Rearrangements of the Gibbane Skeleton during Reactions with 2,3-Dichloro-5,6-dicyanobenzoquinone

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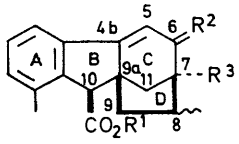
Gibbanes in which ring A is aromatic react with 2,3-dichloro-5,6-dicyanobenzoquinone to give a variety of products which probably arise *via* allylic carbonium ions; the latter are formed by abstraction of a hydride ion from position 4b to give, after elimination of a proton, a 4b(5)-ene which then loses a further hydride ion from C-6. The ions derived from 7-hydroxygibbanes such as methyl allogibberate (5) undergo Wagner–Meerwein rearrangement in which the 7,8-bond migrates to C-6 to give 7-ketones such as (15) in high yield. On the other hand the ions from 7-deoxygibbanes, *e.g.* methyl gibberate (27), give products which are mainly derived from nucleophilic attack at C-6, but which include a low yield of rearrangement product formed by migration of the 9,9a-bond to position 4b, giving 9a(10)-enes, *e.g.* (42). The presence of an 8-hydroxy-group in the allylic carbonium ion leads to cleavage of the 7,8-bond to give ring D seco-compounds, *e.g.* the ketone (49).

In an attempt to improve the preparation of methyl didehydrodihydroallogibberate [1] (1), which was required for another investigation, methyl dihydroallogibberate (4) (mixture of C-8 epimers) was treated with an excess of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in boiling dioxan for *ca.* 16 h. The gummy product, isolated in 95% yield, was a mixture of two epimers, which on column chromatography afforded the pure major epimer as a crystalline compound, $C_{19}H_{20}O_3$. The i.r. spectrum of the latter revealed the presence of both ketone and ester carbonyl groups ($\nu_{max.}$ 1743 and 1722 cm^{-1}) and the absence of a hydroxy-group; its u.v. spectrum [$\lambda_{max.}$ 270, 296, and 305 nm (ε 22,000, 5950, and 4820)] showed that it contained a 4b,5-double bond. The n.m.r. spectrum of this epimer [see compound (10), Table 1] showed the presence of a secondary methyl group and one olefinic proton. Its mass spectrum gave the base peak at *m/e* 254, corresponding to the loss of keten from the molecular ion and suggesting the presence of a $\cdot CH_2 \cdot CO \cdot$ bridge. These spectroscopic data, and degradative evidence which has been briefly reported,[2] are best explained by structure (10). Reduction of the epimer with sodium borohydride gave only one alcohol (11) in the n.m.r. spectrum of which the signal (see Table 1) due to the 8-methyl group had shifted downfield by 0·3 p.p.m. Since attack by borohydride would be expected to take place from the less hindered α-face of the molecule, the alcohol was assigned the β-configuration. Dreiding models show that the 8-methyl group will be deshielded when it has the α-orientation. Hence the major keto-ester has an 8α-methyl group; the other epimer (12) has not been obtained pure.

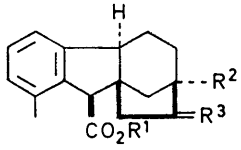
The structure of the keto-ester (10) has been confirmed by chemical degradation. First, on treatment with potassium hydroxide in deuterium oxide, it yielded the trideuterio-derivative (13) which gave no 10-proton signal in its n.m.r. spectrum, but showed two methoxy-signals with a combined integral equivalent to three protons, *i.e.* as expected,[3] partial epimerisation of the ester group had occurred. Its mass spectrum showed M^+ 299 and the base peak at *m/e* 255, corresponding to loss of $CD_2{=}C{=}O$, probably by retro-Diels–Alder breakdown of ring C. Secondly, oxidation of the keto-ester with selenium dioxide gave the α-diketone (14) (*cf.* ref. 4) whose u.v. spectrum showed no evidence of enolisation. Dehydrogenation of the diketone with palladised char-

[1] T. P. C. Mulholland, *J. Chem. Soc.*, 1958, 2693.
[2] B. E. Cross and R. E. Markwell, *J.C.S. Chem. Comm.*, 1972, 442.
[3] J. F. Grove and T. P. C. Mulholland, *J. Chem. Soc.*, 1960, 3007.
[4] B. E. Cross, *J. Chem. Soc.*, 1954, 4670.

coal afforded methyl 1,7-dimethylfluorene-9-carboxylate (17), identical with an authentic sample.[5] These reactions showed that the keto-ester (10) retained the basic hydrofluorene skeleton for rings A, B, and C and excluded the alternative structure (18) (see later). The 10α-proton in the diketone (14) appeared as a singlet in its n.m.r. spectrum, 0·99 p.p.m. downfield from that in the



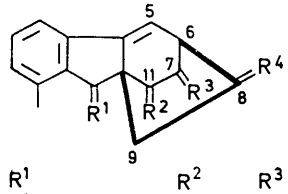
	R^1	R^2	R^3
(1)	Me	H_2	OH
(2)	H	H_2	OH
(3)	Me	H,OEt	H



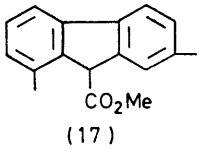
	R^1	R^2	R^3
(4)	Me	OH	H,Me
(5)	Me	OH	CH_2
(6)	Me	H	H,Me
(7)	H	H	Me,OH
(8)	H	H	H,Me
(9)	Me	H	Me,OH

keto-ester (10), thus confirming the α-orientation of the ·CO·CO· bridge.

The mechanism by which the keto-ester (10) is formed can now be considered. The introduction of conjugated double bonds into hydroaromatic systems by DDQ is well known,[6] and further hydride abstraction can then take place leading to allylic carbonium ions.[7,8] In the case of methyl dihydroallogibberate, such a sequence beginning with the abstraction of the 4b-proton by DDQ, would generate the ion (19), which could undergo Wagner–Meerwein rearrangement in either of two ways to give a 4b(5)-ene. Thus, migration of the 7,8-bond to C-6 would give the keto-ester (10), whilst migration of the 7,11-bond to C-6 would give rise to the isomer (18). The driving force for the rearrangement of methyl dihydroallogibberate (4) to the keto-ester (10) is presumably the relief of strain on passing from the bicyclic [3.2.1] system of the former, and of the intermediate 4b(5)-ene (1), to the [2.2.2] ring system of the latter, and is aided by the lone pair on the 7-oxygen atom [see (19)]. The u.v. spectra support this conclusion; the spectrum of the keto-ester (10) shows a higher extinction coefficient (22,000) than does that of didehydrodihydroallogibberic acid[1] (2) (13,500), indicating that the 4b,5-double bond in the former, but not in the latter, can lie in the same plane as ring A.



	R^1	R^2	R^3	R^4
(10)	α-H, β-CO_2Me	H_2	O	β-H, α-Me
(11)	α-H, β-CO_2Me	H_2	α-H,β-OH	β-H, α-Me
(12)	α-H, β-CO_2Me	H_2	O	α-H, β-Me
(13)	α-D, β-CO_2Me / β-D, α-CO_2Me	D_2	O	β-H, α-Me
(14)	α-H, β-CO_2Me	O	O	β-H, α-Me
(15)	α-H, β-CO_2Me	H_2	O	CH_2
(16)	β-H, α-CO_2Me	H_2	O	CH_2



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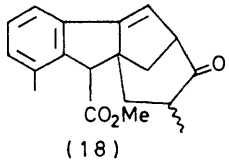

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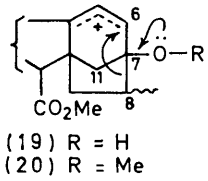
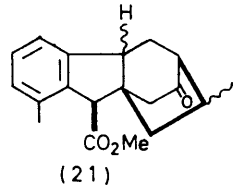


(19) R = H
(20) R = Me



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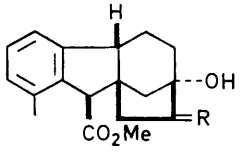
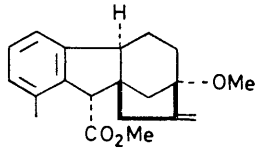


	R
(22)	α-H,β-Me
(23)	β-H,α-Me
(24)	CH_2



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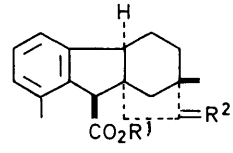
(26)



	R^1	R^2	
(27)	Me	O	
(28)	Me	H_2	
(29)	Me	H,OH	
(30)	Me	O	4bβ-H
(31)	H	H,OH	

[5] B. E. Cross, J. F. Grove, J. MacMillan, and T. P. C. Mulholland, *J. Chem. Soc.*, 1958, 2520.

[6] D. Walker and J. D. Herbert, *Chem. Rev.*, 1967, 153.

[7] I. H. Sadler and J. A. G. Stewart, *Chem. Comm.*, 1969, 773.

[8] F. E. Lutz and E. F. Kiefer, *Tetrahedron Letters*, 1970, 4851.

data (see Table 1 and Experimental section) were in agreement with structure (15). On hydrogenation it gave the tetrahydro-keto-ester (21) which was shown to be a mixture of at least three stereoisomers by g.l.c. This tetrahydro-ester was almost identical (i.r. and

TABLE 1

^{1}H N.m.r. data (τ values; solutions in $CDCl_3$; J in Hz)

Compd.	5-H	6-H	8-Substituent	9-H_2	10-H	Other signals
(10)	3·51(d) J 6	6·91(dd)	8·93(d) J 7		5·95(s)	
(11)	3·56(d) J 7	7·74(m)	8·63(d) J 6		6·12(s)	5·95(m) (7-H)
(15)	3·54(d) J 6·5	6·19(d) J 6·5	4·96(t) and 4·79(t) J 2·5		5·87(s)	
(16)	3·54(d) J 6·5	6·20(d) J 6·5	4·96(t) and 4·79(t) J 2		5·83(s)	
(32)	3·87(d) J 4·5	6·08(d) J 4·5			5·91(s)	8·70(s) (7-Me)
(33)	3·75(s)			7·43(s)	5·82(s)	8·66(s) (7-Me)
(34)	3·98(d) J 3	5·88(d) J 3		7·52(s)	6·02(s)	8·73(s) (7-Me) 8·77(t) and 6·36(q) J 7 (OEt)
(35)	3·95(d) J 4	6·49(d) J 4		7·66(s)	6·10(s)	8·76(s) (7-Me) 8·81(t) and 6·38(q) J 7 (OEt)
(36)	3·94(d) J 3·5	6·23(d) J 3·5		7·67(s)	5·97(s)	8·82(s) (7-Me)
(38)	3·77(s)			8·11(m)	5·90(s)	8·69(s) (7-Me)

n.m.r. spectra) with the tetrahydro-ester prepared by hydrogenation of the keto-ester (10). With 1 mol. equiv. of DDQ at room temperature, methyl allogibberate gave the keto-ester (15) in *ca.* 25% yield and a mixture believed to consist of methyl didehydroallogibberate and the starting ester.

