Preparation and Occurrence of Gibberellins A_{75} and A_{76} and 3-*Epi*-A_{72}

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Three water-soluble compounds were detected in extracts from mature seeds of *Helianthus annuus* by g.l.c.–mass spectrometry. The structures of these putative gibberellins were confirmed by comparison with authentic samples of the 15β-hydroxygibberellins GA_{75}, GA_{76}, and 3-*epi*-GA_{72} prepared from GA_3.

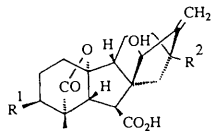
In a previous paper[1] we have reported the occurrence of 10 15β-hydroxygibberellins (GAs) in the ethyl acetate-soluble acids from extracts of seed of *Helianthus annuus* L. We have also described[2] the partial synthesis of four 15β-hydroxyGAs, namely GA_{67} (**1**), GA_{68} (**3**), GA_{72} (**2**) and the unnatural 15β-hydroxyGA_3 (**4**) from GA_3 (**5**). These 15β-hydroxyGAs, particularly the trihydroxy compounds (**2**) and (**4**) showed high water-solubility, suggesting the possibility that other 15β-hydroxyGAs may have escaped detection in our original investigation.[1] This paper reports a re-investigation of the GAs in mature seeds of *H. annuus*, in particular those GAs remaining in an aqueous acidic extract after extraction with ethyl acetate. Three new 15β-hydroxyGAs have been detected by capillary g.c.–m.s. and identified as 15β-hydroxyGA_8 (**6**) (GA_{75}), 15β-hydroxyGA_{29} (**7**) (GA_{76}), and 3-*epi*-GA_{72} (**8**) by partial synthesis from GA_3 (**5**).

Results

Capillary G.c.–m.s. Analyses of Extracts from Mature seeds of Helianthus annuus.—An aqueous methanol extract from mature seeds was partitioned as described in the Experimental section into: (A) a neutral fraction, soluble in ethyl acetate; (B) an acidic fraction, soluble in ethyl acetate; and (C) an acidic fraction, soluble in water and extracted with butanol. Fractions A—C were methylated and trimethylsilylated and analysed by capillary g.c.–m.s. No GAs were detected in Fraction A.. The compounds, identified in Fractions B and C by full scan g.c.–m.s. and Kovats Retention Indices (K_I) are shown in the Table.

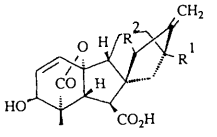
Gibberellins A_{67} (**1**) and A_{72} (**2**) were identified by comparison of the m.s. and K_I with the literature values[1] and 3-hydroxy-2-oxoindol-3-ylacetic acid (**9**) by comparison with published data.[3] Gibberellins A_{75} (**6**) and A_{76} (**7**) and 3-*epi*-GA_{72} (**8**) were identified by direct comparison of the m.s. and K_I data with those of authentic derivatives, prepared as described in the following section.

Partial Syntheses of GA_{75} (**6**), GA_{76} (**7**), *and* 3-epi-GA_{72} (**8**).—The preparation of GA_{75} (**6**) and GA_{76} (**7**) required the introduction of a 15β-hydroxy group into suitably protected derivatives of GA_8 and GA_{29}. The selected derivatives were the methyl ester acetates (**17**) and (**18**) (Scheme 1), the syntheses of which from GA_3 (**5**) are described later. Allylic oxidation of (**17**) and (**18**) introduced a hydroxy group into the 15α-position. It was necessary to invert the alcohol to the required β-orientation. Displacement of the corresponding methanesulphonates by caesium acetate as described by Willis[4] was considered. However a model experiment with the 15α-methylsulphonyl derivative (**11**) of GA_1 methyl ester-3,13-diacetate gave only the S_N2' displacement product (**12**). Hence, the oxidation–reduction procedure of Dolan and MacMillan[2] was employed as shown in Scheme 1. Oxidation of (**19**) and (**20**)



(1) R^1=H, R^2=OH (GA_{67})

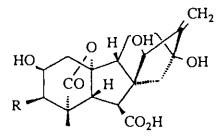
(2) R^1=R^2=OH (GA_{72})



(3) R^1=H, R^2=OH (GA_{68})

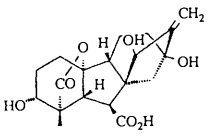
(4) R^1=R^2=OH (15β-OH GA_3)

(5) R^1=OH, R^2=H (GA_3)

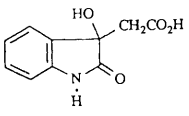


(6) R=OH (GA_{75})

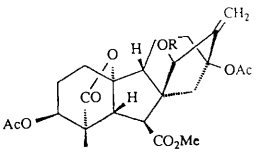
(7) R=H (GA_{76})



(8)

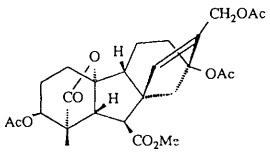


(9)

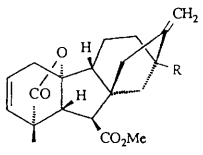


(10) R=H

(11) R=SO_2Me

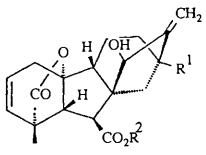


(12)



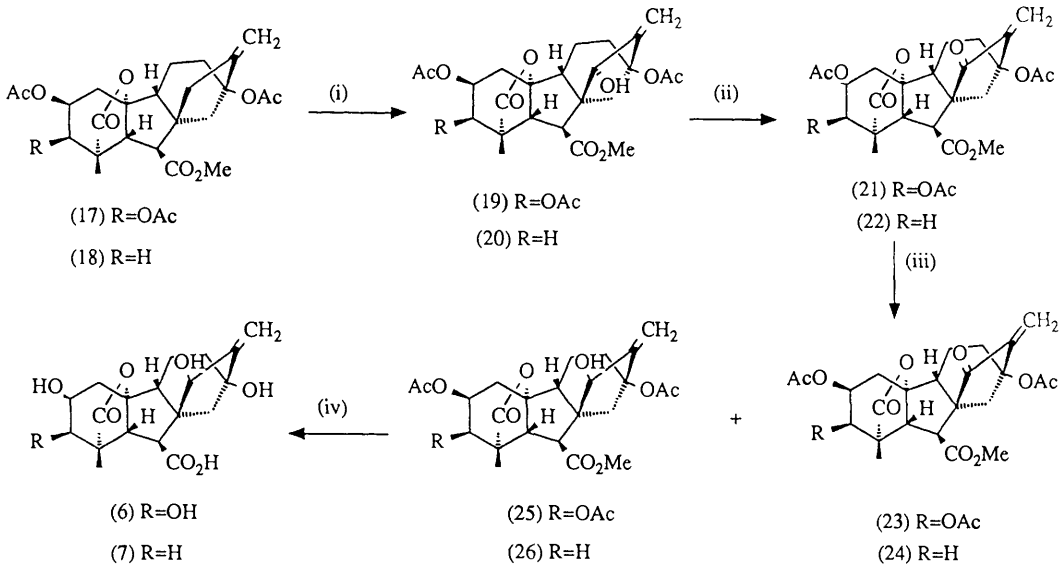
(13) R=OAc

(14) R=OH



(15) R^1=OAc, R^2=Me

(16) R^1=OH, R^2=H



Scheme 1. Conversion of GA_8-triacetate (**17**) and GA_{29}-diacetate (**18**) to GA_{75} (**6**) and GA_{76} (**7**) respectively. *Reagents:* i, SeO_2, Bu^tO_2H, CH_2Cl_2; ii, $(COCl)_2$, Me_2SO, Pr^i_2NEt; iii, Zn, AcOH; iv, K_2CO_3, MeOH, H_2O

Table. Compounds identified in fractions B and C from mature seed of *Helianthus annuus* by full scan g.c./m.s. and K_I

