester (**7**) (1.1 g) which crystallized as prisms, m.p. 130—131 °C (lit.,[11] 133—134 °C) identified from its n.m.r. spectrum.

Sodium Borohydride Reduction of the Ketones (**8**) *and* (**9**).—(*a*) The ketone (**8**)[12] (200 mg) in methanol (50 ml) was treated with sodium borohydride (100 mg) at 0 °C for 1 h. The methanol was evaporated, dilute hydrochloric acid was added, and the product was recovered in ethyl acetate. ent-16β-*Hydroxy*-17-*norgibberell*-2-*ene*-7,19,20-*trioic acid* 7,19,20-*trimethyl ester* (190 mg) crystallized as prisms, m.p. 195—196 °C (Found: C, 65.0; H, 7.3. $C_{22}H_{30}O_7$ requires C, 65.0; H, 7.3%), $\nu_{max.}$ 3 525, and 1 735 cm^{-1}; δ 1.30 (3 H, s, 18-H), 2.30 (1 H, m, 13-H), 2.43 (1 H, d, *J* 13 Hz, 5-H), 3.01 (1 H, dd, *J* 6 and 17 Hz), 3.60, 3.68, and 3.80 (each 3 H, s, OMe), 3.83 (1 H, d, *J* 13 Hz, 6-H), 4.31 (1 H, m, 16-H), 5.62 (1 H, dd, *J* 2 and 10 Hz, 3-H), and 5.85 (1 H, octet, *J* 1.5, 6 and 10 Hz, 2-H). The *acetate*, prepared with acetic anhydride in pyridine, crystallized as prisms, m.p. 113—115 °C (Found: C, 64.3; H, 6.8. $C_{24}H_{32}O_8$ requires C, 64.1; H, 7.1%), $\nu_{max.}$ 1 735 and 1 715 cm^{-1}; δ 1.28 (3 H, s, 18-H), 1.35 (1 H, dt, *J* 3 and 14.4 Hz, 15-H), 1.60 (1 H, d, *J* 2.8 and 12.2 Hz, 14-H), 1.84 (1 H, dd, *J* 10.5 and 14.4 Hz, 15-H), 2.04 (3 H, s, OAc), 2.41 (1 H, d, *J* 12.6 Hz, 5-H), 2.47 (1 H, m, 13-H), 2.96 (1 H, dd, *J* 6 and 16.6 Hz, 1-H), 3.56, 3.65, and 3.76 (each 3 H, s, OMe), 3.80 (1 H, d, *J*

Table 1. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for compound (**5**)

	x	*y*	*z*
Cl	1 173(1)	2 641(1)	2 553(1)
O(1)	4 553(3)	6 901(2)	848(2)
O(2)	2 501(3)	5 952(3)	585(2)
O(3)	6 884(3)	3 093(2)	1 306(2)
O(4)	6 889(4)	2 013(3)	286(2)
C(1)	8 559(5)	4 659(4)	1 546(3)
C(2)	9 418(5)	4 235(5)	875(3)
C(3)	8 602(5)	4 421(5)	144(3)
C(4)	6 928(5)	4 106(4)	179(2)
C(5)	6 266(4)	4 865(3)	776(2)
C(6)	4 568(4)	4 852(3)	900(2)
C(7)	3 901(4)	6 026(3)	765(2)
C(8)	4 321(4)	4 493(3)	1 742(2)
C(9)	5 888(5)	4 643(3)	2 088(2)
C(10)	6 947(4)	4 346(3)	1 469(2)
C(11)	6 010(6)	4 066(4)	2 851(2)
C(12)	4 700(7)	4 469(4)	3 324(2)
C(13)	3 178(5)	4 388(4)	2 934(2)
C(14)	3 197(5)	5 134(3)	2 228(2)
C(15)	3 706(5)	3 249(3)	1 814(2)
C(16)	3 071(5)	3 167(3)	2 605(2)
C(17)	1 945(7)	4 735(5)	3 469(3)
C(18)	6 208(6)	4 112(5)	−574(2)
C(19)	6 876(4)	2 939(3)	557(2)
C(20)	1 719(6)	7 030(5)	521(4)