Since the abstraction of the 4b-proton from gibbanes such as (4) by DDQ should be subject to steric factors, the reaction of methyl dihydroepiallogibberate [3] [(22) + (23)] with the quinone was examined. Under the conditions used with methyl dihydroallogibberate (4) over 50% of its 4b-epimer [(22) + (23)] was recovered. The rearrangement product was shown to consist of the epimeric keto-esters (10) and (12), in the ratio of 1 : 10, by comparison (g.l.c. and n.m.r.) with the products obtained from the ester (4). Since crystallisation of methyl dihydroepiallogibberate gave one pure epimer, it follows from the above rearrangements that this epimer is the 8β-methyl compound (22). In confirmation of the effect of the 4b-stereochemistry upon reaction with DDQ, *ca.* 50% of methyl epiallogibberate [3] (24) was recovered under the usual reaction conditions. The product (*ca.* 30% yield) was the rearranged ester (15) prepared before from methyl allogibberate. The slow reaction of the 4bβ-hydrogen atom in these compounds with DDQ is attributed to steric hindrance by the 10β-methoxycarbonyl group (see also later).

During the rearrangements discussed above, the 7-hydroxy-group is converted into a ketone, and since the loss of the hydroxy-proton might play a part in the mechanism of rearrangement a 7-methoxy-compound was prepared. Treatment of methyl allogibberate with sodium hydride and methyl iodide gave the methyl ether (25) whose n.m.r. spectrum not only revealed the presence of the additional methoxy-group (τ 6·69), but showed that, as expected,[3] the methoxycarbonyl group had epimerised. N.m.r. data show that the relative configurations of the 4b-proton and the ester function at position 10 may be determined from the chemical shift of the former, which is deshielded by about 0·5 p.p.m. when both the hydrogen and the methoxycarbonyl group are on the same side of the molecule (*cf.* ref. 9). Under the usual reaction conditions the methyl ether reacted slowly with an excess of DDQ; *ca.* 45% was recovered and *ca.* 25% of the keto-ester (16) was obtained. The n.m.r. spectrum of the latter (see Table 1) was similar to that of its 10-epimer (15). Treatment of the keto-ester (16) with sodium hydride partially epimerised the methoxycarbonyl group and gave a mixture of the keto-esters (15) and (16) in the ratio of 1 : 3. It is of interest that in the methyl ether (25) the 4bα-proton is sterically hindered by the 10α-methoxycarbonyl group, thus confirming that it is the relative stereochemistries at positions 4b and 10, rather than those of position 4b and ring D, which determine the rate of reaction of these gibbanes with DDQ (*cf.* ref. 10). It was concluded that loss of the proton from the 7-hydroxy-group was not necessary for rearrangement of the ion (19), but that the lone pair on the oxygen atom attached to C-7 in ion (20) was probably essential (see later). Accordingly the reactions of some 7-deoxygibbanes with DDQ were investigated. These gibbanes, on reaction with DDQ, would be expected to give ions such as (26) in which, although migration of the 7,8-bond is unlikely, nucleophilic attack at C-6 would be favoured.

Treatment of methyl gibberate [4] (27) with an excess of DDQ in boiling dioxan gave a complex mixture from which seven compounds were isolated. The major product was the hydroxy-keto-ester (32) whose structure was deduced from its u.v., i.r., and n.m.r. spectra (see Experimental section and Table 1). This structure was confirmed by oxidation with chromic oxide–pyridine–dichloromethane [11] to the diketo-ester (33) whose spectroscopic data [$\lambda_{max.}$ 238, 299, and 325 nm (ε 9200, 20,100, and 14,480); $\nu_{max.}$ 1743, 1732, 1673, and 1631 cm^{-1}; Table 1] were in agreement with those reported [12] for the synthetic (±)-compound. The diketo-ester (33)

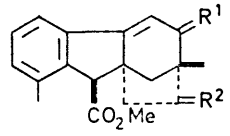
[9] A. J. Baker, A. C. Goudie, U. R. Ghatak, and R. Dasgupta, *Tetrahedron Letters*, 1972, 1103.

[10] J. F. Grove, J. MacMillan, T. P. C. Mulholland, and W. B. Turner, *J. Chem. Soc.*, 1960, 3049.

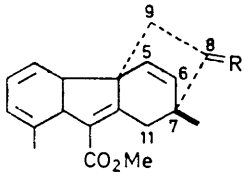
[11] R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, 1970, **35**, 4000.

[12] H. J. E. Loewenthal and S. K. Malhotra, *J. Chem. Soc.*, 1965, 990.

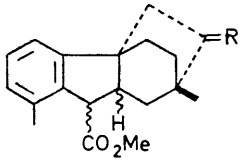
was, not unexpectedly, isolated as one of the products from the DDQ reaction since the quinone is known [6] to oxidise allylic alcohols. The epimeric ethoxy-keto-esters (34) and (35) were also isolated and their structures were deduced from spectroscopic evidence (see Experimental section and Table 1). Their stereochemistries at C-6 followed from comparison of their n.m.r. spectra. The signal given by the 6-proton in the minor epimer (τ 5·88) appeared at lower field than that in the major epimer (τ 6·49). Since the α-proton at C-6 is deshielded by the 8-carbonyl group, the minor and major epimers were assigned structures (34) and (35), respectively. Another



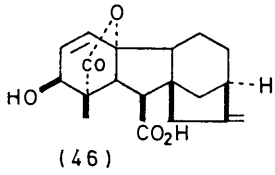
	R^1	R^2
(32)	H,OH	O
(33)	O	O
(34)	α-H, β-OEt	O
(35)	β-H, α-OEt	O
(36)	β-H, α-X	O
(37)	H_2	O
(38)	O	H_2
(39)	H,OH	H_2
(40)	H,OEt	H_2
(41)	H_2	H_2



(42) R = O
(43) R = H_2



(44) R = O
(45) R = H_2



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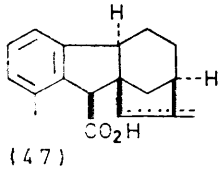

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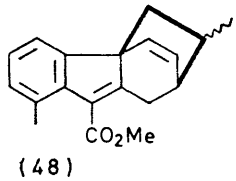

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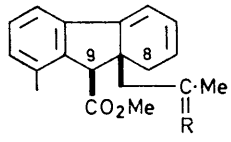
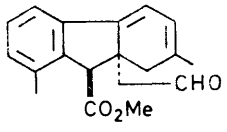


(49) R = O
(50) R = H,OH



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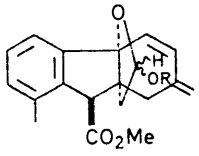
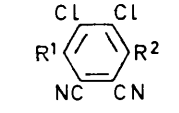
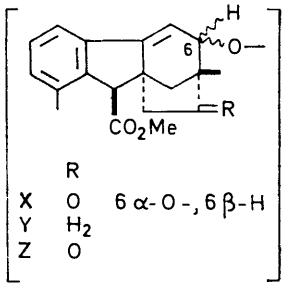


(52) R = Et
(53) R = H



	R^1	R^2
(54)	Y	OH
(55)	Y	Y
(56)	Z	Z
(57)	Z	OH



	R	
X	O	6α-O-, 6β-H
Y	H_2	
Z	O	

product from the DDQ reaction was shown to be a dimer by its molecular weight. Its n.m.r. spectrum (see Table 1) showed only one set of signals for each type of proton and since the 6-proton resonance occurred at τ 6·23 it was assigned structure (36) with β-oriented 6-protons.

All the foregoing products are assumed to arise by nucleophilic attack at C-6 of the allylic carbonium ion (26) or its precursor (see later). Water present in the dioxan would give the hydroxy-ester (32), whilst traces of ethanol, which are usually present in dioxan, would give rise to the ethers (34) and (35). The dimer (36) may be formed by nucleophilic attack by the hydroxy-group of the hydroxy-ester (32) on the ion (26), although dimers formed in other reactions involving DDQ are believed to arise *via* radical mechanisms.[13]

The most interesting product from the reaction between DDQ and methyl gibberate was a keto-ester formed in low yield. Its u.v. spectrum [$\lambda_{max.}$ 234, 281, 292sh, and 300sh nm (ε 12,500, 5360, 4850, and 4420)], which showed that it was not a 4b(5)-ene, was attributed to an αβ-unsaturated ester. In agreement, its i.r. spectrum showed bands at 1725 (ketone), 1714 and 1675 (C=C·CO_2Me), and 712 cm^{-1} (*cis*-olefin), and its n.m.r. spectrum [see compound (42), Table 2], which lacked the normal 10-proton signal, showed doublets at τ 3·62 and 3·85 (J 7·5 Hz) attributed to a *cis*-olefin of the type C–CH=CH–C. Hence this compound was assigned [2] structure (42), and in support hydrogenation gave the tetrahydro-ester (44) [$\lambda_{max.}$ 270 nm (ε 470); $\nu_{max.}$ 1721br cm^{-1} (see Table 2)]. Confirmation of the basic ring structure was provided by oxidation of the unsaturated ester (42) with selenium dioxide which gave the fluorene derivative (17), identical with an authentic specimen.[5] The fluorene (17) was also an unexpected product from the DDQ reaction; the possibility that it was formed *via* the rearrangement product (42) was eliminated when it was found that the latter was recovered after further treatment with DDQ.

When methyl gibberate and DDQ were allowed to react for only 1 h in boiling anhydrous dioxan, the major product was methyl didehydrogibberate (37), which was identified by hydrolysis to didehydrogibberic acid.[5]

[13] H.-D. Becker, *J. Org. Chem.*, 1965, **30**, 982, 989.

The ethoxy-ester (35), the hydroxy-ester (32), and the dimer (36) were also formed, but in low yield. In an attempt to prepare the hydroxy-ester (32) in higher yield, methyl gibberate was treated with DDQ in dioxan containing 6% of water. However the major product was methyl didehydrogibberate and only a small amount of the hydroxy-ester was isolated. Although this may be because the presence of water leads to rapid decomposition of DDQ,[14] dehydrogenations have been carried out in aqueous dioxan.[15]

In contrast to methyl gibberate, methyl epigibberate [4] (30) was stable to DDQ in boiling dioxan; analysis by u.v. spectroscopy showed that less than 0·7% of 4b(5)-ene had been formed. As with methyl epiallogibberate (see before), this unreactivity can be attributed to steric hindrance at position 4b by the 10β-methoxycarbonyl group.