Fraction	Compound	K_I	*m/z* (relative intensites)
B, C	GA_{67} (**1**)	2 613	506 (M^+, 100), 491 (26), 462 (22), 447 (10), 416 (100), 389 (16), 372 (21), 357 (23), 313 (16), 295 (26), 257 (16), 229 (19), and 295 (14)
B, C	3-Hydroxy-2-oxoindol-3-ylacetic acid (**9**)	1 884	293 (M^+, 34), 278 (100), 220 (79), 172 (40), and 89 (55)
C	GA_{72} (**2**)	2 822	594 (M^+, 100), 579 (21), 551 (9), 550 (14), 506 (16), 505 (38), 504 (100), 477 (13), 465 (16), 371 (18), 370 (21), 311 (15), 295 (20), and 203 (19)
C	GA_{75} (**6**)	2 948	682 (M^+, 100), 667 (14), 594 (17), 593 (43), 592 (91), 295 (22), 259 (20), 231 (27), 229 (11), 191 (38), and 147 (19)
C	GA_{76} (**7**)	2 771	594 (M^+, 70), 579 (26), 550 (21), 504 (100), 477 (18), 466 (24), 445 (20), 401 (25), 370 (24), 355 (29), 327 (32), 313 (32), 311 (47), 295 (68), and 281 (43)
C	3-*epi*-GA_{72} (**8**)	2 881	594 (M^+, 77), 550 (21), 504 (100), 465 (15), 457 (12), 430 (11), 370 (14), 315 (12), 282 (13), 258 (16), 247 (13), 206 (17), 115 (14), and 109 (32)

with the activated DMSO complex[5] smoothly gave the enones (**21**) and (**22**) respectively. However reduction of (**21**) and (**22**) gave the 16-en-15β-ols (**25**) and (**26**) as the minor products. In each case, the major products were the saturated ketones (**23**) and (**24**) arising either by 1,4-reduction of the corresponding enone or by acid-catalysed rearrangement of the 16-en-15β-ols (**25**) and (**26**). In the final step, the acetates and methyl esters were hydrolysed by aqueous potassium carbonate to give GA_{75} (**6**) and GA_{76} (**7**). The methyl ester of a gibberellin is usually resistant to hydrolysis under these conditions. For example, treatment of GA_5 methyl ester 13-acetate (**13**) with aqueous potassium carbonate gives GA_5 methyl ester (**14**) as the sole product whereas 15β-hydroxy GA_5 methyl ester 13-acetate (**15**) gives 15β-hydroxyGA_5 (**16**). An investigation of this neighbouring group effect will be described elsewhere.

3-*epi*-Gibberellin A_{72} (**8**) was prepared by base-catalysed epimerisation[6] of the known[2] GA_{72} (**2**) using potassium carbonate in aqueous methanol.

The full scan m.s. and the K_I values for the MeTMSi derivatives of the synthetic GA_{75} (**6**), GA_{76} (**7**), and 3-*epi*-GA_{72} (**8**) were identical with those of the MeTMSi derivatives of the compounds detected by capillary g.c.–m.s. in the butanol-soluble acid fraction from mature seeds of *H. annuus*.

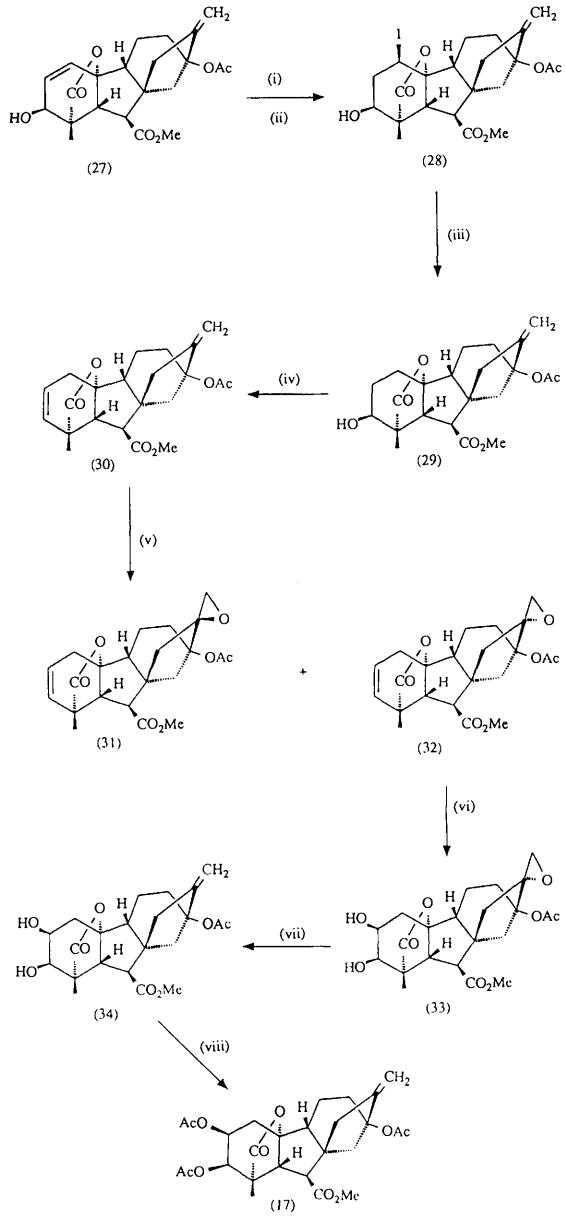
Preparation of Gibberellin A_8 *Methyl Ester Triacetate* (**17**).—The route to GA_8 methyl ester triacetate (**17**) proceeded from GA_3 (**5**) *via* the known[7] GA_3 methyl ester 13-monoacetate (**27**) as shown in Scheme 2. The overall yield from GA_3 was low (~7%), partly because only the 16α,17-epoxide (**32**) gave the corresponding 2β,3β-diol (**33**) on treatment with osmium tetroxide and *N*-methylmorpholine *N*-oxide. The 16β,17-epoxide (**31**) gave an intractable mixture of unidentified products.

Preparation of Gibberellin A_{29} *Methyl Ester Diacetate* (**18**).—The route from the known[8] GA_3 methyl ester 3-monoacetate (**35**) is shown in Scheme 3. It combined and adapted three published procedures. Firstly the mono-acetate (**35**) was converted into the trienoic acid (**36**) following the method of Baynham and Hanson.[9] Secondly the trienoic acid (**36**) was converted into 2-*epi*-GA_{29} methyl ester (**40**) *via* the iodo isolactone (**37**), the isolactone (**38**), and the iodo lactone (**39**) using the procedures described by Beale *et al.*[10] Finally the 2α-hydroxy group in 2-*epi*-GA_{29} methyl ester (**40**) was displaced by acetate by treatment of the 2α-methanesulphonate (**42**) with caesium acetate as described by Willis.[4]

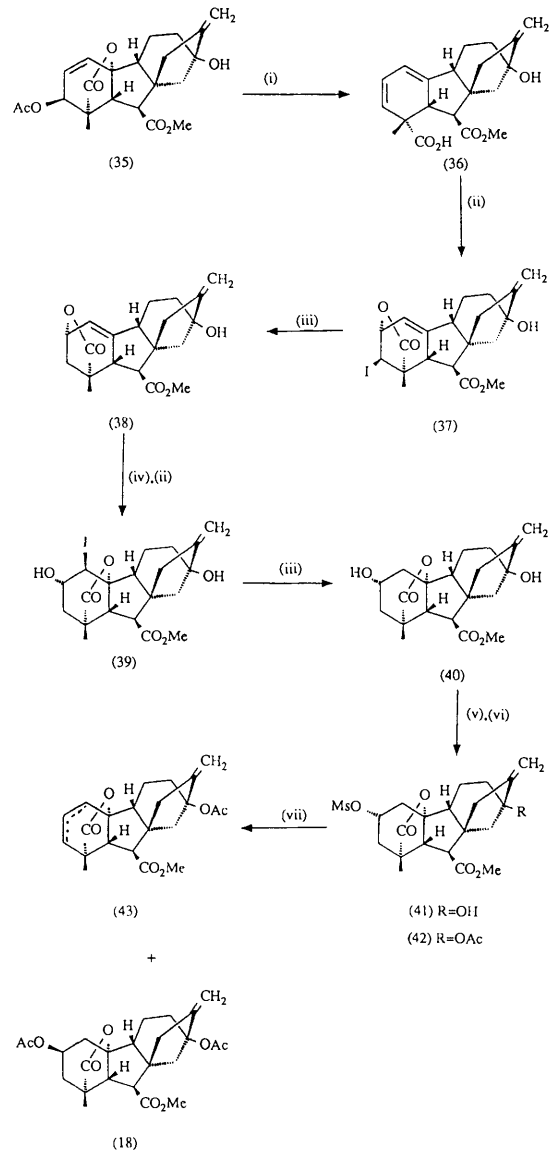
The bioactivities of GA_{75} (**6**) and GA_{76} (**7**) will be reported elsewhere.

