605. *Gibberellic Acid. Part XII.* The Stereochemistry of Allogibberic Acid.*

By JOHN FREDERICK GROVE and T. P. C. MULHOLLAND.

Allogibberic acid and epiallogibberic acid, stereoisomeric degradation products of gibberellic acid, are shown to have the absolute configurations (III) and (XX) respectively.

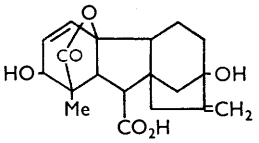
GIBBERELLIC ACID [1] (I), on treatment with dilute mineral acid, yields [2,3] allogibberic acid [4] (III). Allogibberic acid has also been obtained by heating gibberellic acid with water, and from 2,7-dihydroxy-1-methyl-8-methylene-10aξ-gibba-3,4a(4b)-diene-1,10-dicarboxylic acid † (gibberellenic acid [1,5,6]) (II) with boiling water or cold mineral acid.

* Part XI, *J. Sci. Food Agric.*, in the press.

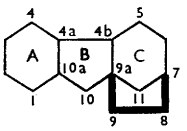
† By agreement with the Editor the name gibbane is used for the fully saturated tetracyclic system (Ia) (8,9-bridge β). The ring system derived from gibbane by inversion at positions 7 and 9a is called 7α-gibbane.

[1] Cross, Grove, MacMillan, Moffatt, Mulholland, Seaton, and Sheppard, *Proc. Chem. Soc.*, 1959, 302.
[2] Cross, *J.*, 1954, 4670.
[3] Brian, Grove, Hemming, Mulholland, and Radley, *Plant Physiol.*, 1958, **33**, 329.
[4] Mulholland, *J.*, 1958, 2693.
[5] Gerzon, Bird, and Woolf, *Experientia*, 1957, **13**, 487.
[6] Moffatt, *J.*, 1960, 3045.

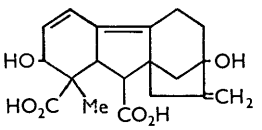
When the acid (I) or (II) was boiled with hydrazine hydrate for 24—26 hr., allogibberic acid and an epimer, epiallogibberic acid, m. p. 244°, were formed. Gibberellic acid, with a reaction time of 6 hr., gave also the acid (II), and this was the main product after 30 minutes' boiling. Allogibberic acid and its epimer thus have a common precursor (II)



(I)



(Ia)



(II)

and must be epimeric at position 4b. In agreement with this formulation epiallogibberic acid gave epigibberic acid when boiled with mineral acid (cf. allogibberic acid ⟶ gibberic acid [2]), gave formaldehyde on ozonolysis, and showed ultraviolet absorption similar to that of allogibberic acid. Epiallogibberic acid was not isolated when gibberellic acid was treated with cold mineral acid but was probably present since the action of hot mineral acid gave [2] both gibberic and epigibberic acid.

The chemistry of allo- and epiallo-gibberic acid is outlined in charts 1 and 2 in terms of the absolute configurations which are deduced below. Tricyclic compounds of type (XI) are fluorene derivatives, numbered as in (XI). Compounds derived from allo- and epiallo-gibberic acid have respectively a 4bα- and a 4bβ-hydrogen atom (see below). In this and subsequent papers dealing with degradation products of gibberellic acid where ring A is aromatic the prefix epi is used to denote compounds in the 4bβ-series.

Allogibberic Acid.—The dibasic keto-acid (XI), obtained by way of the ketol (VII) by ozonolysis [4] of allogibberic acid, is shown below to be the 4bα,8aβ,9β-acid. Six of the eight possible stereoisomers of formula (XI) have been isolated, namely (IX, X, XI, and XVII; chart 1) and (XIX and XXVI; chart 2).

Hydrolysis of the half-ester (XII), obtained by ozonolysis of methyl allogibberate,[4] with cold aqueous potassium hydroxide gave the 9α-dibasic acid (IX) (cf. ref. 4) and the 9β-isomer (XI) in the ratio 85 : 1. The 9β-dibasic acid (XI) was stable to boiling 2N-sodium hydroxide; and epimerisation at position 9 in the methyl ester (XII) but not in the free acid is to be expected.[7,8] The almost exclusive formation of the 9α-acid suggests that this acid has the more stable configuration (see below).

Similar results were obtained on hydrolysis of the methyl esters of allogibberic and gibberic acid, but not with the free acids (which were stable) or with the methyl esters of epiallogibberic, epigibberic, and dehydrogibberic [9] acid which gave the corresponding free acids.

Hydrolysis of methyl allogibberate with boiling 2N-sodium hydroxide gave a gummy acid (V), stereoisomeric with allogibberic acid but differing in the infrared spectrum and specific rotation. That inversion had occurred at position 10 was shown by ozonolysis, which gave the 9α-dibasic keto-acid (IX). Hot hydrochloric acid isomerised the acid (V) to a gummy acid whose infrared spectrum and specific rotation were similar to those of the acidic gum obtained by alkaline hydrolysis of methyl gibberate; the spectrum showed that a 5-ring ketone had been formed, as in the formation of gibberic acid from allogibberic acid. With methanolic sodium hydroxide [7] at room temperature racemisation at position 10 in methyl gibberate proceeded without substantial hydrolysis, giving a little methyl gibberate but mainly a gummy fraction consisting essentially of the 10α-isomer of methyl gibberate. Under these conditions, the specific rotation of methyl epigibberate and methyl epiallogibberate remained constant.