The ease with which the 7,8-bond in 7-oxygibbanes migrates during reaction with DDQ may be attributed to participation by the lone pair on the 7-oxygen atom (see before). The absence of this type of migration in methyl gibberate under similar reaction conditions could be ascribed to the poor migratory aptitude of the keto-group. Consequently methyl deoxogibberate (28) (prepared from deoxogibberic acid [5]), which lacks functionality at both positions 7 and 8, was treated with DDQ under the usual conditions. The major product was the keto-ester (38) (see Table 1), probably formed *via* the hydroxy-ester (39), which was present as a minor product; oxidation of the latter gave the keto-ester (38). The ethoxy-ester (40) was also isolated in low yield. The only other product, isolated in *ca.* 25% yield, was the rearranged ester [2] (43) which showed spectroscopic data (see Experimental section and Table 2) similar to those of the keto-ester (42). Hydrogenation of the ester (43) gave the tetrahydro-derivative (45) (see Table 2).

In the foregoing 7-deoxygibbanes, ring D had the α-configuration. The effect of the stereochemistry of this ring on the reaction with DDQ was studied by preparing the ester (6) from gibberellin A_7 (46).[16] On the small scale, cold dilute mineral acid converted gibberellin A_7 into the hydroxy-acid (7).[16] On a larger scale, only a poor yield of the hydroxy-acid was obtained, and the residual material was not aromatic. When the latter was boiled with dilute mineral acid it gave a gum, shown by its n.m.r. spectrum to be a mixture of the double-bond isomers (47), and which on hydrogenation afforded the acid (8). Reaction of the methyl ester (6) of the latter with DDQ under the usual conditions yielded *ca.* 25% of a gum, shown to be the rearrangement product [2] (48) by spectroscopic data [$\nu_{max.}$ 1713 (C=C·CO_2Me) and 708 cm^{-1} (*cis*-olefin) and see Table 2], and a smaller amount of the ethoxy-ester (3). Thus the stereochemistry of ring D appears to have little, if any, effect on the course of the rearrangement in 7-deoxygibbanes.

The other product from the acid catalysed degradation of gibberellin A_7, *viz.* the hydroxy-acid (7), enabled the effect of an 8-hydroxy-group on the DDQ reactions to be studied. Its methyl ester (9) was treated with DDQ in the usual manner. The major product (*ca.* 35%) was an unstable keto-ester, $C_{19}H_{20}O_3$, whose n.m.r. [τ 8·06 (3H, s, MeCO), 7·53 (2H, s, CH_2·CO), 6·37 (1H, s, 9-H), 6·30 (3H, s, OMe), 6·29 (1H, dd, 8-H), and *ca.* 3·8 (3H, m, vinylic)], i.r., and u.v. spectra (see Experimental section) showed that it had structure [2] (49). The presence of the methyl ketone function was confirmed by reduction with sodium borohydride to the hydroxy-ester (50), which showed new n.m.r. signals at τ 9·01 (3H, d, *J* 6 Hz, CHMe) and 6·35 (1H, m, CH·OH).

Reduction of gibberic acid with sodium borohydride also afforded an 8-hydroxy-acid, *viz.* (31), but when its methyl ester was treated with DDQ under the usual conditions it did not give the expected aldehyde (51). The major product contained an exocyclic methylene group ($\nu_{max.}$ 890 cm^{-1}; τ 5·05), but no n.m.r. signal attributable to the 7-methyl group. Its u.v. spectrum [$\lambda_{max.}$ 238 and 270 nm (ε 18,100 and 2700)] showed that it was not a 4b(5)-ene, but was consistent with a conjugated diene system; its n.m.r. spectrum (see Experimental section) not only revealed that it contained an ethoxy-group but that it was a mixture of epimers. Hence it was assigned the acetal structure (52). The minor product is believed to be a mixture of the epimeric hemiacetals (53) on the basis of spectroscopic data, and because on treatment with ethanol and acetic acid it gave a mixture of the epimeric ethyl acetals (52), identical with that obtained before. An attempt to confirm the acetal structure (52), by oxidation with Jones reagent to the corresponding γ-lactone, failed; the product showed many spots on t.l.c.

TABLE 2

^{1}H N.m.r. data (τ values; solutions in $CDCl_3$; *J* in Hz)

Compound	5-H	6-H	7-Me	9-H_2	CO_2Me	Other signals
(42)	3·85(d) *J* 7·5	3·62(d) *J* 7·5	8·61(s)	7·18(s)	6·14	8·20(d) and 7·33(d) *J* 17·5 (11-H_2)
(43)	3·89(d) *J* 4	3·78(d) *J* 4	8·66(s)	7·49(s)	6·17	
(44)			8·97(s)	7·11(m)	6·33 and 6·26	5·90(d), *J* 10 10-H
(45)			9·14(s)		6·35 and 6·32	6·11(d), *J* 5·5 } (10-H) 6·0(d), *J* 10 }
(48)	*ca.* 3·62(m)	*ca.* 3·62(m)			6·17	9·07(d), *J* 6·5 (8-Me)

[14] S. H. Burnstein and H. J. Ringold, *J. Amer. Chem. Soc.*, 1964, **86**, 4952.

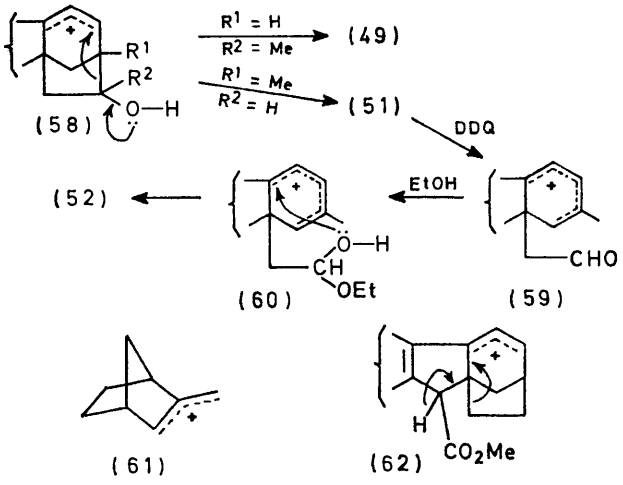
[15] J. W. A. Findlay and A. B. Turner, *J. Chem. Soc.* (*C*), 1971, 23.

[16] B. E. Cross, R. H. B. Galt, and J. R. Hanson, *Tetrahedron*, 1962, **18**, 451.

The mechanism of the reaction of DDQ with 7-oxygenated gibbanes has been discussed already, but that of the 7-deoxy-compounds needs clarification. The reaction of DDQ with the gibbanes may not lead directly to allylic carbonium ions such as (19), but may proceed *via* intermediates incorporating a DDQ residue (*cf.* refs. 7 and 8). To investigate this possibility, the reaction of methyl deoxogibberate (28) and DDQ at room temperature in deuteriochloroform was followed by n.m.r. spectroscopy. Hydride abstraction from position 4b occurred rapidly and after addition of 1 mol. equiv. of DDQ the spectrum [τ 4·10 (1H, t, J 3 Hz, 5-H) and 8·93 (3H, s, 7-Me)] showed the product to be methyl didehydrodeoxogibberate (41). A second mol. equiv. of DDQ was then added to the solution at −25° and as the temperature rose the triplet at τ 4·10 decreased in intensity and new signals appeared at τ 4·34 (m) and 5·05 (m). At 31° the triplet had almost disappeared, the multiplets corresponded to about 0·7—0·8 protons each, and a weak signal had appeared at τ 3·82. Treatment of the solution with a third mol. equiv. of DDQ at 30° for 48 h produced no further change in the spectrum. By analogy with Lutz and Kiefer's work,[8] the intermediate seemed likely to be either the monoether (54) or the diether (55), the signals at τ 4·35 and 5·05 being assigned to the 5- and 6-protons, respectively. The resonance at τ 3·82 is believed to be due to a small amount of the hydroxy-ester (39) and/or the corresponding ketone (38). The persistence of the signal at τ 5·05 in the presence of an excess of DDQ shows that the ether [(54) or (55)] does not undergo further attack by DDQ at C-6 to give an acetal (*cf.* refs. 7 and 8). Addition of ethanol to the reaction mixture caused the instantaneous disappearance of all the low-field signals, apart from those due to the aromatic protons, and one doublet appeared at τ *ca.* 3·9 (J 4 Hz). Isolation of the products gave mainly the ethoxy-ester (40) and a small amount of the keto-ester (38).

When methyl gibberate (27) was treated with DDQ at room temperature in deuteriochloroform, the reactive intermediate was isolated as a gum which was believed to be the diether (56) [$\nu_{max.}$ 2250 cm^{-1} (C≡N); no OH absorption] because (*a*) treatment with ethanol at room temperature for 5 min gave the ethoxy-ester (35), identical with the specimen already prepared, and (*b*) a solution in ethanol had a u.v. spectrum very similar to that of the ethoxy-ester (35), and corresponding in extinction coefficient to the formation of two molecules of the latter from one of the diether, rather than to the breakdown of the monoether (57) to one molecule of the ethoxy-ester. These experiments suggest that the foregoing 6-oxygenated products may arise by nucleophilic displacement of the quinol residue from diethers such as (56), although the mechanism may differ in chloroform and dioxan solutions.

The various rearrangement products probably arise from allylic carbonium ions such as (19). When a 7-oxygen atom is present migration of the 7,8-bond to C-6 proceeds in high yield as depicted for the ion (19). Similarly the lone pair on an 8-hydroxy-group assists



rupture of the 7,8-bond [see ion (58)]. In the case of the 8-hydroxy-compound (29) the initial product is probably the aldehyde (51), which is further attacked by DDQ at C-8 to give the ion (59). The latter is assumed to form a hemiacetal with traces of ethanol present in the solvent and then intramolecular nucleophilic attack [see ion (60)], followed by double-bond migration to the more stable exocyclic position, gives the acetal (52). In the absence of either a 7- or an 8-oxygen substituent the predominant reaction products result from nucleophilic attack at C-6. Nevertheless, in contrast to the allylic carbonium ion [17] (61), ions such as (26) gave about 25% of Wagner–Meerwein rearrangement product by migration of the 9,9a-bond to C-4b, accompanied by loss of a proton from C-10, possibly as depicted for the ion (62).

EXPERIMENTAL

Details of chromatographic materials and conditions used for determination of physical data, *etc.*, are reported in ref. 18. All optical rotations were measured for solutions in chloroform. G.l.c. was carried out on a Varian 1527B gas chromatograph with a stainless steel column (150 × 0·3 cm o.d.) packed with 5% Carbowax SE30 on 80—90 Anakrom at a column temperature of 215°, unless otherwise stated, and a nitrogen gas flow rate of 35—40 ml min^{-1}.

Dioxan was AnalaR grade (Hopkin and Williams) and was filtered through a column of alumina before use. Anhydrous dioxan was prepared as described by Hess and Frahm.[19]

Treatment of Methyl Dihydroallogibberate (4) *with Dichlorodicyanobenzoquinone.*—Dihydroallogibberic acid [4] (500 mg) in methanol (40 ml) was methylated with an excess of ethereal diazomethane and the crude ester in dioxan (30 ml) was heated with the quinone (1·2 g) under reflux for 16 h. The solution was cooled and filtered, the dioxan was

[17] C. W. Jefford and W. Wajnarowski, *Chem. Comm.*, 1968, 129.