Experimental

General experimental details have been described in a previous paper.[12]



Scheme 2. Preparation of GA_8 methyl ester triacetate (**17**). *Reagents:* i, H_2, 10% Pd on $CaCO_3$, MeOH, C_5H_5N; ii, I_2, aq. $NaHCO_3$, THF, CH_2Cl_2; iii, Bu_3SnH, AIBN, toluene; iv, $POCl_3$, C_5H_5N; v, *m*ClpBA, $CHCl_3$; iv, OsO_4, NMMNO, H_2O, Me_2CO; vii, NaI, NaOAc, Zn, AcOH, H_2O; viii, $(MeCO)_2O$, TsOH



Scheme 3. Preparation of GA_{29} methyl ester diacetate (**18**). *Reagents:* i, MeCN, Zn, AcOH; ii, I_2, aq. $NaHCO_3$, THF, CH_2Cl_2; iii, BuSnH, AIBN, toluene; iv, 0.8M KOH, THF; v, $MeSO_2Cl$ (1 equiv.), C_5H_5N; vi, $(MeCO)_2O$, TsOH; vii, CsOAc, 18-crown-6-ether, toluene

Extraction of Mature Seeds of Helianthus annuus.—The seeds (100 g) were macerated in methanol–water (4:1; 500 ml) in a Wareing blender and allowed to stand for 2 days at 20 °C. The extract was recovered by vacuum filtration and the residue was extracted in the same way twice more with methanol–water (4:1; 500 ml), each time for 1 day. The combined filtrates were evaporated to dryness under reduced pressure at 40 °C (toluene being added to remove traces of water azeotropically).

The resultant residue was redissolved in methanol–water (4:1; 100 ml) and washed with light petroleum (3 × 50 ml). The aqueous layer was evaporated to dryness as before. The product was dissolved in pH 8 phosphate buffer solution (200 ml) and shaken for 1 h with poly(vinylpyrrolidone) powder (25 g). The solution was filtered and the solid residues washed with pH phosphate buffer solution (100 ml). The filtrate and washings were combined and extracted with ethyl acetate (2 × 100 ml). The organic phase was washed with water (50 ml) and evaporated to dryness under reduced pressure at 40 °C to give a neutral fraction (A). An aliquot was examined by g.l.c.–mass spectrometry as its MeTMSi derivative, but did not show the presence of any gibberellins.

The aqueous phase was acidified to pH 2.5 (2M HCl) and extracted with ethyl acetate (2 × 100 ml). The organic phase was washed with water (50 ml) and evaporated to dryness under reduced pressure at 40 °C. The residue was dissolved in methanol–water (4:1; 5 ml) and filtered through a micropore membrane of cellulose nitrate. The solvent was evaporated under reduced pressure to give an acidic fraction (B) and an aliquot was derivatised and examined as before; the compounds detected are listed in the Table.

The aqueous phase, at pH 2.5, was extracted with butanol (2 × 100 ml). The solvent was removed under reduced pressure at 40 °C and the residue was dissolved in methanol–water (4:1; 5 ml) and filtered through a micropore membrane of cellulose nitrate. The filtrate was purified by reverse phase h.p.l.c. using a linear gradient elution from methanol–aqueous 1% acetic acid (3:7) to 100% methanol over 25 min at a flow rate of 2.5 ml min^{-1}. The purified fractions (62.5 ml) were combined and evaporated to dryness *in vacuo* at 40 °C to give an acidic fraction (C). An aliquot was derivatised as before and examined by g.l.c.–mass spectrometry. The compounds detected are listed in the Table.

ent-3α,13-*Diacetoxy*-10β-*hydroxy*-15β-*methylsulphonyloxy*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester*-19,10-*Lactone* (**11**).—15α-Hydroxygibberellin A_1 methyl ester diacetate (**10**) (100 mg) and methanesulphonyl chloride (20 μl) in pyridine (2 ml) were set aside for 3 h at room temperature. The product, recovered in the usual way, was purified by flash column chromatography. Elution with ethyl acetate–light petroleum (1:1) yielded the 15-*mesylate* (**11**) (60 mg) (Found: M^+, 540.1647. $C_{25}H_{32}O_{11}$ requires *M*, 540.1665); δ($CDCl_3$) 1.12 (s, 18-H_3), 2.01 and 2.12 (2 s, $OCOCH_3$), 2.66 (d, *J* 9 Hz, 6-H), 2.99 (s, OSO_2CH_3), 3.03 (d, *J* 9 Hz, 5-H), 3.80 (s, CO_2CH_3), 4.97 (br s, 3-H), 5.25 (br s, 15-H), and 5.57 and 5.86 (2 br s, 17-H_2); *m/z* 540 (M^+, 6%), 498 (8), 445 (12), 404 (21), 403 (21), 402 (65), 338 (43), 342 (31), 298 (39), 282 (24), 239 (29), 238 (22), 91 (23), and 43 (100).

Attempted Inversion of Gibberellin A_1 *Methyl Ester* 15α-*Mesylate* 3β,13-*Diacetate* (**11**).—Gibberellin A_1 methyl ester 15-mesylate 3,13-diacetate (**11**) (60 mg), powdered caesium acetate (500 mg), and 18-crown-6-ether (30 mg) in toluene (6 ml) were heated under reflux for 4 h. The reaction mixture was cooled and worked up to yield crude *ent*-3α,13,17-triacetoxy-10β-hydroxygibberell-15-ene-7,19-dioic acid 7-methyl ester 19,10-lactone (**12**) (25 mg); δ($CDCl_3$) 1.07 (s, 18-H_3), 2.01, 2.09, and 2.13 (3 s, $OCOCH_3$), 2.61 (d, *J* 10 Hz, 6-H), 3.16 (d, *J* 10 Hz, 5-H), 4.66 (m, 17-H_2), 4.98 (br s, 3-H), and 5.72 (br s, 15-H); *m/z* 504 (M^+, 8%), 473 (9), 463 (12), 462 (44), 444 (26), 403 (26), 402 (100), 388 (32), 343 (12), 342 (32), 340 (18), 310 (13), 298 (37), 296 (18), 282 (15), 239 (26), 238 (12), and 209 (15).

ent-2α,3α,13-*Triacetoxy*-10β,15β-*dihydroxy*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**19**).—Gibberellin A_8 methyl ester triacetate (**17**) (234 mg) in dichloromethane (15 ml) was stirred with selenium dioxide (72 mg) and t-butyl hydroperoxide (70% in water; 300 μl) for 24 h at room temperature. The crude product, recovered in the usual way, was subjected to flash chromatography. Elution with ethyl acetate–light petroleum (1:1) and (4:6) gave the required 15α-*hydroxy*-GA_8 *methyl ester triacetate* (**19**) (120 mg) (Found: M^+, 520.1958. $C_{26}H_{32}O_{11}$ requires *M*, 520.1944); δ($CDCl_3$) 1.07 (s, 18-H_3), 1.97, 2.04, and 2.19 (3 s, 2-, 3-, and 13-$OCOCH_3$), 2.54 (d, *J* 10.5 Hz, 6-H), 3.30 (d, *J* 10.5 Hz, 5-H), 3.69 (s, CO_2CH_3), 3.79 (d, *J* 8.5 Hz, 15-OH), 4.06 (br d, *J* 8.5 Hz, 15-H), 5.08 (m, 2-H), 5.22 (br s, 17-H), 5.23 (d, *J* 4 Hz, 3-H), and 5.42 (br s, 17-H); *m/z* 520 (M^+, 2%) 460 (13), 447 (29), 446 (100), 400 (18), 356 (19), 340 (26), 308 (15), 296 (17), 295 (25), 236 (11), 235 (13), and 43 (88).