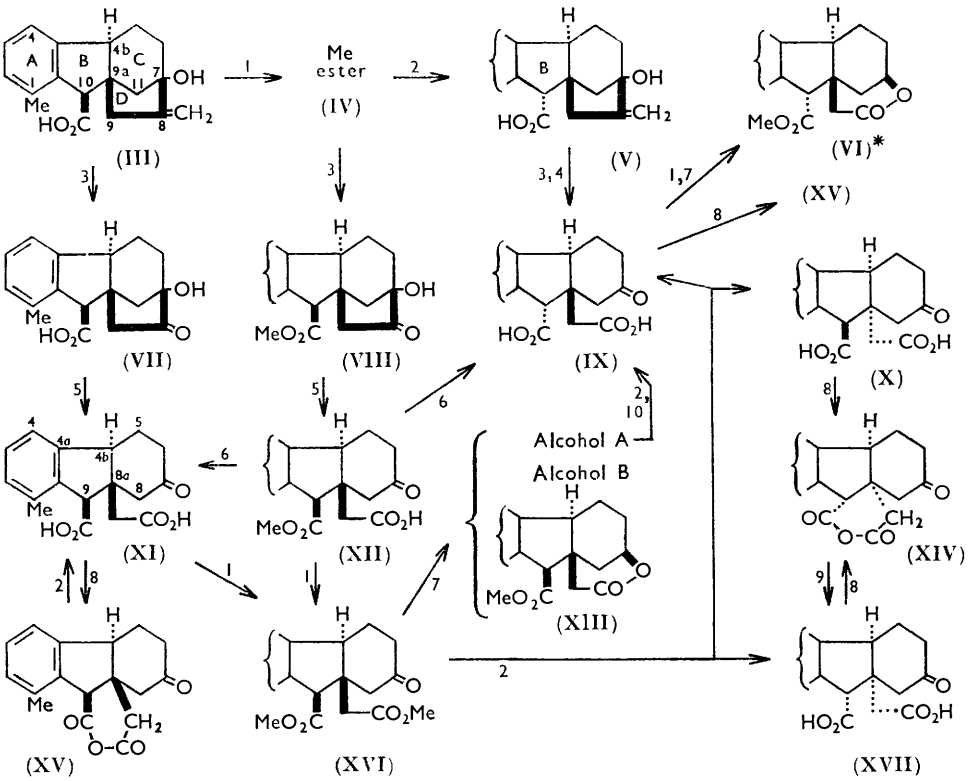
In boiling 2N-sodium hydroxide the dimethyl ester (XVI) of the 9β-acid (XI) gave a

[7] Bickell, *J. Amer. Chem. Soc.*, 1938, **60**, 927.
[8] Kenyon and Young, *J.*, 1940, 216.
[9] Cross, Grove, MacMillan, and Mulholland, *J.*, 1958, 2520.

more complex mixture than did the monomethyl ester (XII). Two new dibasic keto-acids, $C_{17}H_{18}O_5$ (X) and (XVII), were isolated. In addition a substance was obtained which was not resolved by crystallisation but was shown to be a 1 : 1 mixture of the acids (X) and (IX) by comparison with material prepared by crystallising together equimolecular amounts of these two acids (cf. refs. 10, 11). Alkaline hydrolysis of the dimethyl ester of the acid (IX) gave results similar to those obtained from the ester (XVI), but more of the acid (IX) and less of the acid (X) were formed.

Reduction of the 8aβ,9β-dimethyl ester (XVI) with sodium borohydride gave the expected two alcohols, $C_{19}H_{24}O_5$ [(A), m. p. 148—151° and (B), m. p. 152—153°], and a

Chart 1. Degradation of allogibberic acid.

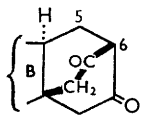


hydroxyl-free neutral compound, $C_{18}H_{20}O_4$, containing one methoxyl group. This compound, also obtained by heating alcohol (A) with acetic acid, must be the lactone (XIII); hence the 7-hydroxyl group in alcohol (A) must be β- (axial), and in alcohol (B) α-orientated. The lactone was also a major product when the ester (XVI) was hydrogenated with Adams catalyst in acetic acid. Alkaline hydrolysis of alcohol (B) followed by oxidation of the gummy product gave only the acid (IX) and a trace of the acid (XI) [isolated as the dimethyl ester (XVI)].

Reduction of the dimethyl ester of the 8aβ,9α-acid (IX) with sodium borohydride also yielded a lactone, $C_{18}H_{20}O_4$ (VI), but the alcohols produced were intractable.

[10] Goodwin and Perkin, *J.*, 1905, **87**, 841.
[11] Bone and Perkin, *J.*, 1896, **69**, 268.

Reduction of the esters of the 8aα-acids (X) and (XVII) was not carried out, but reduction of their antipodes, obtained (below) from epiallogibberic acid, did not give lactones.



(XVIII)

The formation of four dibasic keto-acids, $C_{17}H_{18}O_5$, by degradation of allogibberic acid requires two labile asymmetric centres, one at $C_{(9)}$, the other at $C_{(4b)}$ or $C_{(8a)}$. Neither $C_{(4b)}$ nor $C_{(8a)}$ seemed sufficiently activated for ready inversion to be expected, and it is clear that an intramolecular Claisen condensation could take place at $C_{(6)}$ (we are indebted to Dr. J. MacMillan for this suggestion) giving an alkali-unstable intermediate 1,3-diketone (XVIII).

Fission at the 6,7-bond in (XVIII) then yields compounds of opposite configuration at $C_{(8a)}$. In support of this mechanism it has been shown above that, to obtain the 8aα-acids (X and XVII), (*a*) the 8a-substituent must be esterified, and (*b*) a ketone group must be present at position 7. When the dimethyl ester (XVI) of the 8aβ,9β-acid (XI) was heated with methanolic sodium methoxide it reacted rapidly and gave a little of the dimethyl ester of the 8aα,9α-acid (XVII) together with an intractable gum which may contain the intermediate diketone (XVIII).

Dehydration of the acid (XI) with boiling acetic anhydride gave the anhydride (XV) in good yield.[4] The 9α-acid (IX) also gave this anhydride but less readily. Alkaline hydrolysis [4] of the anhydride gave only the acid (XI), showing that the 9- and 8a-substituents are *cis*-related in this compound and hence these substituents are *trans*-related in the acid (IX). Analogous inversion of a carboxyl group in *trans*-acids is well known.[12] The relatively difficult inversion of the 9-carboxyl group in the acid (IX) compared with other isomers where the 9- and 8a-substituents are also *trans* (see below) is due to the 9α-configuration's being more stable. The 8aα,9β- (X) and 8aα,9α-acid (XVII) yielded the anhydride (XIV) easily and in good yield. Hydrolysis of the anhydride (XIV) gave only the 8aα,9α-acid (XVII), where the 9- and 8a-substituents are therefore *cis* to one another.

Epiallogibberic Acid.—Although hydrogenation of allogibberic acid in methanol with palladised carbon [2] or Adams catalyst [4] gave only one dihydroallogibberic acid, hydrogenation of epiallogibberic acid with Adams catalyst in acetic acid gave two dihydroepiallogibberic acids, $C_{18}H_{22}O_3$, m. p. 234—236° and 178—180°, epimeric at $C_{(8)}$. Hydrogenation with a palladised carbon catalyst in ethyl acetate gave only the acid of m. p. 234—236°. The latter compound, like epigibberic acid, did not react with alkaline permanganate at 0°. Under identical conditions a 4*b*,5-double bond is introduced into gibberic acid [9] and dihydroallogibberic acid.[4]

Ozonolysis of epiallogibberic acid gave formaldehyde and a new dibasic keto-acid, $C_{17}H_{18}O_5$ (XIX). This 4bβ,8aβ,9β-acid, and its 9-monomethyl ester (XXV) obtained from methyl epiallogibberate by ozonolysis, or by fission of the corresponding glycol (XXII) with sodium bismuthate, gave the same crystalline dimethyl ester (XXIV). The dibasic acid (XIX) was stable to boiling 2N-sodium hydroxide. The monomethyl ester, like the analogous ester (XII) from allogibberic acid, was hydrolysed under these conditions to two products, the 8aβ,9β-acid (XIX) and the 9α-isomer (XXVI). In this case the yield of the products (*ca.* 1 : 3) was more nearly equal.