[18] B. E. Cross and R. E. Markwell, *J. Chem. Soc.* (*C*), 1971, 2980.

[19] K. Hess and H. Frahm, *Ber.*, 1938, **71**, 2627.

evaporated off *in vacuo*, and the resultant gum was chromatographed on alumina (30 g). Elution with ethyl acetate–light petroleum (1 : 9) gave a gum (490 mg) which on g.l.c. showed two peaks due to the epimeric keto-esters (10) and (12), retention times 27 and 25 min, respectively, in the ratio 77 : 23 (Found: *m/e* 296. Calc. for $C_{19}H_{20}O_3$: *M*, 296), $\nu_{max.}$ (film) 1732br, 1655, and 1599 cm^{-1}; $\lambda_{max.}$ 249sh, 259, 270, 296, and 305 nm (ε 9850, 17,700, 22,700, 5130, and 6280); τ 9·02 (d, *J* 7 Hz, 8β-Me), 8·93 (d, *J* 7 Hz, 8α-Me), and 3·63 (d, *J* 7 Hz) and 3·51 (d, *J* 6 Hz) (total 1H, 5-H).

The mixture of keto-esters gave a semicarbazone hydrate, which crystallised from chloroform–light petroleum as plates, m.p. 156—158° (Found: C, 64·45, 65·0; H, 6·65, 6·3; N, 10·7, 10·45%; *m/e* 353. Calc. for $C_{20}H_{23}N_3O_3,H_2O$: C, 64·7; H, 6·8; N, 11·3%. Calc. for $C_{20}H_{23}N_3O_3$: *M*, 353).

Chromatography of the mixture of keto-esters (2·3 g) on alumina (100 g) and elution with ethyl acetate–light petroleum (4 : 96) gave fractions which crystallised from ethyl acetate–light petroleum as prisms of the *keto-ester* (10) (1·05 g), m.p. 92—94°, $[\alpha]_D^{24}$ +512° (*c* 0·25), which on g.l.c. showed a single peak at a retention time of 27 min (Found: C, 76·75; H, 6·9. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%), $\nu_{max.}$ 1743 (ester), 1722 (ketone), 1653, and 1592 cm^{-1}; $\lambda_{max.}$ 230sh, 249sh, 259sh, 270, 296, and 305 nm (ε 11,300, 8720, 16,900, 22,000, 5950, and 4820); τ see Table 1 and 7·79 (3H, s, 1-Me), 6·19 (3H, s, OMe), and *ca.* 2·65 (3H, m, aromatic H); *m/e* 296 (37%), 254 (100), 195 (74), 194 (80), 193 (34), 179 (85), and 165 (35).

Later fractions from the column and the mother liquors from the keto-ester (10) gave an intractable gum shown by g.l.c. to be the 8-epimers (10) and (12) in the ratio 1·86 : 1.

Reduction of the Keto-ester (10) *with Sodium Borohydride.*—The keto-ester (140 mg) and sodium borohydride (200 mg) in methanol (10 ml) were left at 0° for 1 h and then at room temperature for 3 h. Acetic acid (0·5 ml) was added, the solution was evaporated *in vacuo*, and the residue was diluted with water (10 ml) and extracted with ethyl acetate to give the *hydroxy-ester* (11), which crystallised from ethyl acetate–light petroleum as rods (101 mg), m.p. 161—163° (Found: C, 76·35; H, 7·35. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·4%), $\nu_{max.}$ 3260, 1742, and 1592 cm^{-1}; $\lambda_{max.}$ 223sh, 254sh, 263, 273, 291, and 303 nm (ε 11,300, 13,600, 18,000, 15,900, 3380, and 3370); τ see Table 1 and 7·83 (3H, s, 1-Me), 6·27 (3H, s, OMe), and *ca.* 2·82 (3H, m, aromatic H); *m/e* 298 (5%), 255 (20), 254 (89), 195 (66), 194 (80), 193 (65), 179 (100), 165 (40), and 149 (40).

The hydroxy-ester showed a single spot on t.l.c. (ethanol–benzene, 5 : 95).

Deuteriation of the Keto-ester (10).—The keto-ester (48 mg) in tetrahydrofuran (3 ml) was heated under reflux with 5% potassium hydroxide in deuterium oxide (5 ml) for 16 h. The tetrahydrofuran was evaporated *in vacuo* and the solution was acidified with dilute hydrochloric acid and extracted with ether. The ethereal solution was methylated with diazomethane to give the trideuterio-keto-ester (13) (45 mg) as a gum (Found: *m/e* 229. Calc. for $C_{19}H_{17}D_3O_3$: *M*, 229), τ 8·92 (3H, d, *J* 7 Hz, 8α-Me), 7·81 (3H, s, 1-Me), 6·93 (1H, dd, 6-H), 6·23 and 6·20 (total 3H, singlets, OMe), and 3·53 (1H, d, *J* 7 Hz, 5-H), no 10-H signal; *m/e* 299 (33%), 256 (27), 255 (100), 220 (23), 196 (50), 195 (35), 194 (23), and 180 (25).

Preparation of the α-Diketone (14).—The keto-ester (10) (150 mg) and selenium dioxide (380 mg) in ethanol (1·5 ml) were heated in a sealed tube at 140° for 5 h. The orange solution was filtered and the filtrate was purified by p.l.c. Development with ethanol–benzene (1 : 199) and recovery of the orange band gave the *α-diketone* (14), which crystallised from ethyl acetate–light petroleum as orange plates (63 mg), m.p. 147—148° (Found: C, 73·75; H, 5·9. $C_{19}H_{18}O_4$ requires C, 73·55; H, 5·85%), $\nu_{max.}$ 1738, 1646, and 1596 cm^{-1}; $\lambda_{max.}$ 227sh, 251sh, 261, 272, 281, 303, and 450 nm (ε 11,100, 9300, 11,600, 11,200, 517, 500, and 436), unchanged on addition of base; τ 8·89 (3H, d, *J* 7 Hz, 8α-Me), 7·77 (3H, s, 1-Me), 6·57 (1H, dd, 6-H), 6·18 (3H, s, OMe), 4·96 (1H, s, 10-H), 3·30 (1H, d, *J* 6·5 Hz, 5-H), and *ca.* 2·61 (3H, m, aromatic H); *m/e* 310 (2%), 254 (100), 196 (70), 195 (80), 180 (57), 179 (100), 178 (48), and 165 (60).

Dehydrogenation of the α-Diketone (14).—The diketone (44 mg) was heated with 10% palladium–charcoal at 220—240° for 1·5 h under nitrogen. The residue was extracted with ether to give a yellow oil which was purified by p.l.c. Development with ethanol–benzene (1 : 199) and recovery of the band showing a blue fluorescence in u.v. light (R_F 0·5) gave methyl 1,7-dimethylfluorene-9-carboxylate (16 mg), which crystallised from methanol as needles (9·1 mg), m.p. 121·5—122·5° (lit.,[5] 121—122°), identical (i.r., u.v., n.m.r., and mass spectra) with an authentic sample.

Treatment of Methyl Allogibberate (5) *with Dichlorodicyanobenzoquinone.*—(a) *With an excess of quinone.* Allogibberic acid (500 mg) in methanol (25 ml) was treated with an excess of ethereal diazomethane in the normal manner, and the resultant gummy methyl ester (5) [τ 7·15 (m, 4b-H)] and the quinone (1·13 g), in dioxan (40 ml), were heated under reflux for 16 h. The recovered products were chromatographed on alumina (50 g). Elution with ethyl acetate–light petroleum (1 : 19) gave the keto-ester (15) (501 mg) as a gum which was shown to be homogeneous by g.l.c.; $[\alpha]_D^{25}$ +258° (*c* 0·65) (Found: *m/e* 294. Calc. for $C_{19}H_{18}O_3$: *M*, 294), $\nu_{max.}$ (film) 1743 (ester), 1733 (ketone), 1649, 1586, and 892 (=CH_2) cm^{-1}; $\lambda_{max.}$ 230sh, 252sh, 261, 272, 293, 304, 312sh, and 322sh nm (ε 12,600, 10,400, 15,900, 18,400, 3720, 4450, 3520, and 2010); τ see Table 1 and 7·79 (3H, s, 1-Me), 6·17 (s, OMe), and *ca.* 2·62 (3H, m, aromatic H); *m/e* 294 (3%), 252 (46), 193 (40), 192 (100), 191 (27), 178 (28), 165 (15), and 119 (30).

Its *semicarbazone* crystallised from chloroform–light petroleum as plates, m.p. 165—166° (Found: C, 68·55; H, 6·05; N, 11·7%; *m/e* 351. $C_{20}H_{21}N_3O_3$ requires C, 68·35; H, 6·0; N, 11·95%; *M*, 351).

(b) *With 1 mol. equiv. of quinone.* Methyl allogibberate (67 mg) and the quinone (50 mg) were kept in dioxan (10 ml) at room temperature for 18 h. The solution was filtered and evaporated *in vacuo* to give a gum which was purified by p.l.c. Development with ethanol–benzene (5 : 95) and recovery of the least polar band (R_F 0·7) gave the keto-ester (15) (16 mg) as a gum, identical (i.r. spectrum) with the sample already prepared.

Recovery of the band of R_F 0·4 gave a mixture of methyl didehydroallogibberate and methyl allogibberate (5), in the ratio of *ca.* 3 : 1, as a gum (38 mg) (Found: *m/e* 298 and 296. Calc. for $C_{19}H_{22}O_3$: *M*, 298. Calc. for $C_{19}H_{20}O_3$: *M*, 296), $\nu_{max.}$ (film) 3410, 1735br, 1658, and 890 cm^{-1}; $\lambda_{max.}$ 250sh, 258, 269, 288, and 299 nm (ε 7800, 10,200, 8800, 1930, and 1660); τ 7·85 (3H, s, 1-Me), 6·24 (3H, s, OMe), 6·05 [*ca.* 0·25H, s, 10-H in (5)] and 5·88 (*ca.* 0·75H, s, 10-H), 5·24 (t, *J* 2 Hz), 5·04 (m) and 4·73 (t, *J* 2 Hz) (total 2H, =CH_2), 4·13 (*ca.* 0·75H, t, *J* 3 Hz, 5-H), and *ca.* 2·9 (3H, m, aromatic H).

Hydrogenation of the Keto-ester (15).—The ester (436 mg)

in ethyl acetate (25 ml) was hydrogenated over 5% palladium–charcoal (300 mg) until uptake of hydrogen ceased. Recovery of the product gave the tetrahydro-ester (21) (393 mg) as a gum, shown to contain three isomers by g.l.c. analysis (at 184°) (Found: *m/e* 298·1556. Calc. for $C_{19}H_{22}O_3$: *M*, 298·1569), $\nu_{max.}$ (film) 1734br and 1601 cm^{-1}; $\lambda_{max.}$ 265 nm (ε 300); τ 9·0 (3H, m, 8-Me), 7·78 (3H, s, 1-Me), 7·02 (1H, m, 4b-H), 6·2 (4H, m, OMe and 10-H), and *ca.* 2·75 (3H, m, aromatic H).