ent-2α,3α,13-*Triacetoxy*-10β-*hydroxy*-15-*oxo*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**21**).—Oxalyl chloride (200 μl) and dimethyl sulphoxide (400 μl) in dichloromethane (5 ml) were stirred at −78 °C for 5 min under nitrogen gas. 15α-HydroxyGA_8 methyl ester triacetate (**19**) (64 mg) in dichloromethane (2 ml) was added and the mixture was stirred for a further 1 h at −78 °C. Di-isopropylethylamine (1 ml) was added and the solution was allowed to warm to room temperature, with stirring, over 1 h. The crude product, recovered in the usual way, was subjected to flash chromatography. Elution with ethyl acetate–light petroleum (1:1) gave the required 15-*oxo* GA_8 *methyl ester triacetate* (**21**) (35 mg) (Found: M^+, 518.1757. $C_{26}H_{30}O_{11}$ requires *M*, 518.1788); δ($CDCl_3$) 1.14 (s, 18-H_3), 1.98, 2.11, and 2.22 (3 s, 2-, 3-, and 13-$OCOCH_3$), 2.61 (d, *J* 10 Hz, 6-H), 3.09 (d, *J* 11 Hz, 14-H), 3.45 (d, *J* 10 Hz, 5-H), 3.63 (s, CO_2CH_3), 5.09 (m, 2-H), 5.27 (d, *J* 4 Hz, 3-H), and 5.63 and 6.12 (2 s, 17-H_2); *m/z* 518 (M^+, 9%), 487 (18), 476 (21), 458 (12), 430 (34), 416 (12), 356 (19), 324 (12), 311 (22), 310 (12), 266 (13), 265 (11), 251 (15), 129 (41), 114 (26), and 43 (100).

ent-2α,3α,13-*Triacetoxy*-10β,15α-*dihydroxy*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**25**).—15-Oxo-GA_8 methyl ester triacetate (**21**) (32 mg) in acetic acid (0.5 ml) was stirred with activated zinc[2] (120 mg) for 1 h at room temperature. The reaction mixture was filtered and the zinc was washed with ethyl acetate (30 ml). The combined filtrate and washings were evaporated to dryness under reduced pressure and the residue was flash chromatographed. Elution with ethyl acetate–light petroleum (1:1) gave 16ζ,17-dihydro-15-oxo-GA_8 methyl ester triacetate (**22**) (20 mg); elution with ethyl acetate–light petroleum (6:4) gave the required 15β-hydroxy GA_8 methyl ester triacetate (**25**) (10 mg).

15β-*Hydroxy* GA_8 *methyl ester triacetate* (**25**). (Found: M^+, 520.1963. $C_{26}H_{32}O_{11}$ requires *M*, 520.1944); δ($CDCl_3$) 1.07 (s, 18-H_3), 1.97, 2.01, and 2.19 (3 s, 2-, 3-, and 13-$OCOCH_3$), 2.71 (d, *J* 11 Hz, 6-H), 3.15 (d, *J* 11 Hz, 5-H), 3.79 (s, CO_2CH_3), 4.26 (br s, 15-H), 5.09 (m, 2-H), and 5.25 (br s, 17-H_2 masking signal due to 3-H); *m/z* 520 (M^+, 43%), 478 (17), 460 (29), 447 (11), 446 (36), 428 (15), 400 (15), 369 (23), 340 (16), 296 (22), 295 (22), 253 (18), 237 (16), and 43 (100).

16ζ,17-Dihydro-15-oxo GA_8 methyl ester triacetate (**23**): δ($CDCl_3$) 1.12 (s, 18-H_3), 1.15 (d, *J* 7 Hz, 17-H_3), 1.98, 2.06, and 2.20 (3 s, 2-, 3-, and 13-$OCOCH_3$), 2.57 (d, *J* 10.5 Hz, 6-H), 3.18 (d, *J* 11.5 Hz, 14-H), 3.39 (d, *J* 10.5 Hz, 5-H), 3.63 (s, CO_2CH_3), and 5.10 (m, 2-H), 5.26 (d, *J* 4 Hz, 3-H); *m/z* 520 (M^+, 39%), 478 (11), 461 (27), 460 (97), 432 (38), 429 (28), 341 (35), 340 (17), 281 (19), 268 (21), 256 (23), 209 (21), 188 (35), and 43 (100).

ent-2α,3α,10β,13,15α-*Pentahydroxy*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 19,10-*Lactone* (GA_{75}) (**6**).—15β-Hydroxy GA_8 methyl ester triacetate (**25**) (20 mg) in methanol (2 ml) was stirred with potassium carbonate (60 mg) in water (1.2 ml) for 40 h. The reaction mixture was acidified with 2M hydrochloric acid and extracted with butanol (3 × 20 ml). The solvent was distilled under reduced pressure to yield 15β-*hydroxy* GA_8 (GA_{75}) (**6**) (10 mg); δ_H(CD_3OD) 1.15 (s, 18-H_3), 2.56 (d, *J* 11 Hz, 6-H), 3.24 (d, *J* 11 Hz, 5-H), 3.58 (d, *J* 4 Hz, 3-H), 3.70 (m, 2-H), 4.28 (br s, 15-H), and 5.15 and 5.31 (2 br d, *J* 2 Hz, 17-H_2); δ_C(CD_3OD), 15.4 (C-18), 17.6 (C-11), 36.5 (C-12), 40.5 (C-14), 42.1 (C-1), 43.4 (C-5 and C-9), 53.4 (C-6), 55.3 (C-8), 56.2 (C-4), 68.4 (C-2), 73.5 (C-3), 76.2 (C-15), 76.9 (C-13), 95.6 (C-10), 109.4 (C-17), 161.7 (C-16), and 179.9 (C-7 and C-19); g.l.c.–m.s. (as the methyl ester trimethylsilyl ether); *m/z* 682 (M^+, 40%), 667 (6), 593 (19), 592 (37), 548 (6), 533 (6), 309 (6), 295 (14), 257 (7), 231 (14), 229 (10), 147 (18), and 75 (100) and K_I = 2 947.

ent-2α,13-*Diacetoxy*-10β,15β-*dihydroxy*-20-*norgibberell*-16-*ene*-7,19-*Dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**20**).—Gibberellin A_{29} methyl ester diacetate (**18**) (140 mg) in dichloromethane (15 ml) was stirred with selenium dioxide (35 mg) and t-butyl hydroperoxide (70% in water; 160 μl) for 18 h at room temperature. The crude product was recovered in the usual way and purified by flash chromatography. Elution with

ethyl acetate–light petroleum (4:6) gave recovered GA_{29} methyl ester diacetate (**18**) (70 mg) and elution with ethyl acetate–light petroleum, (6:4) gave the required 15α-*hydroxy* GA_{29} *methyl ester diacetate* (**20**) (79 mg) (Found: M^+, 462.1831. $C_{24}H_{30}O_9$ requires *M*, 462.1889); δ($CDCl_3$) 1.13 (s, 18-H_3), 2.02 and 2.04 (2 s, 2- and 13-$OCOCH_3$), 2.55 (d, *J* 10 Hz, 6-H), 2.75 (d, *J* 10 Hz, 5-H), 3.69 (s, CO_2CH_3), 3.77 (d, *J* 8.5 Hz, 15-OH), 4.02 (br d, *J* 8.5 Hz, 15-H), 4.96 (m, 2-H), and 5.20 and 5.41 (br 2 s, 17-H_2); *m/z* 462 (M^+, 1%), 430 (4), 402 (5), 389 (25), 388 (100), 342 (23), 310 (10), 282 (12), 262 (8), 237 (16), and 209 (7).