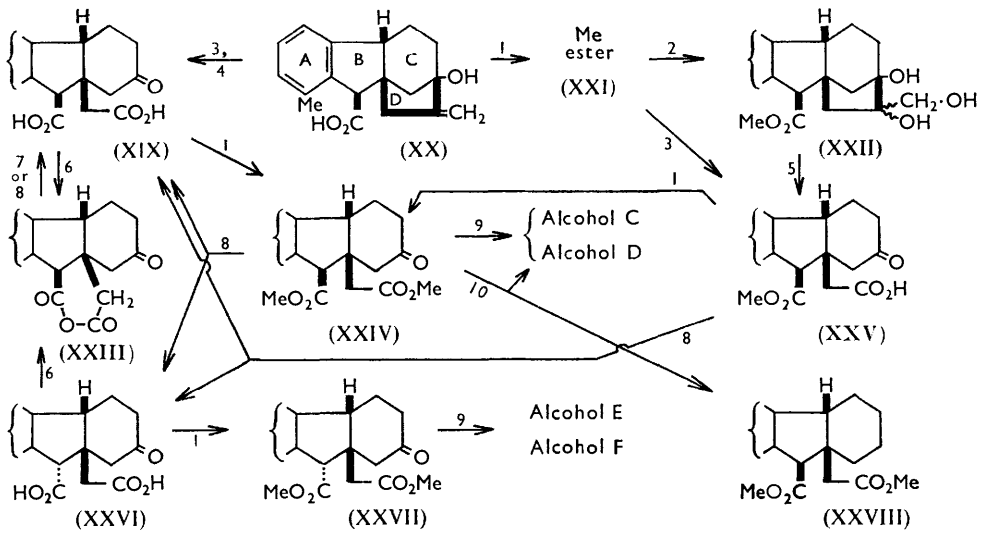
Hydrolysis of the dimethyl ester (XXIV) gave the same two acids as did the monomethyl ester (XXV). Thus in this series derived from epiallogibberic acid, although there was the expected lability at position 9, there were no products resulting from inversion at $C_{(8a)}$. When the 4bβ,8aβ,9β-dimethyl ester (XXIV) was boiled with methanolic sodium methoxide the ester was only attacked slowly and 58% was recovered under conditions in which the 4bα,8aβ,9β-ester (XVI) reacted completely.

Reduction of the ester (XXIV) with sodium borohydride gave two epimeric alcohols, $C_{19}H_{24}O_5$, (C), m. p. 95—96°, and (D), m. p. 134°; hydrogenation gave the same products and in low yield a dimethyl ester, $C_{19}H_{24}O_4$ (XXVIII), which is a hydrogenolysis product. Reduction of the ester (XXVII) with sodium borohydride gave two oily alcohols E and F.

[12] Cook and Linstead, *J.*, 1934, 956.

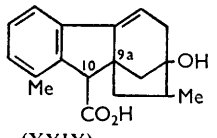
The 9β- and 9α-acids (XIX) and (XXVI) readily gave the same anhydride (XXIII) with acetic anhydride. Since hydrolysis of this anhydride with water or dilute sodium hydroxide gave only the acid (XIX) the 9- and 8a-substituents are *cis*-related in this acid and *trans* in the epimeric acid (XXVI).

Chart 2. Degradation of epiallogibberic acid.



Reagents: 1, CH_2N_2; 2, OsO_4; 3, O_3; 4, H_2O_2; 5, $NaBiO_3$; 6, Ac_2O; 7, H_2O; 8, NaOH; 9, $NaBH_4$; 10, H_2–Pt.

The dibasic acids (XIX) and (XXVI) were antipodes of the acids (XVII) and (X) respectively. Their infrared spectra and m. p.s were identical, their specific rotations were equal but of opposite sign, and the optical rotatory dispersion curves were mirror-images (see Fig. 1). The enantiomeric nature of the two pairs of curves is more convincing than the comparison of individual values of rotation at a single wavelength. The anhydrides (XXIII) and (XIV) were also antipodes. These relations are to be expected if the acids (XI) and (XIX) differ only in the configuration at position 4b. Inversion of the remaining two asymmetric centres (9 and 8a) in (XI) will give (XVII), a mirror image of (XIX). It follows from this and what has been said previously that allo- and epiallo-gibberic acid differ only in the configuration at the 4b-centre and that the 8,9-bridge and 10-carboxyl substituent are *cis* to each other in both compounds.


(XXIX)

Hydrogenation of dehydrodihydroallogibberic acid[4] (XXIX), under acidic, neutral, and basic conditions with palladium or platinum catalysts, gave only dihydroallogibberic acid. Since reduction will occur at the less hindered side of the molecule, opposite to the 10- and 9a-substituents, and since the original stereochemistry at position 4b is regenerated, rings B and C must be *trans*-fused in allogibberic acid and therefore *cis*-fused in epiallogibberic acid.

A study of Courtauld space-filling models of tricyclic structures of general formula (XI) shows that when rings B and C are *trans*-fused the 9-carboxyl substituent is less hindered when the 9- and the 8a-substituent are *trans*, and this then represents the more stable configurational relationship at these two centres. But when rings B and C are *cis*-fused there is little to choose, on steric grounds, between the two possible configurations for the 9-carboxyl substituents. The ready inversion at position 9 in the esters of the 4bα,8aβ,9β-acid (XI) and the ready racemisation at position 9 in the esters of the 4bβ,8aβ,9β-acid (XIX) are consistent with these observations.

Relief of steric compression may also be a factor in the ready transformation of the

dimethyl esters of the 4bα,8aβ-acids (IX) and (XI) into the 4bα,8aα-acids (X) and (XVII) *via* the diketone (XVIII). The stability of the 8a-centre in the 4bβ,8aβ-dimethyl ester (XXIV) under similar conditions may be due to the difficulty of formation of the intermediate diketone; the distance between $C_{(6)}$ and the appropriate methoxycarbonyl group is greater in those compounds with rings B/C *cis*-fused and ring C in the chair conformation. The failure of the intramolecular condensation with the ester (XXIV) cannot be attributed to ring C's adopting the alternative conformation where the 8a-substituent is equatorial, for it is shown below that the esters of this type exist preferentially in the conformation where the 8a-substituent is axial and the 8a,9-bond equatorial. Models of

FIG. 1. FIG. 2. FIG. 3.