Chromatography on alumina gave a number of fractions containing the tetrahydro-ester (21) which all showed several peaks on g.l.c.

Hydrogenation of the Keto-ester (10).—The ester (240 mg) in ethyl acetate (20 ml) was hydrogenated over 5% palladium–charcoal (200 mg) until uptake of hydrogen ceased. Recovery of the product gave a gum (238 mg) which was almost identical (i.r. and n.m.r. spectra) with the tetrahydro-ester (21) already prepared.

Treatment of Methyl Dihydroepiallogibberate [(22) *and* (23)] *with Dichlorodicyanobenzoquinone.*—Methyl dihydro-epiallogibberate [shown by g.l.c. to be a mixture of the 8-epimers (22) and (23) in the ratio of 9 : 1] (230 mg) and the quinone (510 mg) in dioxan (30 ml) were heated under reflux for 15 h. Chromatography of the recovered products on alumina (50 g) and elution with ethyl acetate–light petroleum (1 : 19) gave the epimeric keto-esters (12) and (10) as a gum (63 mg) which on g.l.c. showed two peaks at retention times 25 and 27 min (relative intensity *ca.* 10 : 1) (Found: *m/e* 296. Calc. for $C_{19}H_{20}O_3$: *M*, 296), $\nu_{max.}$ 1741 (ester), 1728 (ketone), 1653, and 1592 cm^{-1}; τ 9·02 (3H, d, *J* 7 Hz, 8β-Me), 7·79 (3H, s, 1-Me), 6·89 (1H, dd, 6-H), 6·19 (3H, s, OMe), 5·94 (1H, s, 10-H), 3·63 (1H, d, *J* 7 Hz, 5-H), and *ca.* 2·65 (3H, m, aromatic H).

Elution with ethyl acetate–light petroleum (3 : 17) gave a fraction which crystallised from light petroleum to give *methyl* 1,8β-*dimethyl*-7-*hydroxyepigibba*-1,3,4a(10a)-*triene*-10β-*carboxylate* (22) (pure by g.l.c.) (102 mg), m.p. 97—98° (Found: C, 76·2; H, 7·75%; *m/e* 300. $C_{19}H_{24}O_3$ requires C, 76·0; H, 8·05%; *M*, 300), $\nu_{max.}$ 3460, 3380, 1738, 1719, and 1596 cm^{-1}; τ 8·90 (3H, d, *J* 7 Hz, 8-Me), 7·73 (3H, s, 1-Me), 6·53 (1H, t, *J* 6 Hz, 4b-H), 6·29 (4H, s, OMe and 10-H), and *ca.* 2·82 (3H, m, aromatic H).

The preceding mixture of keto-esters (12) and (10) gave a semicarbazone which crystallised from chloroform–light petroleum as plates, m.p. 164—165° (Found: C, 67·85; H, 6·45; N, 11·8. Calc. for $C_{20}H_{23}N_3O_3$: C, 68·0; H, 6·55; N, 11·9%), $\lambda_{max.}$ 230sh, 258sh, 264, 274, 290, and 302 nm (ε 20,300, 17,700, 22,100, 24,000, 535, and 490).

Treatment of Methyl Epiallogibberate (24) *with Dichlorodicyanobenzoquinone.*—Methyl epiallogibberate (238 mg) [τ 6·53 (t, *J* 6 Hz, 4b-H)] and the quinone (540 mg) in dioxan (25 ml) were heated under reflux for 19 h and the recovered products were chromatographed on alumina (20 g). Elution with ethyl acetate–light petroleum (5 : 95) gave the keto-ester (15) (77 mg) as a gum identical (i.r. spectrum) with the specimen prepared from methyl allo-gibberate. Elution with ethyl acetate–light petroleum (15 : 85) gave methyl epiallogibberate (113 mg).

Preparation of the Methyl Ether (25).—Methyl allo-gibberate (3·0 g) and sodium hydride (1·0 g; 1 : 1 mixture with oil) in dry tetrahydrofuran (30 ml) were heated under reflux for 1·5 h. Methyl iodide (10 ml) was added; the solution was maintained at 30—40° for 1 h, then more methyl iodide (5 ml) was added and the solution was left at room temperature overnight. The mixture was evaporated *in vacuo* and the residue was diluted with water (30 ml) and extracted with ethyl acetate to give a gum which was chromatographed on alumina (40 g). Elution with ethyl acetate–light petroleum (1 : 19) gave the *methyl ether* (25), which crystallised from light petroleum as prisms (1·98 g), m.p. 111—112° (Found: C, 77·1; H, 7·6. $C_{20}H_{24}O_3$ requires C, 76·9; H, 7·75%), $\nu_{max.}$ 1736, 1663, 1600, and 883 cm^{-1}; τ 7·78 (3H, s, 1-Me), 6·69 (3H, s, 7-OMe), 6·5 (m, 4b-H), 6·38 (s, 10-H), 6·32 (s, OMe), 5·13 (2H, m, $=CH_2$), and *ca.* 2·85 (3H, m, aromatic H); *m/e* 312 (86%), 297 (17), 283 (13), 280 (7), 253 (32), 240 (17), 239 (14), 237 (23), 223 (100), and 221 (40).

Treatment of the Methyl Ether (25) *with Dichlorodicyanobenzoquinone.*—The ether (1·5 g) and the quinone (3·1 g) in anhydrous dioxan (50 ml) were heated under reflux for 18 h and the recovered products were chromatographed on alumina (120 g). Elution with ethyl acetate–light petroleum (1 : 19) followed by crystallisation from light petroleum gave the unchanged methyl ether as prisms (592 mg). Elution with ethyl acetate–light petroleum (15 : 85) gave the keto-ester (16) (296 mg) as a gum (Found: *m/e* 294. Calc. for $C_{19}H_{18}O_3$: *M*, 294), $\nu_{max.}$ (film) 1735, 1725, 1648, 1590, and 890 cm^{-1}; $\lambda_{max.}$ 230sh, 252sh, 260, 271, 292, 303, 310sh, and 320 nm (ε 10,900, 9980, 14,200, 17,300, 4150, 4800, 3610, and 2180); τ see Table 1 and 7·79 (3H, s, 1-Me), 6·24 (3H, s, OMe), and *ca.* 2·62 (3H, m, aromatic H); *m/e* 294 (7%), 266 (3), 253 (12), 252 (54), 193 (47), and 192 (100).

Its *semicarbazone* crystallised from chloroform–light petroleum as plates, m.p. 213—214° (Found: C, 68·25; H, 5·9; N, 11·8. $C_{20}H_{21}N_3O_3$ requires C, 68·35; H, 6·0; N, 11·9%).

Treatment of the Keto-ester (16) *with Sodium Hydride.*—The ester (120 mg) and sodium hydride (240 mg; 1 : 1 mixture with oil) in dry tetrahydrofuran (20 ml) were heated under reflux for 3 h under nitrogen. The solution was cooled, water (10 ml) was added dropwise, the tetrahydrofuran was evaporated off *in vacuo*, and the product was recovered in ether and chromatographed on alumina (50 g). Elution with ethyl acetate–light petroleum (8 : 92) gave a gum (105 mg), shown by its n.m.r. spectrum to be a mixture of the keto-esters (15) and (16) in the ratio of *ca.* 1 : 3, τ 7·79 (3H, s, 1-Me), 6·17 (4H, m, 2 × epimeric-CO_2Me and 6-H), 5·87 (*ca.* 0·25H, s, 10-αH), 5·83 (*ca.* 0·75H, s, 10-βH), 4·96 (1H, t, *J* 2 Hz) and 4·79 (1H, t, *J* 2 Hz) ($=CH_2$), 3·54 (1H, d, *J* 6·5 Hz, 5-H), and *ca.* 2·62 (3H, m, aromatic H).

Treatment of Methyl Gibberate (27) *with Dichlorodicyanobenzoquinone.*—(a) *In dioxan for* 21 *h.* Methyl gibberate (300 mg) [τ 6·92 (t, *J* 7 Hz, 4b-H)] and the quinone (860 mg) in dioxan (25 ml) were heated under reflux for 21 h. The products were recovered in the usual manner and were chromatographed on alumina (80 g). Elution with ethyl acetate–light petroleum (1 : 19) gave a gum which was purified by p.l.c. (ethanol–benzene, 1 : 99). Recovery of the band with R_F 0·75 gave methyl 1,7-dimethylfluorene-9-carboxylate (6·2 mg), which crystallised from light petroleum as plates, m.p. 122—123°, $[\alpha]_D^{25}$ 0°, identical (i.r., u.v., and mass spectra) with an authentic sample.[5]

Recovery of the band with R_F 0·5 gave the *keto-ester* (42) (10 mg), which crystallised from light petroleum as prisms, m.p. 88—90°, $[\alpha]_D^{24}$ +528° (*c* 0·17) (Found: C, 77·6; H, 6·2. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·15%), $\nu_{max.}$ 1725, 1714, 1675, and 712 (*cis*-olefin) cm^{-1}; $\lambda_{max.}$ 234, 281, 292sh, and 300sh nm (ε 12,500, 5360, 4850, and 4420); τ see Table 2

and 7·54 (3H, s, 1-Me) and *ca.* 2·78 (3H, m, aromatic H); *m/e* 294 (30%), 252 (76), 220 (12), 194 (23), 193 (100), 192 (17), 191 (13), 179 (12), 178 (17), and 165 (10).

Recovery of the band with R_F 0·35 gave the *ethoxy-keto-ester* (35), which crystallised from light petroleum as needles (23 mg), m.p. 124—125° (Found: C, 74·25; H, 7·05. $C_{21}H_{24}O_4$ requires C, 74·1; H, 7·1%), $\nu_{max.}$ 1742, 1730, 1658, and 1596 cm^{-1}; $\lambda_{max.}$ 254sh, 262, 271, 288, and 299 nm (ε 11,300, 15,400, 15,400, 4030, and 3400); τ see Table 1 and 7·79 (3H, s, 1-Me), 6·34 (s, OMe), and *ca.* 2·78 (3H, m, aromatic H); *m/e* 340 (100%), 325 (10), 308 (25), 298 (50), 281 (30), 280 (60), 271 (80), 240 (80), and 194 (100).