ent-2α,13-*Diacetoxy*-10β-*hydroxy*-15-*oxo*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**22**).—Oxalyl chloride (160 μl) and dimethyl sulphoxide (400 μl) in dichloromethane (5 ml) were stirred at −78 °C for 5 min under nitrogen gas. 15α-Hydroxy GA_{29} methyl ester diacetate (**20**) (100 mg) in dichloromethane (2 ml) was added and the mixture was stirred for a further 1 h at −78 °C. Di-isopropylethylamine (1 ml) was added and the solution was allowed to warm to room temperature with stirring over 1 h. The reaction was worked up in the usual way and the recovered material was flash chromatographed. Elution with ethyl acetate–light petroleum (45:55) gave the required 15-*oxo*GA_{29} *methyl ester diacetate* (**22**) (57 mg) (Found: M^+, 460.1760. $C_{24}H_{28}O_9$ requires *M*, 460.1733); δ($CDCl_3$) 1.18 (s, 18-H_3), 2.03 and 2.11 (2 s, 2- and 13-$OCOCH_3$), 2.25 (d, *J* 11.5 Hz, 14-H), 2.59 (d, *J* 10.5 Hz, 6-H), 2.88 (d, *J* 10.5 Hz, 5-H), 3.07 (d, *J* 11.5 Hz, 14-H), 3.63 (s, CO_2CH_3), 4.97 (m, 2-H), 5.61 and 6.10 (2 s, 17-H_2); *m/z* 460 (M^+, 15%), 429 (31), 418 (35), 40 (20), 373 (18), 372 (56), 359 (23), 358 (87), 326 (32), 312 (46), 298 (24), 280 (39), 253 (48), and 43 (100).

ent-2α,13-*Diacetoxy*-10β,15α-*dihydroxy*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**26**).—15-OxoGA_{29} methyl ester diacetate (**22**) (57 mg) in acetic acid (3.5 ml) was stirred with activated zinc[2] (390 mg) for 2 h at room temperature. The filtrate from the reaction mixture was combined with the washings of the zinc with methanol (30 ml) and ethyl acetate (30 ml) and distilled to dryness *in vacuo*. The residue was flash chromatographed. Elution with ethyl acetate–light petroleum (4:6) gave 16ζ,17-dihydro-15-oxogibberellin A_{29} methyl ester diacetate (**24**) (27 mg) and elution with ethyl acetate–light petroleum (45:55) yielded 15β-hydroxyGA_{29} methyl ester diacetate (**26**) (10 mg).

15β-*Hydroxy*GA_{29} *methyl ester diacetate* (**26**). (Found: M^+, 462.1881. $C_{24}H_{30}O_9$ requires *M*, 462.1889); δ($CDCl_3$) 1.12 (s, 18-H_3), 2.01 and 2.02 (2 s, 2- and 13-$OCOCH_3$), 2.64 (d, *J* 10.5 Hz, 6-H), 2.71 (d, *J* 10.5 Hz, 5-H), 3.79 (s, CO_2CH_3), 4.24 (br s, 15-H), 4.97 (m, 2-H), 5.22 and 5.24 (2 d, *J* 3 Hz, 17-H_2); *m/z* 462 (M^+, 40%), 420 (16), 402 (39), 388 (22), 370 (33), 360 (20), 342 (44), 310 (33), 298 (23), 282 (29), 281 (21), 238 (29), 237 (54), 183 (22), 105 (21), aand 43 (100).

16ζ,17-*Dihydro*-15-*oxo*GA_{29} *methyl ester diacetate* (**24**). (Found: M^+,462.1878. $C_{24}H_{30}O_9$ requires *M*, 462.1889); δ($CDCl_3$) 1.13 (d, *J* 7 Hz, 17-H_3), 1.16 (s, 18-H_3), 2.03 and 2.05 (2 s, 2- and 13-$OCOCH_3$), 2.14 (d, *J* 12 Hz, 14-H), 2.58 (d, *J* 10 Hz, 6-H), 2.81 (d, *J* 10 Hz, 5-H), 3.16 (d, *J* 12 Hz, 14-H), 3.62 (s, CO_2CH_3), and 4.97 (m, 2-H); *m/z* 462 (M^+, 29%), 403 (24), 402 (87), 374 (36), 371 (27), 342 (60), 314 (28), 282 (44), 271 (25), 270 (22), 258 (23), 255 (25), 238 (21), 211 (22), 55 (23), and 43 (100).

ent-2α,10β,13,15α-*Tetrahydroxy*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (GA_{76}) (**7**).—15β-HydroxyGA_{29} methyl ester diacetate (**25**) (30 mg) in methanol (2 ml) was stirred with potassium carbonate (60 mg) in water (1.2 ml) for 28 h at room temperature. The reaction mixture (pH 11) was acidified to pH 4.0 with 0.5M hydrochloric acid and extracted with ethyl acetate (3 × 20 ml). Recovery from the ethyl acetate extract gave 15β-hydroxyGA_{29} methyl ester (1 mg). Extraction of the aqueous (pH 4.0) layer with butanol (3 × 20 ml) and recovery from the butanol gave 15β-*hydroxy*GA_{29} (GA_{76}) (**7**) (20 mg); δ_H(CD_3OD) 1.13 (s, 18-H_3), 3.78 (m, 2-H), 4.32 (br s, 15-H), 5.15 and 5.29 (2 d, *J* 2 Hz, 17-H_2); δ_C(CD_3OD) 17.6 (C-11 and C-18), 29.6 (C-5), 40.5 (C-12 and C(14), 42.3 (C-3), 43.7 (C-9), 44.6 (C-1), 56.1 (C-4 and C-8), 6.13 (C-6), 66.7 (C-2), 77.0 (C-13 and C-15), 95.9 (C-10), 109.2 (C-17), 161.2 (C-16), 181.1 (C-7 and C-19); g.l.c.–m.s. (as the methyl ester trimethylsilyl ether); *m/z* 594 (M^+, 47%) 579 (20), 550 (13), 505 (12), 229 (15), 205(13), 75 (100), and 73 (98); K_I = 2 771.

ent-3β,10β,13-15α-*Tetrahydroxy*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 19,10-*Lactone* (3-*epi*GA_{72}) (**8**).—Gibberellin A_{72} (**2**) (1 mg) in methanol (0.5 ml) was stirred with potassium carbonate (30 mg) in water (0.5 ml) for 24 h. The reaction mixture was acidified with 0.5M hydrochloric acid and extracted with butanol (3 × 5 ml). The solvent was distilled under reduced pressure and the resultant gum was treated with ethereal diazomethane and derivatised with hexamethyldisilazane–trimethylchlorosilane–pyridine (2:1:1) prior to analysis by g.l.c.–m.s. This showed, in a ratio of 1:1; 3-*epi*-GA_{72} methyl ester trimethylsilyl ether and GA_{72} methyl ester trimethyl silyl ether. 3-*Epi*-Gibberellin A_{72} methyl ester trimethylsilyl ether had KRI 2 881 and *m/z* 594 (M^+, 50%), 579 (17), 550 (16), 505 (29), 504 (58), 465 (18), 463 (17), 457 (17), 375 (16), 311 (18), 295 (29), 257 (23), 229 (21), 147 (20), 129 (20), 76 (22), 75 (100), 74 (21), and 73 (99).