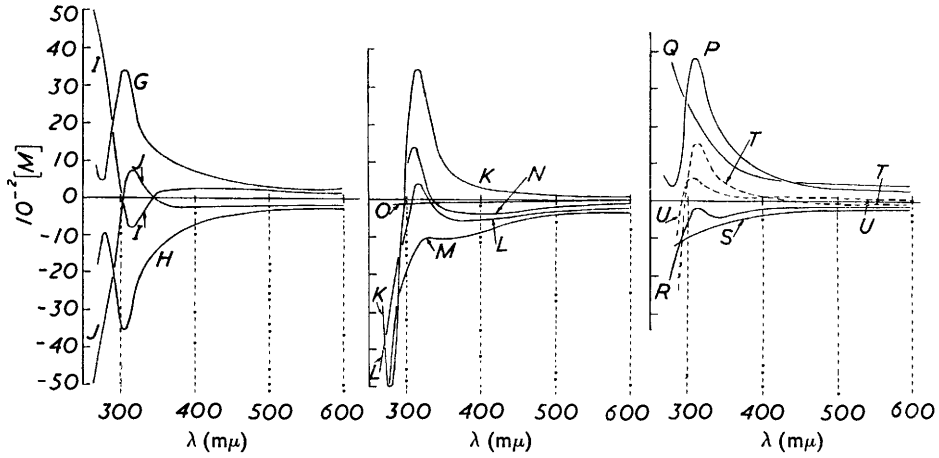


FIG. 1. *Optical rotatory dispersion curves of compounds* XIX (*G*), XVII (*H*), X (*I*), *and* XXVI (*J*).

FIG. 2. *Optical rotatory dispersion curves for compounds* XVI (*K*), XII (*L*), *and* XI (*M*), *dimethyl ester of* IX (*N*), *and the* 7α*-alcohol B* (*O*) *from* XVI.

FIG. 3. *Optical rotatory dispersion curves for* XXIV (*P*), *alcohol C* (*Q*), XXVII (*R*), *alcohol E* (*S*), *and subtraction curves P — Q* (*T*) *and R — S* (*U*).

the tetracyclic structures with an aromatic ring A show that, when rings B/C are *trans*-fused (allogibberic acid), the less hindered configuration of the 10-carboxyl substituent is *trans* to the 8,9-bridge [as in the acid (V)], consistently with the lability of the centre 10 in methyl allogibberate; when rings B/C are *cis*-fused the less hindered configuration of the carboxyl group is *cis* to the 8,9-bridge although there is little difference between the two possibilities. The stability to alkali of the 10-centre in methyl epiallogibberate is therefore not wholly explained in terms of steric hindrance of the methoxycarbonyl substituent in the two alternative configurations. The 4bβ,8aβ,9β-configuration (epiallogibberic acid) is less hindered and presumably more stable than the 4bα,8aβ,9β-configuration (allogibberic acid).

The relative configurations of the four asymmetric centres in allogibberic and epiallogibberic acid have been established by the work described above. The absolute configurations of the acids follow from studies of optical rotatory dispersion carried out by Dr. W. Klyne, Postgraduate Medical School, London, W. 12. It has been shown by examination of the model compounds (+)-*cis*-[13,14] and (—)-*trans*-hexahydro-8-methylindan-5-one [15] and of (+)-*trans*-hexahydroindan-5-one [16] that no major conformational distortion is produced in the cyclohexane ring by fusion with a five-membered ring: the shapes and

[13] Conroy and Cohen, *J. Org. Chem.*, 1958, **23**, 616.
[14] Acklin and Prelog, *Helv. Chim. Acta*, 1959, **42**, 1239.
[15] Djerassi, Marshall, and Nakano, *J. Amer. Chem. Soc.*, 1958, **80**, 4853.
[16] Bourn and Klyne, *J.*, 1960, 2044.

amplitudes of the optical rotatory dispersion curves obtained were similar to those for standard decalones of known absolute configuration and were largely unaffected by the presence of a methyl substituent at the ring junction. The curve for the ester (XVI) (Fig. 2) showed a positive Cotton effect, indicating by simple analogy with the model hexahydroindanones or by application of the octant rule,[17,18] that this compound has the 4bα,8aβ-absolute configuration shown (chart 1). It follows that allogibberic acid has the (4b*S*,7*S*,9a*S*,10*R*)-absolute configuration (III).*

The curves (Fig. 3) for the dimethyl esters (XXIV) and (XXVII) both showed positive Cotton effects; taken with the known relations of these esters to the 4bα,8aβ-ester (XVI), this indicates that the compounds have the 4bβ-8aβ-configuration and (cf. the octant rule [17,18]), the conformation in which the 4bβ-hydrogen atom is equatorial and the 8aβ-substituent axial. The amplitudes of the curves for ketones derived from epiallogibberic acid were generally smaller than those derived from allogibberic acid and this fact (although arguments based on amplitudes need to be treated with caution) supports the *cis*-B/C-configuration for the epiallo-series. Epiallogibberic acid therefore has the (4b*R*,7*S*,9a*S*,10*R*)-absolute configuration (XX).

The curves of the keto-acids and esters of general formula (XI) show several points of interest. The remarkable difference in the shape of curves *P* and *R* (Fig. 3) for the 4bβ,8aβ-esters (XXIV) and (XXVII) respectively is due to the fact that inversion at position 9 alters the sign of the plain curve on which the Cotton effects are superimposed. Thus, alcohol C derived from the ester (XXIV) shows a positive plain curve [21] rising steeply towards shorter wavelengths, whereas alcohol E derived from (XXVII) shows a negative flatter plain curve. The subtraction curves *T* and *U* (Fig. 3) give a more realistic estimate of the Cotton effect due to the carbonyl group in the two cases and are not dissimilar. Similar differences in shape can be discerned in the curves for the 4bα,8aβ-compounds. The 7α-alcohol B derived from the 9β-ester (XVI) shows a very weakly negative plain curve (*O*, Fig. 2) and in consequence the curve (*K*, Fig. 2) for the ester (XVI) is roughly symmetrical about the wavelength axis. The positive Cotton effect in the ester of the 9α-acid (IX) is superimposed on a more strongly negative plain curve, giving the unsymmetrical curve (*N*, Fig. 2).