Table 2. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for compound (**10**)

	x	*y*	*z*
O(1)	4 271(3)	3 346(0)	2 134(3)
O(2)	6 183(3)	4 452(2)	2 249(2)
O(3)	9 165(3)	3 956(2)	7 522(3)
O(4)	9 132(3)	2 921(2)	9 321(3)
O(5)	6 031(3)	5 464(2)	5 572(2)
O(6)	6 516(3)	5 044(2)	7 963(2)
O(7)	8 466(3)	249(2)	2 864(4)
C(1)	6 539(4)	1 846(3)	7 535(4)
C(2)	5 395(4)	2 478(3)	7 934(4)
C(3)	4 738(4)	3 354(3)	7 276(4)
C(4)	5 016(3)	3 847(3)	5 991(3)
C(5)	5 980(3)	3 095(2)	5 444(3)
C(6)	6 811(3)	3 445(2)	4 420(3)
C(7)	5 585(4)	3 727(3)	2 837(3)
C(8)	7 880(3)	2 524(3)	4 408(3)
C(9)	8 118(4)	1 890(3)	5 859(4)
C(10)	7 342(4)	2 501(3)	6 754(3)
C(11)	9 932(5)	1 561(3)	6 772(5)
C(12)	10 658(5)	1 137(4)	5 738(5)
C(13)	10 181(4)	1 754(3)	4 259(5)
C(14)	9 561(4)	2 809(3)	4 444(4)
C(15)	7 179(4)	1 840(3)	2 974(4)
C(16)	8 680(4)	1 331(3)	2 887(4)
C(18)	3 326(4)	4 084(3)	4 694(4)
C(19)	5 922(3)	4 874(3)	6 465(3)
C(20)	8 629(4)	3 217(3)	7 881(4)
C(21)	7 449(5)	5 983(3)	8 476(4)
C(22)	10 351(6)	3 563(5)	10 461(5)
C(23)	5 147(7)	4 755(4)	717(4)

12.6 Hz, 6-H), 5.00 (1 H, octet, *J* 3.5, 6.8, and 10.5 Hz, 16-H), 5.57 (1 H dd, *J* 2 and 10 Hz, 3-H), and 5.78 (1 H, octet, *J* 1.5, 6, and 10 Hz, 2-H).

(*b*) The diketone (**9**) (300 mg) was treated as above to afford ent-1β,16β-*dihydroxy*-17-*norgibberell*-2-*ene*-7,19,20-*trioic acid* 7,19,20-*trimethyl ester* (**12**) (285 mg) which crystallized as prisms, m.p. 166—168 °C (Found: C, 62.5; H, 7.1. $C_{22}H_{30}O_8$ requires C, 62.55; H, 7.1%), $\nu_{max.}$ 3 580, 3 540, 1 730, and 1 710 cm^{-1}; δ 1.30 (3 H, s, 18-H), 2.43 (1 H, d, 12 Hz, 5-H), 3.65, 3.70, and 3.79 (each 3 H, s, OMe), 3.70 (1 H, d, *J* 12 Hz, 6-H), 4.12 (1 H, dd, 2 and 12 Hz, 1-H, the 12 Hz coupling was removed by exchange with ^2H_2O), 4.28 (1 H, octet, *J* 3.5, 6.5, and 10 Hz, 16-H), 5.62 (1 H, dd, *J* 2 and 10 Hz, 2-H), and 5.84 (1 H, dd, *J* 1 and 10 Hz, 3-H).

Deuteriation of the Ketone (**8**).—The ketone (**8**) (300 mg) in dioxane (10 ml) was stirred with 2M-sodium [^{2}H] hydroxide (6 ml) for 15 h at room temperature. The solution was acidified and the product recovered in ethyl acetate. The solvent was evaporated and the residue methylated with diazomethane and recrystallized to afford the [^{2}H]ketone (**8**), identified from its n.m.r. spectrum. Signals at δ 1.35 and 1.84 were absent in the deuteriated sample.

Crystallographic Data.—(*a*) *ent*-16α-Chloro-10β-hydroxy-13-methyl-17,20-bisnor-8,13-isogibberellane-7,19-dioic acid 19,10β-lactone 7-methyl ester (**5**): $C_{20}H_{27}ClO_4$, M = 366.9, orthorhombic, a = 9.032(1), b = 11.663(2), c = 17.910(4) Å, U = 1 886.6 Å^3, Z = 4, D_C = 1.29 g cm^{-3}, $F(000)$ = 784. Mo-K_α radiation, λ = 0.710 69 Å, μ = 2.3 cm^{-1}. Space group $P2_12_12_1$ from systematic absences of $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd. Final atomic co-ordinates are given in Table 1.

(*b*) *ent*-16β-Hydroxy-17-norgibberell-2-ene-7,19,20-trioic acid 7,19,20-trimethyl ester (**10**): $C_{22}H_{30}O_7$, M = 406.5, monoclinic, a = 9.033(2), b = 13.197(2), c = 9.704(2) Å, β = 115.10(2)° U = 1 047.6 Å^3 Z = 2, D_C = 1.29 g cm^{-3}, $F(000)$ = 436. Monochromated Cu-K_α radiation λ = 1.5418 Å μ = 7.9 cm^{-1}. Space group $P2_1$ from systematic absences of $0k0$ for k odd and successful structure refinement. Final atomic co-ordinates are given in Table 2. Details of the crystal structure determinations, intramolecular distances and angles, lists of temperature factors, hydrogen atom positions, and final structure factors have been deposited as Supplementary Publication No SUP 23878 (34 pp.).*

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