Further elution of the column with ethyl acetate–light petroleum (1 : 19) gave the *ethoxy-keto-ester* (34), which crystallised from light petroleum as prisms (11 mg), m.p. 171—175° (decomp.) (Found: C, 74·35; H, 7·15%; *m/e* 340. $C_{21}H_{24}O_4$ requires C, 74·1; H, 7·1%; *M*, 340), $\nu_{max.}$ 1750, 1733, 1662, and 1599 cm^{-1}; $\lambda_{max.}$ 253sh, 260, 270, 288, and 299 nm (ε 11,300, 15,900, 14,200, 3320, and 2990); τ see Table 1 and 7·88 (s, 1-Me), 6·32 (s, OMe), and *ca.* 2·8 (3H, m, aromatic H).

Elution with ethyl acetate–light petroleum (3 : 22 and 3 : 17) gave a gum which was purified by p.l.c. Development with ethanol–benzene (2 : 98) and recovery of the least polar band gave the *dimer* (36) (36 mg), which crystallised from ethyl acetate–light petroleum as plates, m.p. 256—258° [Found: C, 75·1; H, 6·3%; *M* (osmometric), 560. $C_{38}H_{38}O_7$ requires C, 75·25; H, 6·3%; *M*, 606], $\nu_{max.}$ 1742, 1664, and 1599 cm^{-1}; $\lambda_{max.}$ 267sh, 276, 288, and 300 nm (ε 16,100, 18,850, 8220, and 5870); τ see Table 1 and 7·76 (6H, s, 2 × 1-Me), 6·34 (6H, s, 2 × OMe), and *ca.* 2·74 (6H, m, aromatic H); *m/e* 312 (5%), 311 (13), 296 (5), 295 (7), 254 (10), 253 (8), 209 (15), 194 (33), 193 (100), 179 (16), and 178 (16).

Recovery of the most polar band gave the diketo-ester (33) (32 mg) as a gum (Found: *m/e* 310. Calc. for $C_{19}H_{18}O_4$: *M*, 310), $\nu_{max.}$ (film) 1743, 1732, 1673, 1631, and 1599 cm^{-1}; $\lambda_{max.}$ 238, 290sh, 299, and 325 nm (ε 9200, 16,200, 20,100, and 14,480); τ see Table 1 and 7·69 (3H, s, 1-Me), 6·28 (3H, s, OMe), and *ca.* 2·6 (3H, m, aromatic H); *m/e* 310 (100%), 286 (7), 282 (7), 278 (17), 268 (17), 251 (20), 241 (100), 208 (28), 209 (28), and 165 (28).

Its *dioxime* crystallised from chloroform as plates, m.p. 236—239° (Found: C, 67·4; H, 6·0; N, 7·55%; *m/e* 340. $C_{19}H_{20}N_2O_4$ requires C, 67·05; H, 5·9; N, 8·25%; *M*, 340), $\nu_{max.}$ 1731 cm^{-1}.

Elution of the column with ethyl acetate–light petroleum (1 : 1) gave the hydroxy-keto-ester (32) (74 mg) as a gum (Found: *m/e* 312. Calc. for $C_{19}H_{20}O_4$: *M*, 312), $\nu_{max.}$ (film) 3420, 1741, and 1725 cm^{-1}; $\lambda_{max.}$ 262, 271, 288, and 300 nm (ε 12,800, 12,800, 3620, and 3160); τ see Table 1 and 7·71 (3H, s, 1-Me), 6·23 (3H, s, OMe), and *ca.* 2·6 (3H, m, aromatic H); *m/e* 312 (34%), 184 (10), 180 (9), 270 (70), 253 (17), 252 (20), 243 (15), 212 (18), 211 (100), 210 (30), 209 (21), and 183 (47).

Its *semicarbazone* crystallised from chloroform–light petroleum as plates, m.p. 164—166° (Found: C, 64·55; H, 6·2; N, 11·2. $C_{20}H_{23}N_3O_4$ requires C, 65·0; H, 6·3; N, 11·4%).

In a second experiment, under identical conditions but with a reaction time of 15 h, the hydroxy-ester (32) was isolated in about 60% yield.

(b) *In dioxan for* 1 *h.* Methyl gibberate (150 mg) and the quinone (320 mg) in anhydrous dioxan (20 ml) were heated under reflux for 1 h and the products were recovered and chromatographed on alumina (40 g). Elution with ethyl acetate–light petroleum (1 : 24) gave a gum which was purified by p.l.c. Development with ethanol–benzene (1 : 99) and recovery of the major band gave *methyl didehydrogibberate* (37) (88 mg) as a gum (Found: *m/e* 296·1419. $C_{19}H_{20}O_3$ requires *M*, 296·1412), $\nu_{max.}$ 1745br, 1677, and 1603 cm^{-1}; $\lambda_{max.}$ 250sh, 260, 270, 288, and 299 nm (ε 10,700, 14,400, 12,750, 2860, and 2480); τ 8·76 (3H, s, 7-Me), 7·92 (2H, s, 11-H_2), 7·72 (3H, s, 1-Me), 7·66 (2H, d, *J* 4 Hz, 6-H_2), 7·51 (2H, s, 9-H_2), 6·23 (3H, s, OMe), 5·90 (1H, s, 10-H), 3·95 (1H, t, *J* 4 Hz, 5-H), and *ca.* 2·65 (3H, m, aromatic H); *m/e* 296 (100%), 254 (60), 237 (36), 209 (40), 195 (65), 194 (87), 193 (72), 180 (29), 179 (55), 178 (46), 167 (35), and 165 (50).

Recovery of a more polar band gave the ethoxy-ester (35) (20 mg), identical (i.r. and mass spectra) with the sample prepared in (a).

Elution of the column with ethyl acetate–light petroleum (1 : 5) gave the dimer (36) (8 mg), identical (i.r. spectrum) with the specimen prepared in (a). Elution with ethyl acetate–light petroleum (1 : 1) gave the hydroxy-ester (32) (13·5 mg), identical (i.r. spectrum) with the specimen prepared in (a).

(c) *In aqueous dioxan for* 16 *h.* Methyl gibberate (600 mg) and the quinone (1·28 g) in dioxan (50 ml) and water (3 ml), were heated under reflux under nitrogen for 16 h and the products were recovered and were chromatographed on alumina (150 g). Elution with ethyl acetate–light petroleum (1 : 19) gave a gum which was purified by p.l.c. Development with ethanol–benzene (1 : 99) and recovery of the major band gave methyl didehydrogibberate (37) (212 mg). Recovery of a more polar band gave the ethoxy-ester (35) (28 mg).

Elution of the column with ethyl acetate–light petroleum (1 : 5) gave a gum which was purified by p.l.c. Development with ethanol–benzene (1 : 99) and recovery of the major band gave the diketo-ester (33) (68 mg). Elution of the column with ethyl acetate gave the hydroxy-ester (32) (28 mg).

Oxidation of the Hydroxy-ester (32).—The ester (170 mg) in dichloromethane (10 ml) was added to a stirred solution of chromium trioxide (1·8 g) in dry pyridine (3·0 ml) and dichloromethane (45 ml), and the mixture was stirred for 15 min at room temperature. The organic layer was decanted and the residue was washed with ethyl acetate. The combined organic solutions were washed with sodium hydroxide solution, dilute hydrochloric acid, sodium hydrogen carbonate solution, and water, and evaporated to give a gum which was purified by p.l.c. Development with ethanol–benzene (1 : 49) and recovery of the major band gave the diketo-ester (33) (52 mg), identical (i.r. and mass spectra) with the sample prepared before.

Hydrolysis of Methyl Didehydrogibberate (37).—Methyl didehydrogibberate (42 mg) and 5% potassium hydroxide solution (5 ml) were heated under reflux under nitrogen for 2 h. Isolation of the acidic fraction gave didehydrogibberic acid (32·5 mg), which crystallised from benzene–light petroleum as prisms, m.p. 220—222° (decomp.) [lit.,[5] 222—224° (decomp.)], identical (i.r. spectrum) with an authentic sample.

Hydrogenation of the Keto-ester (42).—The keto-ester (14·5 mg) in ethyl acetate (5 ml) was hydrogenated over 10% palladium–charcoal (15 mg) until uptake of hydrogen ceased. Recovery gave the *tetrahydro-keto-ester* (44) (10 mg), which crystallised from light petroleum as prisms,

m.p. 81—83° (Found: C, 76·6; H, 7·7. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·5%), $\nu_{max.}$ 1721br and 1605 cm^{-1}; $\lambda_{max.}$ 270 nm (ε 470); τ see Table 2 and 7·79 (3H, s, 1-Me), 6·33 and 6·26 (singlets, ratio 3 : 1, total 3H, epimeric CO_2Me groups), and *ca.* 2·87 (3H, m, aromatic H); *m/e* 298 (90%), 270 (60), 255 (15), 254 (30), 239 (45), 238 (45), 211 (50), 210 (37), 209 (44), 195 (75), and 155 (100).

Oxidation of the Keto-ester (42) *with Selenium Dioxide.*—The ester (60 mg) and selenium dioxide (150 mg) in ethanol (1·25 ml) were heated in a sealed tube at 140° for 4 h. The recovered products were purified by p.l.c. Development with ethanol–benzene (1 : 99) and recovery of the band showing a blue fluorescence in u.v. light (R_F 0·75) gave methyl 1,7-dimethylfluorene-9-carboxylate (22 mg), m.p. 120—121°, identical (i.r. and u.v. spectra) with an authentic sample.[5]

Treatment of the Keto-ester (42) *with Dichlorodicyanobenzoquinone.*—The ester (25 mg) was recovered (22 mg) after treatment with the quinone (40 mg) in dioxan (20 ml) under reflux for 15 h.

Treatment of Methyl Epigibberate (30) *with Dichlorodicyanobenzoquinone.*—Methyl epigibberate[4] (45 mg) [τ 6·47 (m, 4b-H)] and the quinone (115 mg) in anhydrous dioxan (20 ml) were heated under reflux for 16 h and the products were recovered. Chromatography followed by crystallisation from ethyl acetate–light petroleum gave methyl epigibberate (39 mg), m.p. 95·5—96·5°. The mother liquors were shown by u.v. spectroscopy (ε_{265} 600) to contain <0·31 mg of methyl didehydrogibberate (37).

Preparation of Methyl Deoxogibberate (28).—Deoxogibberic acid[5] (600 mg) in ether was treated with an excess of ethereal diazomethane in the normal manner. Recovery gave *methyl deoxogibberate* (28) which crystallised from light petroleum as prisms (450 mg), m.p. 107—108° (Found: C, 80·15; H, 8·45. $C_{19}H_{24}O_2$ requires C, 80·25; H, 8·5%), $\nu_{max.}$ 1735 and 1604 cm^{-1}; τ 8·98 (3H, s, 7-Me), 7·87 (3H, s, 1-Me), 7·16 (1H, t, *J* 6·5 Hz, 4b-H), 6·29 (3H, s, OMe), 6·02 (1H, s, 9-H), and *ca.* 2·9 (3H, m, aromatic H); *m/e* 284 (43%), 255 (3), 252 (4), 226 (32), 225 (100), 224 (20), 195 (13), 169 (20), 165 (13), 157 (20), and 155 (44).