The curves (*L* and *M*, Fig. 2) for the acids (XII) and (XI) respectively are difficult to interpret. Their imperfect nature may be due in part to the shape of the negative plain curves on which the positive Cotton effects are superimposed, but it may also be related to the depression in amplitude of the Cotton-effect curves of some ketones by ketal formation.[22] This effect, found with acids in the 4bα,8aβ-series, was not nearly so pronounced with acids where rings B/C were *cis*-fused, and, analogously to the failure of the ester (XXIV) to undergo intramolecular condensation, may be due to the greater distance in these compounds between the carboxyl group of the 8a-acetic acid residue and the 7-ketone group. Thus, the optical rotatory dispersion curves for the acid (XXVI) (curve *J*, Fig. 1) and its dimethyl ester (XXVII) (curve *R*, Fig. 3) were not dissimilar, and the curves for the acids (XIX) (curve *G*, Fig. 1) and (XXV) were almost identical with that for the ester (XXIV) (curve *P*, Fig. 3).

Experimental

M. p.s are corrected. Alumina was of grade II, with pH 4.[23] Specific rotations were determined for EtOH solutions in a 1 dm. micropolarimeter tube unless stated otherwise.

* This conclusion has already been reported briefly.[19] While this paper was in preparation an identical conclusion was published independently by Stork and Newman.[20]

[17] Djerassi, *Rec. Chem. Progr.*, 1959, **20**, 101.
[18] Moffitt, Moscovitz, Woodward, Djerassi, and Klyne, unpublished work.
[19] Cross, Grove, McCloskey, Mulholland, and Klyne, *Chem. and Ind.*, 1959, 1345.
[20] Stork and Newman, *J. Amer. Chem. Soc.*, 1959, **81**, 3168.
[21] Djerassi and Klyne, *Proc. Chem. Soc.*, 1957, 55.
[22] Djerassi, Mitscher, and Mitscher, *J. Amer. Chem. Soc.*, 1959, **81**, 947.
[23] Mulholland and Ward, *J.*, 1954, 4676.

Optical rotatory dispersion curves were obtained in methanol (*c* 0·1 for plain curves; *c* 0·01 for Cotton-effect curves). Light petroleum had b. p. 40—60°.

Hydrogenation of the Dehydro-derivative of Dihydroallogibberic Acid.—Crude dihydroallogibberic acid [4] had m. p. 200—203° (decomp.), $[\alpha]_D^{25}$ −72° (*c* 0·90), and after one recrystallisation, m. p. 203—206° (decomp.), $[\alpha]_D^{28}$ −71° (*c* 0·96). The dehydro-derivative [4] ($C_{18}H_{20}O_3$,CH_3·OH) had $[\alpha]_D^{24}$ −24° (*c* 0·78); hydrogenation was carried out at room temperature and pressure.

(i) The compound (35 mg.) in ethyl acetate (6 ml.) with 10% palladium–charcoal (32 mg.) gave dihydroallogibberic acid (34 mg.), $[\alpha]_D^{28}$ −65° (*c* 0·93), m. p. 198—200° (decomp.), raised to 204—206° (decomp.) by one crystallisation from ethyl acetate–light petroleum.

(ii) The compound (34 mg.) in methanol (6 ml.) with Adams catalyst (31 mg.) gave dihydroallogibberic acid (33 mg.), $[\alpha]_D^{26}$ −72° (*c* 1·03), m. p. 198—201° (decomp.), raised to 198—202° (decomp.) by crystallisation.

(iii) The compound (33 mg.) in acetic acid (6 ml.) with Adams catalyst (30 mg.) gave dihydroallogibberic acid (32 mg.), $[\alpha]_D^{28}$ −67° (*c* 1·09), m. p. 190—195° (decomp.), raised to 196—200° (decomp.) by crystallisation.

(iv) The compound (35 mg.) in ethyl acetate (7 ml.) containing concentrated hydrochloric acid (0·05 ml.) with Adams catalyst (50 mg.) gave, after washing of the filtered solution and recovery, dihydroallogibberic acid (32 mg.), $[\alpha]_D^{26}$ −70° (*c* 1·09), m. p. 196—200 (decomp.), raised to 204—208° (decomp.) by crystallisation.

(v) The compound (33 mg.) in 0·1N-sodium hydroxide (5 ml.) with 2% palladium–strontium carbonate [24] (55 mg.) gave, after filtration, acidification, and recovery in ethyl acetate, dihydroallogibberic acid (28 mg.), $[\alpha]_D^{21}$ −70° (*c* 1·00), m. p. 198—201° (decomp.), raised to 199—202° (decomp.) by crystallisation.

The products were identified by mixed m. p. and the infrared spectra.

Ozonolysis of Allogibberic Acid (cf. ref. 4). *Decomposition of the Ozonide with Hydrogen peroxide.*—(i) The compound (2·00 g.) in acetic acid (50 ml.) was ozonised at room temperature (absorption, 1·1 mol.). 20% Hydrogen peroxide (20 ml.) was added and the mixture was kept at room temperature for 18 hr. Water (50 ml.) was added and the solution was concentrated *in vacuo* to *ca.* 30 ml. After addition of more water (50 ml.) the mixture was extracted with ether, and the extract was freed from peroxides by shaking it with ferrous sulphate solution. Recovery gave a sticky solid which crystallised from ethyl methyl ketone–light petroleum, giving needles (0·56 g.), m. p. 230—240° (decomp.), of the crude ketol (VII). The residue recovered from the mother-liquor crystallised from ether, giving crude 9β-carboxy-4bα,5,6,7,8,8a-hexahydro-1-methyl-7-oxofluoren-8aβ-ylacetic acid (XI) [0·66 g.; m. p. 204—210° (decomp.)].

(ii) Repetition of experiment (i), but with the product kept in hydrogen peroxide for 2·5 days, gave the crude ketol (26 mg.) and keto-acid (1·1 g.).

The keto-acid (XI) was recovered after 2 hr. in boiling 2N-sodium hydroxide. The dimethyl ester [4] (XVI) formed needles (from methanol), $[\alpha]_D^{24}$ +17° (*c* 0·20 in $COMe_2$).

Action of Alkali on the Ester (XVI).—The compound (500 mg.) was heated under reflux with 2N-sodium hydroxide (50 ml.) for 2·5 hr. The solution was washed with ether and acidified and the gummy product (0·43 g.), recovered in ether, was crystallised from ether, giving a solid (A) (267 mg.). The residue from the mother-liquor was kept for 18 hr. with ethyl acetate, giving prisms (B), m. p. 208—214° (20 mg.), and, on recovery from the mother-liquor, a gum (C).

Fractional crystallisation of products A and B from ethyl methyl ketone alone or mixed with light petroleum gave prisms (D) and more soluble needles (E).