Gibberellin A_{72} methyl ester trimethylsilyl ether had KRI 2 822 and *m/z* 594 (M^+, 100%), 579 (21), 550 (14), 506 (16), 505 (38), 504 (100), 465 (16), 445 (11), 414 (10), 371 (18), 370 (21), 311 (15), 297 (10), 295 (20), 257 (12), 203 (19), 175 (22), 97 (32), and 73 (18).

ent-13-*Acetoxy*-3α,10β-*dihydroxy*-1α-*iodo*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**28**). The known[7] GA_3methyl ester 13-acetate (**27**) (1.2 g) in methanol (50 ml) and pyridine (1 ml) was stirred for 0.5 h at room temperature with 10% palladium on calcium carbonate (40 mg) in an atmosphere of hydrogen gas. The reaction mixture was filtered *in vacuo* and the catalyst was washed with methanol (50 ml) and ethyl acetate (50 ml). The combined filtrate and washings were evaporated under reduced pressure to yield crude hydrogenolysis product (1.68 g), identified by ^1H n.m.r. spectroscopy.

Crude hydrogenolysis product (5.0 g), from several experiments, in dichloromethane (20 ml) and freshly distilled tetrahydrofuran (10 ml) was stirred vigorously with saturated aqueous hydrogen carbonate (20 ml) and iodine (1.63 g) for 1.5 h at room temperature. The reaction mixture was allowed to settle for 10 min after which the organic phase was removed and the aqueous phase was acidified to pH 3 and extracted with ethyl acetate (3 × 50 ml). The organic extracts were combined, washed with saturated aqueous sodium thiosulphate (2 × 50 ml), dried (Na_2SO_4), and evaporated under reduced pressure. Purification of the residue by flash chromatography eluting with ethyl acetate–light petroleum (1:1) gave 1β-iodoGA_1 methyl ester 13-acetate (**28**) (3.02 g), m.p. 171—174 °C (lit.,[7] m.p. 163—165 °C); δ($CDCl_3$) 1.19 (s, 18-H_3), 2.03 (s, $OCOCH_3$), 2.69 (d, *J* 10 Hz, 6-H), 3.75 (s, CO_2CH_3), 3.85 (d, *J* 10 Hz, 5-H), 3.98 (d, *J* 4 Hz, 3-H), 4.41 (d, *J* 5 Hz, 1-H), and 5.04 and 5.17 (2 br s, 17-H_2); *m/z* 530 (M^+, 51%), 489 (24), 488 (100), 470 (18), 429 (24), 371 (10), 343 (15), 329 (14), 301 (14), 297 (14), 281 (23), 221 (24), and 43 (50).

ent-13-*Acetoxy*-3α,10β-*dihydroxy*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester*-19,10-*Lactone* (**29**).—To the

iodide (**28**) (3.0 g) in refluxing toluene (75 ml) was added tributylstannane (3 ml) and 2,2′-azo-2-methylpropionitrile, (30 mg). The reaction mixture was heated under reflux for 2.5 h after which the solvent was removed under reduced pressure. The residue was purified by flash chromatography. Elution with ethyl acetate–light petroleum (6:4) yielded the required GA_1 methyl ester 13-acetate (**29**) (2.2 g), m.p. 148—151 °C (lit.,[14] m.p. 137—140 °C); δ($CDCl_3$) 1.13 (s, 18-H_3), 2.03 (s, $OCOCH_3$), 2.69 (d, *J* 10.5 Hz, 6-H), 3.22 (d, *J* 10.5 Hz, 5-H), 3.72 (s, CO_2CH_3), 3.83 (br s, 3-H), and 4.99 and 5.15 (2 br s, 17-H_2); *m/z* 404 (M^+, 27%), 373 (12), 372 (11), 363 (23), 362 (100), 344 (31), 330 (21), 312 (11), 303 (19), 302 (21), 284 (21), 282 (32), 256 (19), and 43 (52).

ent-13-*Acetoxy*-10β-*hydroxy*-20-*norgibberell*-2,16-*diene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**30**).—Gibberellin A_1 methyl ester 13-acetate (**29**) (2.2 g) and phosphoryl chloride (1.2 ml) in pyridine (20 ml) were heated under reflux for 0.5 h. The reaction mixture was slowly diluted with water and worked up. The crude product was flash chromatographed. Elution with ethyl acetate–light petroleum (4:6) gave the required GA_5 methyl ester 13-acetate (**30**) (1.5 g), m.p. 130—132 °C (lit.,[13] m.p. 125—127 °C); δ($CDCl_3$) 1.22 (s, 18-H_3), 2.02 (s, $OCOCH_3$), 2.66 (d, *J* 10 Hz, 6-H), 2.81 (d, *J* 10 Hz, 5-H), 3.73 (s, CO_2CH_3), 4.98 and 5.13 (2 br s, 17-H_2), 5.67 (br d, *J* 9.5 Hz, 3-H), and 5.81 (dt, *J* 9.5 and 3 Hz, 2-H); *m/z* 386 (M^+, 13%), 344 (25), 319 (11), 303 (10), 300 (10), 285 (12), 283 (28), 282 (100), 267 (10), 223 (22), 222 (20), 207 (14), 155 (13), 105 (17), and 43 (51).

Epoxidation of Gibberellin A_5 *Methyl Ester* 13-*Acetate* (**30**).—Gibberellin A_5 methyl ester 13-acetate (**30**) (1.5 g) and 3-chloroperbenzoic acid (910 mg, 1.2 equiv.) in chloroform (100 ml) were allowed to stand for 16 h at room temperature. The reaction mixture, diluted with chloroform (100 ml), was washed with saturated aqueous sodium hydrogen carbonate (3 × 50 ml). The chloroform was removed by distillation under reduced pressure and the residue was purified by flash chromatography. Elution with ethyl acetate–light petroleum (45:55) yielded the 16β,17-epoxide (**31**) (230 mg); elution with ethyl acetate–light petroleum (1:1) gave the 16α,17-epoxide (**32**) (660 mg); and elution with ethyl acetate–light petroleum (4:6) gave recovered starting material (**25**) (124 mg).

The 16α,17-epoxide (**32**), m.p. 174—176 °C (previously isolated as a gum[14]); δ($CDCl_3$) 1.23 (s, 18-H_3), 2.00 (s, $OCOCH_3$), 2.70 (d, *J* 10 Hz, 6-H), 2.74 (d, *J* 5 Hz, 17-H), 2.81 (d, *J* 10 Hz, 5-H), 3.10 (d, *J* 5 Hz, 17-H), 3.73 (s, CO_2CH_3), 5.68 (br d, *J* 9.5 Hz, 3-H), and 5.83 (dt, *J* 9.5 and 3 Hz, 2-H); *m/z* 402 (M^+, 1%), 371 (20), 360 (14), 357 (11), 316 (14), 299 (12), 298 (28), 280 (17), 267 (14), 266 (12), 257 (10), 256 (13), 255 (16), 238 (28), 155 (27), 118 (25), and 43 (100).