Treatment of Methyl Deoxogibberate (28) *with Dichlorodicyanobenzoquinone.*—Methyl deoxogibberate (200 mg) and the quinone (450 mg) in anhydrous dioxan (30 ml) were heated under reflux for 22 h under nitrogen and the recovered products were chromatographed on alumina (50 g). Elution with ethyl acetate–light petroleum (3 : 97) gave a gum which was purified by p.l.c. Development with ethanol–benzene (1 : 99) and recovery of the major band gave the *ester* (43), which crystallised from light petroleum as prisms (39 mg), m.p. 87—88° (Found: C, 81·25; H, 7·15. $C_{19}H_{20}O_2$ requires C, 81·4; H, 7·2%), $\nu_{max.}$ 1717, 1604, and 700 cm^{-1} (*cis*-CH=CH); $\lambda_{max.}$ 233, 275, 290sh, and 299sh nm (ε 13,350, 7450, 5260, and 4150); τ see Table 2 and 7·54 (3H, s, 1-Me), and *ca.* 2·85 (3H, m, aromatic H); *m/e* 280 (34%), 252 (47), 220 (13), 193 (100), and 178 (15).

Recovery of a more polar band gave the *ethoxy-ester* (40) as a gum (17 mg) which sublimed at 105° (bath) and 10^{-4} mmHg (Found: C, 77·25; H, 8·2. $C_{21}H_{26}O_3$ requires C, 77·25; H, 8·05%), $\nu_{max.}$ (film) 1729, 1662, and 1600 cm^{-1}; $\lambda_{max.}$ 250sh, 259, 268, 287, and 296 nm (ε 11,650, 15,700, 13,000, 2670, and 2350); τ 8·84 (t, *J* 7 Hz, O·CH_2·CH_3), 8·78 (s, 7-Me), 7·82 (3H, s, 1-Me), 6·43 (1H, d, *J* 4·5 Hz, 6-H), 6·43 (q, *J* 7 Hz, O·CH_2·CH_3), 6·42 (s, OMe), 6·11 (1H, s, 10-H), 3·75 (1H, d, *J* 4·5 Hz, 5-H), and *ca.* 2·78 (3H, m, aromatic H); *m/e* 326 (52%), 311 (41), 281 (30), 271 (54), 266 (69), 252 (30), 209 (27), 193 (100), 179 (36), 178 (30), 165 (17), and 155 (13).

Elution of the column with ethyl acetate–light petroleum (1 : 19) gave the *keto-ester* (38), which crystallised from ethyl acetate–light petroleum as cubes (63 mg), m.p. 162—163° (Found: C, 76·7; H, 6·7. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%), $\nu_{max.}$ 1733, 1660, 1630, and 1599 cm^{-1}; $\lambda_{max.}$ 229, 235, 286sh, 295, and 315 nm (ε 11,300, 11,400, 18,850, 23,400, and 15,350); τ 8·69 (3H, s, 7-Me), 7·73 (3H, s, 1-Me), 6·35 (3H, s, OMe), 5·90 (1H, s, 10-H), 3·77 (1H, s, 5-H), and *ca.* 2·62 (3H, m, aromatic H); *m/e* 296 (58%), 268 (35), 241 (100), 237 (42), 209 (40), 208 (35), 193 (30), and 165 (28).

Elution of the column with ethyl acetate–light petroleum (1 : 1) gave a gum (33 mg), believed to contain the hydroxy-ester (39), $\nu_{max.}$ 3430 and 1720 cm^{-1}. T.l.c. in ethanol–benzene (7 : 93) showed several spots.

Oxidation of the Hydroxy-ester (39).—The foregoing impure hydroxy-ester (28 mg) in dichloromethane (2 ml) was added to chromium trioxide (400 mg) in dry pyridine (0·8 ml) and dichloromethane (10 ml), and the mixture was stirred for 15 min. The product (recovered in the normal manner) crystallised from ethyl acetate as the keto-ester (38) (10 mg), identified by its i.r. spectrum.

Hydrogenation of the Ester (43).—The ester (26 mg) in ethyl acetate (15 ml) was hydrogenated over 10% palladium–charcoal (25 mg) until uptake of hydrogen ceased. Recovery gave the *tetrahydro-ester* (45) (22 mg), which crystallised from light petroleum as prisms, m.p. 53—56° (Found: C, 80·25; H, 8·6. $C_{19}H_{24}O_2$ requires C, 80·25; H, 8·5%), $\nu_{max.}$ 1736 and 1599 cm^{-1}; $\lambda_{max.}$ 266 and 273 nm (ε 400 and 380); τ see Table 2 and 7·84 (3H, s, 1-Me), 7·35 (2H, m), 6·35 and 6·32 (total 3H, singlets, ratio 1 : 6, epimeric CO_2Me groups), and *ca.* 3·0 (3H, m, aromatic H); *m/e* 284 (67%), 255 (33), 224 (30), 214 (100), and 155 (60).

Treatment of Gibberellin A_7 (46) *with Acid* (cf. *ref.* 16).—Gibberellin A_7 (containing 7% of gibberellin A_4) (5·4 g) in tetrahydrofuran (30 ml) was added to concentrated hydrochloric acid (100 ml) in water (1·0 l) and the solution was left at room temperature for 5 days. Recovery in ethyl acetate gave a gum which was chromatographed on silica gel (130 g). Elution with ethyl acetate–light petroleum (2 : 3) and crystallisation from acetone gave needles (520 mg) of the hydroxy-acid (7), m.p. 228—231° (lit.,[16] 220—225°). All other fractions gave intractable gums.

Its *methyl ester* (9) crystallised from ethyl acetate–light petroleum as rods, m.p. 155—156° (Found: C, 76·15; H, 8·05. $C_{19}H_{24}O_3$ requires C, 75·95; H, 8·05%), $\nu_{max.}$ 3450, 1726, and 1592 cm^{-1}; τ 8·72 (3H, s, 8-Me), 7·83 (3H, s, 1-Me), 6·22 (3H, s, OMe), 6·05 (1H, s, 10-H), and *ca.* 3·0 (3H, m, aromatic H); *m/e* 300 (1%), 282 (80), 242 (43), 225 (27), 223 (35), 222 (42), 197 (100), 183 (93), 182 (84), and 155 (80).

The combined intractable fractions, in tetrahydrofuran (25 ml), were added to concentrated hydrochloric acid (45 ml) in water (450 ml) and the solution was heated under reflux for 1 h. Recovery in ethyl acetate gave a gum which was chromatographed on silica gel (100 g). Elution with ethyl acetate–light petroleum (1 : 9) gave a gum (1·25 g) which was a mixture of the isomeric acids (47) (Found: *m/e* 268. Calc. for $C_{18}H_{20}O_2$: *M*, 268), $\nu_{max.}$ (film) 2600br, 1715, 1698, and 1596 cm^{-1}; τ 8·35 (d, *J* 1·5 Hz, 8-Me), 7·78 (3H, s, 1-Me), 6·17 and 6·09 (total 1H, singlets, 10-H), 5·25 (*ca.* 0·45H, m, $=CH_2$), 4·71 (*ca.* 0·75H, q, *J* 1·5 Hz, 9-H), and *ca.* 3·08 (3H, m, aromatic H).

Elution with ethyl acetate–light petroleum (1 : 1) gave the hydroxy-acid (7) which crystallised from acetone–light petroleum as needles (240 mg).

Preparation of the Acid (8).—The mixture of acids (47) (1·10 g) in ethyl acetate (30 ml) was hydrogenated over 10% palladium–charcoal (250 mg) until uptake of hydrogen ceased (14 h). Recovery gave the *acid* (8), which crystallised from ethyl acetate–light petroleum as needles (590 mg), m.p. 137—138° (decomp.) (Found: C, 80·25; H, 8·1. $C_{18}H_{22}O_2$ requires C, 79·95; H, 8·2%), $\nu_{max.}$ 2620—3100, 1710, and 1595 cm^{-1}; τ 9·08 and 9·03 (total 3H, doublets, *J* 6·5 Hz, epimeric 8-Me groups), 7·75 (3H, s, 1-Me), 7·25 (1H, m, 4b-H), 6·01 (1H, s, 10-H), and 2·96 (3H, m, aromatic H); *m/e* 270 (100%), 255 (8), 241 (7), 227 (25), 226 (16), 225 (64), 224 (34), 209 (8), 200 (12), 195 (8), 183 (20), 181 (28), and 155 (47).

Its methyl ester (6) was a gum (Found: *m/e* 284. Calc. for $C_{19}H_{24}O_2$: *M*, 284), $\nu_{max.}$ (film) 1740, 1730, and 1592 cm^{-1}; τ 9·09 and 9·04 (total 3H, doublets, *J* 6·5 Hz, epimeric 8-Me groups), 7·83 (3H, s, 1-Me), 7·35 (1H, m, 4b-H), 6·25 (3H, s, OMe), 6·08 (1H, s, 10-H), and *ca.* 3·02 (3H, m, aromatic H).

Treatment of the Methyl Ester (6) *with Dichlorodicyanobenzoquinone.*—The ester (540 mg) and the quinone (1·22 g) in anhydrous dioxan (25 ml) were heated under reflux for 16 h and the products were recovered and were chromatographed on alumina (100 g). Elution with ethyl acetate–light petroleum (1 : 19) gave a gum which was purified by p.l.c. Development with ethanol–benzene (1 : 99) and recovery of the major band gave the *ester* (48) (132 mg) as a gum which sublimed at 90° (bath) and 3×10^{-3} mmHg (Found: C, 81·1; H, 7·15. $C_{19}H_{20}O_2$ requires C, 81·4; H, 7·2%), $\nu_{max.}$ (film) 1713, 1600, 1589, and 708 (*cis*-HC=CH) cm^{-1}; $\lambda_{max.}$ 234, 274, 280sh, and 300sh nm (ε 12,900, 7200, 7050, and 4120); τ see Table 2 and 7·53 (3H, s, 1-Me), and *ca.* 2·86 (3H, m, aromatic H); *m/e* 280 (20%), 239 (10), 238 (40), 224 (8), 206 (11), 195 (8), 180 (20), 179 (100), 178 (35), 165 (13), and 152 (12).

Recovery of a more polar band gave the *ethoxy-ester* (3) as a gum (36 mg) which sublimed at 110° (bath) and 3×10^{-3} mmHg (Found: C, 77·0; H, 7·95. $C_{21}H_{26}O_3$ requires C, 77·25; H, 8·05%), $\nu_{max.}$ (film) 1722, 1660, and 1595 cm^{-1}; $\lambda_{max.}$ 250sh, 259, 268, 287, and 298 nm (ε 13,050, 17,500, 14,650, 2860, and 2500); τ 8·8 (6H, m, O·CH_2·CH_3 and 8-Me), 7·82 (3H, s, 1-Me), 7·50 (1H, m), 6·41 (s, OMe), 6·41 (q, *J* 6·5 Hz, O·CH_2·CH_3), 6·11 (1H, s, 10-H), 4·03 (1H, m, 5-H), and *ca.* 2·80 (3H, m, aromatic H); *m/e* 326 (35%), 311 (42), 297 (5), 282 (15), 281 (12), 267 (25), 266 (100), 195 (35), 179 (100), and 165 (20).