The prisms (D) (79 mg.), m. p. 218—220°, $[\alpha]_D^{22}$ +25° (*c* 0·61) consisted of 9β-*carboxy*-4bα,5,6,7,8,8a-*hexahydro*-1-*methyl*-7-*oxohydrofluoren*-8aα-*ylacetic acid* (X) [Found: C, 67·3; H, 6·2%; equiv., 159. $C_{17}H_{18}O_5$ requires C, 67·5; H, 6·0%; equiv. (dibasic), 151]. The infrared spectrum [$\nu_{max.}$ 3235, 1735, 1699 (sh), 1683 cm.$^{-1}$] was identical with that of the antipode (XXVI) (see below).

The *dimethyl ester*, obtained with diazomethane, was a gum, $[\alpha]_D^{23}$ +55° (*c* 1·07) {[*M*]; negative Cotton effect curve (600 mμ) +200°; (340) +500°; (312·5, peak) +300°; (275) +2300°} (Found: C, 68·9; H, 6·8; OMe, 18·7. $C_{19}H_{22}O_5$ requires C, 69·1; H, 6·7; 2OMe, 18·8%), $\nu_{max.}$ 1740, 1727 (sh) cm.$^{-1}$ in CCl_4.

The needles (E) crystallised from ethyl methyl ketone–light petroleum in needles (125 mg.), m. p. 140—175° (gas evolution) with further melting at 190—197°, $[\alpha]_D^{20}$ −26° (*c* 0·46); these

[24] Martin and Robinson, *J.*, 1943, 491.

were a 1 : 1 mixture of the above acid (X) and 9α-carboxy-4bα,5,6,7,8,8a-*hexahydro*-1-methyl-7-oxofluoren-8aβ-ylacetic acid [4] (IX). The mixture could not be separated into its components by crystallisation but was identical with material prepared by crystallising a 1 : 1 mixture of the above two acids.

The gum (C) crystallised from ethyl acetate, to give large prisms (36 mg.), m. p. 196—203°. Recrystallisation from ethyl acetate–light petroleum gave 9α-*carboxy*-4bα,5,6,7,8,8a-*hexahydro*-1-*methyl*-7-*oxofluoren*-8aα-*ylacetic acid* (XVII) as prisms (27 mg.), m. p. 205—207° (yellow at the m. p.), $[\alpha]_D^{23}$ −76·5° (*c* 1·11), which became opaque on drying at 100° [Found: C, 67·7; H, 6·2%; equiv., 140. $C_{17}H_{18}O_5$ requires C, 67·5; H, 6·0%; equiv. (dibasic), 151].

The *dimethyl ester*, prepared with diazomethane, crystallised from methanol in needles or prisms, m. p. 167—169°, $[\alpha]_D^{24}$ −78° (*c* 0·68 in $COMe_2$) {[*M*]; negative Cotton effect curve (600 mμ) −300°; (310, peak) −3500°; (275, trough) −250°; (270) −1400°} (Found: C, 68·7; H, 6·8; OMe, 20·8. $C_{19}H_{22}O_5$ requires C, 69·1; H, 6·7; 2OMe, 18·8%). The m. p. was not depressed on mixture with the antipode (XXIV) (see below) and the infrared spectra were identical.

Action of Methanolic Sodium Methoxide on the Ester (XVI).—The compound (63 mg., 1·0 mol.), was heated under reflux with sodium (6·5 mg.; 1·5 g.-atom) in methanol (1·0 ml.) for 1 hr. The crystals dissolved quickly. After storage at room temperature for 16 hr. the solution was evaporated *in vacuo* at 100°. The residue was mixed with water (3 ml.), and the crystals (4 mg.; m. p. 165—170°) were filtered off. Recrystallisation from ethyl acetate–light petroleum gave needles (2 mg.), m. p. 166—168°, identified as the dimethyl ester of the acid (XVII) by the infrared spectrum and specific rotation.

The aqueous mother-liquor was washed with ether and acidified with hydrochloric acid, and the amorphous precipitate (13 mg.) filtered off. A further 11 mg. of gum was recovered by ether-extraction. The combined product ($\nu_{max.}$ 1737, 1722, 1704, 1595 cm.$^{-1}$) was intractable. It was insoluble in cold dilute sodium hydroxide, and gave no colour with alcoholic ferric chloride and a doubtfully positive colour reaction for a 1,3-diketone with *o*-phenylenediamine.

Reduction of the Ester (XVI).—(i) *With sodium borohydride.* The ester (200 mg.) in methanol (80 ml.) was treated portionwise with sodium borohydride (104 mg.) in methanol (10 ml.). The solution, initially at 10°, was cooled to 0° when about half the reagent had been added. After storage at 0° for 15 min., excess of reagent was decomposed with acetic acid, and the mixture was evaporated *in vacuo*. The residue was mixed with water and extracted with ether. The extract, after being washed with sodium carbonate solution and with water, was dried and evaporated, giving a gum (191 mg.). Crystallisation from ether gave needles (Y) (80 mg.; m. p. 190—203°). The mother-liquor was chromatographed on alumina (30 × 1·2 cm.), the following main fractions being recovered: (i—iii) (by ether, 30 ml.), a gum (19 mg.); (iv) (by ether, 10 ml.), a gum (6 mg.); (v—viii) (by ether, 40 ml.), a solid (13 mg.; m. p. *ca.* 200°); (ix) (by ether–methanol, 3 : 1, 50 ml.), a gum (72 mg.).

Fraction Y and the product from fractions (v—viii) were combined and crystallised from ethyl acetate–light petroleum, giving 4bα,5,6,7,8,8a-*hexahydro*-7β-*hydroxy*-9β-*methoxycarbonyl*-1-*methylfluoren*-8aβ-*ylacetic acid lactone* (XIII) as needles (78 mg.), m. p. 202—204° (Found: C, 71·8, 71·95; H, 6·8, 6·8; OMe, 10·6, 10·5. $C_{18}H_{20}O_4$ requires C, 72·0; H, 6·7; OMe, 10·3%), $\nu_{max.}$ 1726, 1596 cm.$^{-1}$ (OH and ethylenic C=C absent); in CCl_4, 1744 cm.$^{-1}$.

Fractions (i—iii) in ether–light petroleum crystallised, to give needles of the lactone (XIII) and prisms. The latter (7 mg., m. p. 147—153°) were separated and recrystallised from ethyl acetate–light petroleum, giving alcohol A, *methyl* 4bα,5,6,7,8,8a-*hexahydro*-7β-*hydroxy*-9β-*methoxycarbonyl*-1-*methylfluoren*-8aβ-*ylacetate*,as prisms, m. p. 148—151°, $[\alpha]_D^{22}$ −16° (*c* 0·43) (Found: C, 69·1; H, 7·6. $C_{19}H_{24}O_5$ requires C, 68·65; H, 7·3%), $\nu_{max.}$ 3530, 1731, 1591 cm.$^{-1}$.