The 16β,17-epoxide (**31**), m.p. 167—169 °C (previously isolated as a gum[14]); δ($CDCl_3$) 1.22 (s, 18-H_3), 1.99 (s, $OCOCH_3$), 2.65 (d, *J* 10 Hz, 6-H), 2.80 (d, *J* 10 Hz, 5-H), 2.80 (d, *J* 5 Hz, 17-H), 3.02 (d, *J* 5 Hz, 17-H), 5.67 (br d, *J* 9.5 Hz, 3-H), and 5.82 (dt, *J* 9.5 and 3 Hz, 2-H); *m/z* 402 (M^+, 6%), 371 (21), 358 (16), 314 (18), 303 (19), 299 (15), 298 (46), 280 (12), 271 (20), 239 (28), 238 (54), 197 (26), 155 (29), 105 (24), 91 (23), and 43 (100).

ent-13-*Acetoxy*-2α,3α,10β-*trihydroxy*-16β,17-*epoxy*-20-*norgibberellane*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**33**).—To the 16α,17-epoxide (**32**) (660 mg) in acetone (90 ml) and water (30 ml) was added osmium tetroxide (10 mg) and *N*-methylmorpholine *N*-oxide (30% in water; 0.9 ml). After 64 h at room temperature, the acetone was removed by distillation under reduced pressure and the remaining aqueous solution was stirred with aqueous saturated sodium metabisulphite (100 ml) for 0.5 h. After acidification to pH 3.0 with 2M hydrochloric acid, the aqueous solution was extracted with ethyl acetate (3 × 50 ml). The ethyl acetate extract was washed with water (50 ml), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by flash chromatography. Elution with ethyl acetate–light petroleum (8:2) and (9:1) yielded the required GA_8 *methyl ester* 13-*acetate* 16α,17-*epoxide* (**33**) (384 mg) (Found: M^+, 436.1733. $C_{22}H_{28}O_9$ requires *M*, 436.1746); δ($CDCl_3$) 1.19 (s, 18-H_3), 2.01 (s, $OCOCH_3$), 2.70 (d, *J* 10.5 Hz, 6-H), 2.76 (d, *J* 5 Hz, 17-H), 3.09 (d, *J* 5 Hz, 17-H), 3.27 (d, *J* 10.5 Hz, 5-H), 3.72 (s, CO_2CH_3 masking signal due to 3-H), and 3.89 (br s, 2-H); *m/z* 436 (M^+, 8%), 405 (12), 395 (18), 394 (79), 393 (31), 378 (10), 376 (24), 344 (21), 337 (21), 328 (29), 305 (28), 300 (34), 283 (32), 282 (42), 223 (47), 91 (28), 59 (27), 55 (34), and 43 (100).

ent-13-*Acetoxy*-2α,3α,10β-*trihydroxy*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**34**).—To sodium iodide (1.0 g) sodium acetate (1.86 g), and activated zinc (1.2 g), in acetic acid (8 ml) was added the 16α,17-epoxide (**33**) (380 mg) in acetone (8 ml). After being stirred for 4.5 h at room temperature, the reaction mixture was filtered to remove the zinc residues and the filtrate was worked up as usual to give a residue which was subjected to flash chromatography. Elution with ethyl acetate–light petroleum (6:4) and (7:3) gave GA_8 methyl ester 13-acetate (**34**) (220 mg) as a gum; δ($CDCl_3$) 1.17 (s, 18-H_3), 2.02 (s, $OCOCH_3$), 2.66 (d, *J* 10.5 Hz, 6-H), 3.26 (d, *J* 10.5 Hz, 5-H), 3.73 (s, CO_3CH_3 masking due to 3-H), 3.87 (m, 2-H), 4.99 and 5.15 (2 br s, 17-H_2); *m/z* 420 (M^+, 25%), 389 (10), 379 (19), 378 (81), 361 (11), 360 (35), 319 (18), 318 (20), 300 (15), 221 (14), 105 (14), 91 (27), 77 (17), and 43 (100).

ent-2α,3α,13-*Triacetoxy*-10β-*hydroxy*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**17**).—Gibberellin A_8 methyl ester 13-acetate (**34**) (220 mg) and 4-methylbenzenesulphonic acid (10 mg) in acetic anhydride (20 ml) were allowed to stand for 16 h at room temperature. Work-up gave GA_8 *methyl ester triacetate* (**17**) (242 mg) (Found: M^+, 504.1995. $C_{26}H_{32}O_{10}$ requires *M*, 504.2023); δ($CDCl_3$) 1.06 (s, 18-H_3), 1.98, 2.03, and 2.20 (3 s, 2-, 3-, and 13-$OCOCH_3$), 2.66 (d, *J* 10.5 Hz, 6-H), 3.30 (d, *J* 10.5 Hz, 5-H), 3.73 (s, CO_2CH_3), 5.00 (br s, 17-H), 5.10 (m, 2-H), 5.17 (br s, 17-H), and 5.24 (d, *J* 4 Hz, 3-H); *m/z* 504 (M^+, 27%), 473 (10), 463 (12), 462 (43), 444 (13), 402 (13), 385 (11), 384 (11), 356 (10), 342 (18), 281 (15), 280 (26), 221 (20), and 43 (100).

ent-2β,13-*Dihydroxy*-3α-*iodo*-20-*norgibberell*-1(10)16-*diene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,2-*Lactone* (**37**).—To the known[8] GA_3 methyl ester 3-acetate (**35**) (1.0 g) in refluxing acetonitrile (40 ml) was added activated zinc (10 g) and acetic acid (1 ml). Further activated zinc (5 g) was added to the refluxing solution after 0.7 h and again after 1.25 h. After a total of 2 h under reflux, the reaction mixture was cooled and filtered. The filtrate and ethyl acetate washings (2 × 30 ml) of the zinc residues were combined and evaporated under reduced pressure to yield the crude diene (**36**) (1.1 g) as a gum. A repeat experiment gave further diene (0.8 g). The combined diene (**36**) (1.9 g) in dichloromethane (20 ml) and freshly distilled tetrahydrofuran (10 ml) was stirred vigorously with saturated aqueous sodium hydrogen carbonate (20 ml) and iodine (760 mg) for 1.5 h at room temperature. After being allowed to settle for 10 min, the organic phase was removed and the aqueous phase was acidified to pH 3 with 2M hydrochloric acid and extracted with ethyl acetate (3 × 50 ml). The organic extracts were combined, washed with saturated aqueous sodium thiosulphate (2 × 50 ml), dried (Na_2SO_4), and evaporated under reduced pressure to yield the required iodolactone (**37**) (2.16 g); δ($CDCl_3$) 1.16 (s, 18-H_3), 3.75 (s, CO_2CH_3), 4.52 (d, *J* 5 Hz, 3-H), 4.94 (t, *J* 5 Hz, 2-H), 4.98 and 5.01 (2 br s, 17-H_2), and

5.79 (m, 1-H); *m/z* 470 (M^+, 1%), 439 (3), 403 (2), 360 (3), 343 (11), 311 (26), 229 (22), 298 (19), 297 (28), 283 (45), 240 (28), 239 (100), 238 (29), and 237 (31).

ent-2β,13-*Dihydroxy*-20-*norgibberell*-1(10),16-*diene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,2-*Lactone* (**38**).—To the 3β-iodide (**37**) (1.6 g) in refluxing toluene (100 ml) was added tributylstannane (1.6 ml) and 2,2′-azo-2-methylpropionitrile (30 mg). After the mixture had been heated under reflux for 1 h, further tributylstannane (1 ml) and 2,2′-azo-2-methylpropionitrile (10 mg) were added. After 2 h the reaction mixture was allowed to cool and toluene was removed under reduced pressure. The residue was flash chromatographed; elution with ethyl acetate–light petroleum (4:6) and (1:1) gave the required 19,2-lactone (**38**) (780 mg); δ($CDCl_3$) 1.26 (s, 18-H_3), 3.74 (s, CO_2CH_3), 4.86 (t, *J* 5 Hz, 2-H), 4.97 and 5.12 (2 br s, 17-H_2), and 5.94 (m, 1-H); *m/z* 344 (M^+, 95%), 326 (31), 313 (31), 312 (79), 300 (27), 299 (21), 298 (30), 294 (27), 284 (44), 240 (30), 239 (100), 238 (37), 221 (27), and 211 (30).