Treatment of the Hydroxy-ester (9) *with Dichlorodicyanobenzoquinone.*—The ester (487 mg) and the quinone (1·03 g) in anhydrous dioxan (25 ml) were heated under reflux for 16 h and the products were recovered and chromatographed on alumina (80 g). Elution with ethyl acetate–light petroleum (1 : 19) gave the *keto-ester* (49) (165 mg), which crystallised from light petroleum as needles, m.p. 104—106° (Found: C, 77·2; H, 6·75. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%), $\nu_{max.}$ 1729 (ester), 1715 (ketone), 1660, and 1590 cm^{-1}; $\lambda_{max.}$ 233, 240, 248, 295sh, 308, 320, and 333sh nm (ε 8060, 8400, 6600, 10,380, 13,500, 14,800, and 11,400); τ 8·06 (3H, s, MeCO), 7·83 (3H, s, 1-Me), 7·53 (2H, s, CH_2·CO), 6·37 (1H, s, 9-H), 6·30 (3H, s, OMe), 6·29 (1H, dd, 8-H), *ca.* 3·8 (3H, m, olefinic H), and *ca.* 2·75 (3H, m, aromatic H); *m/e* 296 (1%), 239 (80), 206 (6), 193 (8), 179 (100), 165 (19), and 152 (9).

The keto-ester (49) was unstable at room temperature; after 2 days t.l.c. showed several new spots.

Reduction of the Keto-ester (49) *with Sodium Borohydride.*—The keto-ester (40 mg) in methanol (8 ml) was treated with sodium borohydride (150 mg) at 0° for 15 min and then left at room temperature for 1 h. Recovery of the product gave a gum which was purified by p.l.c. Development with ethanol–benzene (1 : 24) and recovery of the major band gave the hydroxy-ester (50) (15 mg) as a gum, $\nu_{max.}$ (film) 3410, 1725, and 1590 cm^{-1}; τ 9·01 (3H, d, *J* 6 Hz, *Me*CH·OH), 7·82 (3H, s, 1-Me), 6·35 (2H, m, 9-H and C*H*·OH), 6·22 (3H, s, OMe), *ca.* 3·17 (3H, m, olefinic H), and *ca.* 2·79 (3H, m, aromatic H).

The hydroxy-ester (50) was unstable at room temperature; after 24 h t.l.c. showed several new spots.

Preparation of the Hydroxy-acid (31).—Sodium borohydride (3·0 g) was added to gibberic acid (2·0 g) in methanol (35 ml) at 0° over 1 h, and then the solution was left at room temperature overnight. Recovery gave the *hydroxy-acid* (31) (2·05 g) as a foam (Found: C, 75·55; H, 7·8. $C_{18}H_{22}O_3$ requires C, 75·5; H, 7·75%), $\nu_{max.}$ 3320, 2600, 1708, and 1601 cm^{-1}; τ 8·86 (3H, s, 7-Me), 7·78 (3H, s, 1-Me), 6·0 (1H, s, 10-H), 5·7 (1H, m, 8-H), and *ca.* 2·98 (3H, m, aromatic H); *m/e* 286 (8%), 268 (92), 223 (30), 200 (100), 197 (28), 195 (35), 156 (38), and 155 (94).

Its *methyl ester* crystallised from acetone–light petroleum as prisms, m.p. 98—99° (Found: C, 76·15; H, 8·05. $C_{19}H_{24}O_3$ requires C, 75·95; H, 8·05%), $\nu_{max.}$ 3450, 1726, and 1592 cm^{-1}; τ 8·72 (3H, s, 8-Me), 7·83 (3H, s, 1-Me), 6·22 (3H, s, OMe), 6·05 (1H, s, 10-H), and *ca.* 3·0 (3H, m, aromatic H); *m/e* 300 (1%), 282 (80), 242 (42), 197 (100), 183 (93), 182 (84), and 155 (80).

Treatment of the Methyl Ester of the Acid (31) *with Dichlorodicyanobenzoquinone.*—The hydroxy-ester (1·05 g) and the quinone (2·7 g) in anhydrous dioxan (40 ml) were heated under reflux for 17 h under nitrogen. The products were recovered and were chromatographed on silica gel (150 g). Elution with ethyl acetate–light petroleum (8 : 92) gave the epimeric acetals (52) as a gum (222 mg) which sublimed at 90° (bath) and 4×10^{-3} mmHg (Found: C, 74·2; H, 6·9. Calc. for $C_{21}H_{24}O_4$: C, 74·1; H, 7·1%), $\nu_{max.}$ (film) 1730, 1720, 1638, 1600, and 890 cm^{-1} (=CH_2); $\lambda_{max.}$ 218, 238, and 270 nm (ε 16,300, 18,100, and 2700); τ 9·09 and 8·83 (total 3H, triplets, *J* 6·5 Hz, epimeric O·CH_2*Me* groups), 7·84 (3H, s, 1-Me), 6·66 (2H, m, epimeric O·CH_2·Me groups), 6·40 and 6·34 (total 3H, singlets, OMe), 5·05 (2H, m, =CH_2), 4·86 and 4·78 [total 3H, triplets, *J* 3 Hz, epimeric CH_2·C*H*$(OR)_2$ groups], 3·84 (2H, m, olefinic H), and *ca.* 2·75 (3H, m, aromatic H); *m/e* 340 (3%), 295 (20), 294 (65), 252 (35), 251 (75), 250 (37), 207 (50), 206 (35), 193 (65), 192 (100), 191 (35), 178 (25), and 165 (20).

Elution with ethyl acetate–light petroleum (1 : 4) gave the epimeric hemiacetals (53) as a gum (62 mg) (Found: *m/e* 312. Calc. for $C_{19}H_{20}O_4$: *M*, 312), $\nu_{max.}$ (film) 3420, 1738, 1722, 1641, 1602, and 890 cm^{-1} (=CH_2); $\lambda_{max.}$ 219, 238, and 270 nm (ε 16,000, 17,900, and 2700); τ 7·86 (3H, s, 1-Me), 6·38 and 6·34 (total 3H, singlets, OMe), 5·03 (2H, m, =CH_2), 4·50 [1H, m, CH_2·C*H*(OH)(OR)], 3·85 (2H, m, olefinic H), and *ca.* 2·75 (3H, m, aromatic H); *m/e* 312 (8%), 310 (4), 294 (63), 268 (20), 252 (32), 251 (57), 250 (34), 209 (44), 208 (37), 207 (42), 206 (41), 205 (24), 193 (58), 192 (100), and 191 (52).

Treatment of the Hemiacetals (53) *with Ethanol.*—The hemiacetals (30 mg) in ethanol (3 ml) and acetic acid (2 drops) were heated under reflux for 20 h. The solvents

were evaporated off *in vacuo* to give a gum (32 mg), identical (i.r. and mass spectra) with the epimeric acetals (52) prepared before.

Oxidation of the Mixture of Acetals (52) *with Jones Reagent.*—The acetals (80 mg) in acetone (10 ml) at 0° were treated with Jones reagent (0·30 ml) for 30 min. Recovery of the products in the normal manner gave a gum (70 mg) which showed several spots on t.l.c. (chloroform–light petroleum, 1 : 1).

Treatment of Methyl Deoxogibberate (28) *with Dichlorodicyanobenzoquinone in Deuteriochloroform.*—The ester (16 mg) and the quinone (12·9 mg, 1 mol. equiv.) in deuteriochloroform (0·5 ml) were left at room temperature for 5 min and then the solution was filtered. The filtrate, which exhibited the n.m.r. spectrum expected for methyl didehydrodeoxogibberate (41), τ 8·83 (3H, s, 7-Me), 7·79 (3H, s, 1-Me), 6·33 (3H, s, OMe), 6·10 (1H, s, 10-H), 4·10 (1H, t, J 4 Hz, 5-H), and *ca.* 2·8 (3H, m, aromatic H), was cooled to −25° and a second mol. equiv. of quinone was added; the solution went dark green. Its n.m.r. spectrum was run at intervals as the temperature was gradually allowed to rise. Reaction was slow below 0°; at 18° the triplet at τ 4·10 had diminished to 50% of its original intensity; at 31° the n.m.r. spectrum suggested that the major product was the bis-ether (55), τ 8·83 and 8·54 (singlets, 7-Me), 7·78 and 7·81 (total 6H, singlets, 1-Me), 6·38 (6H, s, OMe), 6·01 (2H, m, 10-H), 5·06 (*ca.* 1·4H, m, 6-H), 4·34 (*ca.* 1·6H, m, 5-H), 4·10 (*ca.* 0·2H, t, J 4 Hz), and 3·82 (*ca.* 0·4H, m).

A third mol. equiv. of quinone was added and the solution was left at 30° for 48 h. Its n.m.r. spectrum was virtually unchanged, but after addition of ethanol (1 drop) the only signal between τ 3·5 and 5·5 was a doublet (J *ca.* 4 Hz) at *ca.* τ 3·9. The product was recovered and purified by p.l.c. Development with chloroform–light petroleum (1 : 1), and recovery of the major band, gave the ethoxy-ester (40) as a gum (10·5 mg), identical (i.r. and n.m.r. spectra) with an authentic sample. Recovery of a more polar band gave the keto-ester (38) (2 mg) which crystallised from ethyl acetate–light petroleum as cubes, m.p. 159—161°, identical (i.r. spectrum) with an authentic sample.

Treatment of Methyl Gibberate (27) *with Dichlorodicyanobenzoquinone in Deuteriochloroform.*—Methyl gibberate (62·4 mg) and the quinone (95 mg) in deuteriochloroform (1·5 ml) were left at room temperature for 24 h. The solution was filtered and the filtrate [τ 5·05 (m, 6-H) and 4·3 (m, 5-H)] was evaporated *in vacuo* at 0° to give a gum, believed to be the bis-ether (56), $\nu_{max.}$ (film) 2250 (CN) and 1730br cm^{-1}. A solution in ethanol showed $\lambda_{max.}$ 260, 269, 288, 298, 348, and 390 nm (ε 30,800, 28,800, 10,500, 8200, 3400, and 1250).

The bis-ether was kept in ethanol (0·5 ml) at room temperature for 5 min and the product was purified by p.l.c. Development with ethanol–benzene (1 : 199) and recovery of the major band gave the ethoxy-keto-ester (35), which crystallised from light petroleum as needles (19 mg), m.p. 122—124°, identical (i.r. spectrum) with an authentic sample.

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