Fraction (ix) crystallised from ether–light petroleum as prisms (61 mg.) of the *epimeric* 7α-*alcohol* (*B*), m. p. 145—151°, raised to 152—153° by recrystallisation, $[\alpha]_D^{21}$ −5° (*c* 1·02). The m. p. was depressed on admixture with alcohol (A) (Found: C, 68·9; H, 7·4; OMe, 18·4%), $\nu_{max.}$ 3490, 1738 cm.$^{-1}$.

(ii) *By hydrogenation.* The ester (50 mg.) in acetic acid (8 ml.) was shaken with hydrogen at room temperature and pressure in the presence of Adams catalyst (30 mg.) for 5 hr., then left under hydrogen for 2 days. Recovery gave a semi-solid product (48 mg.) which crystallised from methanol in needles (26 mg.), m. p. 196—203°, raised to 201—203° by recrystallisation from ethyl acetate–light petroleum, identified (mixed m. p. and infrared spectrum) as the lactone (XIII).

Action of Acetic Acid on Alcohol A.—The alcohol and acetic acid were heated under reflux for 3 hr. The solid obtained by evaporation crystallised from ethyl acetate–light petroleum

in needles, m. p. 202—204°, identified as the lactone (XIII) by mixed m. p. and the infrared spectrum.

Hydrolysis and Oxidation of Alcohol B.—The compound (65 mg.) was boiled with 2N-sodium hydroxide (7 ml.) for 3 hr. The cooled mixture was washed with ether, acidified, and extracted with ether and ethyl acetate. The dried extracts were washed with water and evaporated to a foam (59 mg.). This, in acetic acid (1 ml.), was treated portionwise with chromic oxide (28 mg.) in water (0·25 ml.) and acetic acid (0·5 ml.) during 10 min., with warming after each addition. After storage for 10 min. at 20° the mixture was diluted with water and extracted with ether and ethyl acetate. The product (44 mg.) recovered from the extracts was washed with ether, giving a solid (27 mg.), m. p. 242—248° (decomp.), $[\alpha]_D^{20}$ −79° (*c* 0·96), which crystallised from ethyl methyl ketone–light petroleum, yielding the keto-acid (IX), m. p. 249—252° (decomp.), $[\alpha]_D^{20}$ −77° (*c* 0·51), identified by the infrared spectrum.

The material recovered from the ether-washings above was methylated with diazomethane, and the product crystallised from methanol giving a few prisms, m. p. 199—202°, not depressed on admixture with the dimethyl ester (XVI).

Ozonolysis of Methyl Allogibberate.—Methyl allogibberate (1·78 g.) in acetic acid (50 ml.) was ozonised at 20° (uptake 1·1 mol.). The mixture was kept with 20% hydrogen peroxide (18 ml.) for 66 hr., then worked up as described above for allogibberic acid. The product was separated into neutral and acidic fractions in the usual way. The latter crystallised from ether, giving fractions of crude 4bα,5,6,7,8,8a-hexahydro-9β-methoxycarbonyl-1-methyl-7-oxofluoren-8aβ-ylacetic acid (XII) 629 mg.), not melting under 230°. Purification[4] gave prisms, m. p. 243 246° (decomp.), $[\alpha]_D$ −66° (*c* 1·37).

Alkaline Hydrolysis of the Acid (XII).—(i) The acid (34 mg.) was boiled with 2N-sodium hydroxide (3·5 ml.) for 2 hr. After acidification the gummy product (36 mg.) was recovered in ether and crystallised from ether, giving a solid (25 mg.), m. p. 208—218°. Recrystallisation from ethyl methyl ketone–light petroleum gave prisms (19 mg.), m. p. 247—250° (decomp.), identified as the acid (IX), by the infrared spectrum.

(ii) The acid (0·72 g.) was kept with 20% aqueous potassium hydroxide solution (25 ml.) at room temperature for 4 days. The product, isolated as described previously,[4] was crystallised from ether, then fractionally crystallised from ethyl methyl ketone–light petroleum and ether, giving (i) large prisms (588 mg.), m. p. 242—255° (decomp.), $[\alpha]_D$ −78°, and (ii) small prisms (6 mg.), m. p. 210—215° (decomp.), $[\alpha]_D^{25}$ −101° (*c* 0·56), which, with diazomethane, gave the dimethyl ester (XVI) as prisms, m. p. 204—207°, identified by the infrared spectrum and mixed m. p.

Fraction (i) crystallised from ethyl methyl ketone–light petroleum as prisms, m. p. 252—255° (decomp.), $[\alpha]_D^{18}$ −76° (*c* 0·89) {[*M*]; positive Cotton effect curve (600 mμ) −300°, (370) −650°; (315, peak) +500°; (270) −9000°}, identified as the acid (IX) by the infrared spectrum.

The *dimethyl ester* was a gum, $[\alpha]_D^{24}$ −53° (*c* 1·21) (Found: C, 69·3; H, 6·9; OMe, 17·9. $C_{19}H_{22}O_5$ requires C, 69·1; H, 6·7; 2OMe, 18·8%).

Hydrolysis of the Dimethyl Ester of the Acid (IX).—The ester (200 mg.) was hydrolysed with 2N-sodium hydroxide (20 ml.) for 2 hr. at 100°. The yellow gummy product (0·17 g.) was recovered as described above for the ester (XVI); it crystallised from ether as prisms (A) [36 mg.; m. p. 240—248° (decomp.)], then needles (B) [42 mg.; m. p. 150—200° (decomp.)], and a residue, which crystallised from ethyl acetate as prisms (C) (17 mg.; m. p. 190—200°).

Fraction (A) crystallised from ethyl methyl ketone in prisms, m. p. 247—250° (decomp.), identified as the acid (IX) by mixed m. p. and the infrared spectrum. Fraction (B) crystallised from ethyl acetate–light petroleum, giving needles of the 1 : 1 mixture of the acids (IX) and (X) (see above), identified by the infrared spectrum and specific rotation. Fraction (C) crystallised from ethyl acetate–light petroleum in prisms, m. p. 200—204°, of the acid (XVII), identified by mixed m. p., infrared spectrum and specific rotation.