ent-2β,10β,13-*Trihydroxy*-1α-*iodo*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**39**).—The 19,2-lactone (**38**) (750 mg) in freshly distilled tetrahydrofuran (12 ml) was treated with 0.8M aqueous potassium hydroxide (11 ml) for 16 h at room temperature. The pH of the solution was adjusted to 9.0 with 2M hydrochloric acid. Iodine (360 mg) in dichloromethane (20 ml) was added and the mixture was stirred vigorously for 1.5 h at room temperature. After being allowed to settle for 10 min, the organic phase was removed and the aqueous phase was acidified to pH 3 with 2M hydrochloric acid and extracted with ethyl acetate (3 × 50 ml). The organic extracts were combined, washed with saturated aqueous sodium thiosulphate (2 × 50 ml), dried (Na_2SO_4), and evaporated under reduced pressure to give the required iodide (**39**) (700 mg); δ($CD_3)_2CO$ 1.04 (s, 18-H_3), 2.59 (d, *J* 10 Hz, 6-H), 3.34 (d, *J* 10 Hz, 5-H), 3.73 (s, CO_2CH_3), 4.59 (m, 2-H), 4.60 (d, *J* 1.5 Hz, 1-H), 4.91 and 5.21 (2 br s, 17-H_2); *m/z* 488 (M^+, 21%), 457 (9), 438 (9), 429 (32), 361 (40), 359 (23), 343 (24), 329 (25), 315 (36), 312 (24), 311 (41), 301 (51), 283 (46), 269 (29), 257 (32), 256 (28), and 255 (100).

ent-2β,10β,13-*Trihydroxy*20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**40**).—To the 1β-iodide (**39**) (680 mg) in refluxing toluene (100 ml) was added tributylstannane (1 ml) and 2,2′-azo-2-methylproprionitrile (40 mg). The reaction mixture was heated under reflux for 1 h and additional tributylstannane (0.5 ml) and 2,2′-azo-2-methylpropnitrile (20 mg) were added. After heating under reflux for a further 1 h the solvent was removed under reduced pressure and the residue was subjected to flash chromatography. Elution with ethyl acetate–light petroleum (8:2) yielded the required 2-*epi*-GA_{29} methyl ester (**40**) (362 mg); δ($CD_3)_2CO$ 0.99 (s, 18-H_3), 2.59 (d, *J* 10 Hz, 6-H), 2.64 (d, *J* 10 Hz, 5-H), 3.71 (s, CO_2CH_3), 4.25 (br s, 2-H), and 4.85 and 5.18 (2 br s, 17-H_2); *m/z* 362 (M^+, 48%), 344 (18), 331 (29), 330 (27), 316 (20), 313 (24), 312 (100), 303 (60), 302 (27), 285 (21), 284 (37), 258 (19), 239 (26), 231 (25), and 197 (16).

ent-13-*Acetoxy*-10β-*hydroxy*-2β-*methylsulphonyloxy*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**42**).—2-*epi*-Gibberellin A_{29} methyl ester (**40**) (500 mg) and methanesulphonyl chloride (130 μl) in pyridine (3 ml) were allowed to stand for 1.25 h at room temperature. The products, recovered in the usual way, were purified by flash chromatography. Elution with ethyl acetate–light petroleum (7:3) gave the required 2-monomesylate (**41**) (360 mg) and elution with ethyl acetate–light petroleum (8:2) and (9:1) yielded recovered 2-*epi*-GA_{29} methyl ester (**40**) (150 mg). The 2-monomesylate (**41**); δ($CDCl_3$) 1.12 (s, 18-H_3), 2.64 (d, *J* 10 Hz, 6-H), 2.74 (d, *J* 10 Hz, 5-H), 3.02 (s, OSO_2CH_3), 3.73 (s, CO_2CH_3), 4.96 (br s, 17-H), 5.24 (m, 2-H), and masked by 5.26 (br s, 17-H); *m/z* 440 (M^+, 100%), 409 (39), 408 (88), 381 (29), 345 (63), 344 (67), 313 (39), 312 (89), 303 (55), 300 (67), 289 (30), 285 (40), 284 (53), 271 (34), and 270 (37).

The 2-monomesylate (**41**) (250 mg) and 4-methylbenzenesulphonic acid (30 mg) in acetic anhydride (6 ml) were allowed to stand for 2 h at room temperature. Work-up gave the required 2-*epi*-GA_{29} methyl ester 2-mesylate 13-acetate (**42**) (280 mg); δ($CDCl_3$) 1.11 (s, 18-H_3), 2.02 (s, $OCOCH_3$), 2.64 (d, *J* 10 Hz, 6-H), 2.74 (d, *J* 10 Hz, 5-H), 3.02 (s, OSO_2CH_3), 3.73 (s, CO_2CH_3), 4.98 and 5.15 (2 br s, 17-H_2), and 5.24 (br t, *J* 4 Hz, 2-H); *m/z* 482 (M^+, 41%), 451 (13), 441 (26), 440 (100), 422 (19), 378 (24), 344 (22), 326 (18), 312 (32), 284 (26), 283 (20), 282 (38), 267 (15), and 256 (17).

ent-2α,13-*Diacetoxy*-10β-*hydroxy*-20-*norgibberell*-16-*ene*-7,19-*dioic Acid* 7-*Methyl Ester* 19,10-*Lactone* (**18**).—Powdered caesium acetate (1.0 g) and 18-crown-6-ether (30 mg) in toluene (10 ml) were heated under reflux. The 2-mesylate (**42**) (170 mg) in acetone (0.3 ml) was added and heating under reflux was continued for a further 2 h. The reaction mixture was cooled and worked up as normal. The product, combined with that from an identical experiment using the 2-mesylate (160 mg), was purified by flash chromatography. Elution with ethyl acetate–light petroleum (4:6) gave olefinic products (**43**) (40 mg); elution with ethyl acetate–light petroleum (1:1) gave the required GA_{29} methyl ester 2,13-diacetate (**18**) (177 mg); δ($CDCl_3$) 1.11 (s, 18-H_3), 2.02 and 2.03 (2 s, 2- and 13-$OCOCH_3$), 2.66 (d, *J* 10 Hz, 6-H), 2.75 (d, *J* 10 Hz, 5-H), 3.73 (s, CO_2CH_3), 4.96 (m, 2-H), and 4.98 and 5.14 (2 br s, 17-H_2); *m/z* 446 (M^+, 43%), 415 (14), 405 (20), 404 (77), 386 (22), 344 (26), 326 (30), 298 (20), 294 (16), 284 (29), 283 (29), 282 (61), 239 (22), 223 (20), 91 (16), and 43 (100).

Hydrolysis of GA_5 *Methyl Ester* 13-*Acetate* (**13**) *and* 15β-*Hydroxy*GA_5 *Methyl Ester* 13-*Acetate* (**15**) *with Aqueous Potassium Carbonate*.—Gibberellin A_5 methyl ester 13-acetate (**13**) (30 mg) in methanol (2 ml) and aqueous potassium carbonate (0.5 ml) at pH 11 was stirred for 14 h at room temperature. Work-up gave, after crystallisation from ethyl acetate–light petroleum, GA_5 methyl ester (**14**) (19 mg), m.p. 192—194 °C (lit.,[11] m.p. 191—193 °C); δ 1.24 (s, 18-H_3), 2.66 (d, *J* 10 Hz, 5-H), 2.79 (d, *J* 10 Hz, 6-H), 3.75 (s, CO_2CH_3), 4.96 and 5.25 (2 br s, 17-H_2), 5.67 (ddd, *J* 2, 2.5, 9 Hz, 3-H), and 5.81 (dt, *J* 3 and 9 Hz, 2-H).

15β-Hydroxygibberellin A_5 methyl ester 13-acetate (**15**) (60 mg) in methanol (2 ml) and aqueous potassium carbonate (1 ml) at pH 11 was stirred for 14 h at room temperature. Work-up followed by flash chromatography eluting with ethyl acetate–light petroleum (3:1) and 1% acetic acid gave 15β-hydroxyGA_5 (**16**) as a gum (43 mg); δ($CD_3)_2CO$ 1.19 (s, 18-H_3), 2.60 and 2.72 (both d, *J* 10 Hz, 5- and 6-H), 4.40 (t, *J* 2.5 Hz, 15-H), 5.12 and 5.30 (2 br s, 17-H_2), 5.70 (dt, *J* 1.8, 9.5 Hz, 3-H), and 5.88 (dt, *J* 1.8 and 9.5 Hz, 2-H); *m/z* 346 (M^+, 1%), 328 (3), 309 (13), 277 (29), 239 (100), 156 (11), 129 (9), and 91 (84).

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