Reduction of the Dimethyl Ester of the Acid (IX).—The above ester (96 mg.) in methanol (10 ml.) was treated portionwise with sodium borohydride (49 mg.) in methanol (5 ml.) at 0° during 30 min. After 15 min. at 0°, excess of acetic acid was added. Recovery of the product as described above for reduction of the ester (XVI) gave a gum (96 mg.), which could not be separated into its components on alumina but crystallised from ethyl acetate–light petroleum, giving prisms (25 mg.), m. p. 165—167°, raised to 167—168° by further crystallisation, of 4bα,5,6,7,8,8a-*hexahydro*-7β-*hydroxy*-9α-*methoxycarbonyl*-1-*methylfluoren*-8aβ-*ylacetic acid lactone* (VI) (Found: C, 71·55; H, 6·8; OMe, 11·9. $C_{18}H_{20}O_4$ requires C, 72·0; H, 6·7; OMe, 10·3%),

$\nu_{max.}$ 1725, 1595 cm.$^{-1}$ (OH absent). The alcoholic gum (52 mg.), $\nu_{max.}$ 3475, 1723 cm.$^{-1}$, recovered from the mother-liquor was intractable.

Alkaline Hydrolysis of Methyl Allogibberate.—The ester {250 mg., m. p. 98—99°, $[\alpha]_D^{22}$ −82° (*c* 0·94)} was hydrolysed with 2N-sodium hydroxide (25 ml.) at 100° for 2 hr. Recovery as described for the ester (XVI) above gave a gum (203 mg.). The gum was kept in ether–light petroleum at 0°, yielding needles (*ca.* 1 mg.) of an unidentified product melting at 140—155° to a gum which liquefied at 200—205°, $\nu_{max.}$ (broad and ill-defined) ~3350, ~1698, ~1654, 1550 cm.$^{-1}$. The residue was distilled on to a cold finger at 10^{-4} mm., giving gums (*a*) bath to 165° (114 mg.), $[\alpha]_D^{22}$ −149° (*c* 0·93), essentially the 10α-*isomer* of allogibberic acid (V) (Found: C, 76·15; H, 7·2. $C_{18}H_{20}O_3$ requires C, 76·0; H, 7·1%), $\nu_{max.}$ 3380 (broad), 1705 cm.$^{-1}$ (the spectrum was distinct from that of allogibberic acid or its hydrate or epiallogibberic acid), and (*b*) bath to 220° (48 mg.), material whose infrared spectrum was almost identical with that of fraction (*a*). Neither fraction crystallised.

Degradation of the Acid (V).—(a) *Ozonolysis.* The crude acid (0·50 g., $[\alpha]_D$ −147°) in acetic acid (20 ml.) was ozonised at 20° until absorption became slow (uptake 1·2 mol.). The solution was kept with 20% hydrogen peroxide (5 ml.) for 45 hr. Recovery of the product as described for allogibberic acid (above) gave a gum which crystallised from ether, yielding fractions (i) (75 mg.), m. p. 200—220° (decomp.), softening 180°, and (ii) (81 mg.), m. p. 228—240° (decomp.). Fractional crystallisation of the products from ethyl methyl ketone–light petroleum and from ethyl methyl ketone–light petroleum–ether gave the acid (IX) as prisms (116 mg.), m. p. 249—251° (decomp.), $[\alpha]_D^{23}$ −78° (*c* 1·16). The infrared spectrum was identical with that of authentic material (see above).

(b) The crude acid (88 mg.) was boiled with 3N-hydrochloric acid (4 ml.) for 2 hr. The cooled emulsion was extracted with ether, and the product recovered from the extract was distilled on to a cold finger (bath, 130—140°/10^{-4} mm.), giving an intractable gum (51 mg.), $[\alpha]_D^{19}$ −53° (*c* 0·99). The infrared spectrum [$\nu_{max.}$ 3100 (broad), 1736 (5-ring ketone), 1704 (CO_2H) cm.$^{-1}$] was almost identical with that of the acidic gum obtained by alkaline hydrolysis of methyl gibberate (see below).

Formation of Anhydrides.—(*a*) The acid (IX) (30 mg.) was boiled with acetic anhydride (0·4 ml.) for 60 min. Evaporation *in vacuo* gave an intractable gum, $\nu_{max.}$ 1809, 1734, 1714 cm.$^{-1}$ with some absorption due to carboxylic OH.

(*b*) The acid (IX) (75 mg.) was boiled with acetic anhydride (1·2 ml.) for 2 hr. The gum recovered was sublimed at 10^{-4} mm. (bath-temp. to 220°), and the sublimate (64 mg.) crystallised from ethyl acetate–light petroleum, giving (i) prisms (6 mg.), m. p. 283—286° (decomp.), (ii) prisms (5 mg.), m. p. 278—285° (decomp.), and intractable fractions with a wide range of m. p. Products (i) and (ii) were identified as the anhydride [4] (XV) by their infrared spectra.

(*c*) The acid (X) (39 mg.) was boiled with acetic anhydride (0·6 ml.) for 60 min. Recovery gave a solid, m. p. 140—152°, which crystallised from ethyl methyl ketone–light petroleum (charcoal) to give the *anhydride* (XIV) as prisms (29 mg.), m. p. 154—155°, $[\alpha]_D^{22}$ +190° (*c* 0·69 in $COMe_2$) (Found: C, 72·0; H, 5·9. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·7%), $\nu_{max.}$ in Nujol 1806, 1764, 1714 cm.$^{-1}$ (OH absent) or, in $CHCl_3$, 1816, 1768, 1720 cm.$^{-1}$. In solution the spectrum was identical with that of the antipode (XXIII) (see below).

(*d*) The acid (XVII) (15 mg.) was boiled with acetic anhydride (0·5 ml.) for 60 min. The product, m. p. 145—151°, crystallised from ethyl methyl ketone–light petroleum in prisms (11 mg.), m. p. 154°, $[\alpha]_D^{24}$ +188° (*c* 0·43 in $COMe_2$), identified as the above anhydride (XIV) by mixed m. p. and the infrared spectrum in $CHCl_3$.

Hydrolysis of the Anhydride (XIV).—The anhydride (70 mg.; $[\alpha]_D$ +190°) was boiled with water (8 ml.) for 60 min. The product recovered by ether-extraction crystallised under ethyl acetate as prisms (71 mg.), m. p. 203—206°, $[\alpha]_D^{21}$ −73° (*c* 0·05). Recrystallisation from ethyl methyl ketone–light petroleum gave prisms (65 mg.), m. p. 204—206° (yellow at the m. p.), $[\alpha]_D^{23}$ −76° (*c* 1·00), identified as the acid (XVII), by mixed m. p., infrared spectrum, and methylation to the dimethyl ester, m. p. 166—169°, $[\alpha]_D^{24}$ −82° (*c* 0·50 in $COMe_2$) (mixed m. p. and infrared spectrum).

Preparation of Epiallogibberic Acid (XX) (with Dr. B. E. Cross).—(i) Gibberellic acid (19·40 g.) was boiled with 100% hydrazine hydrate (25 ml.) for 26 hr. The mixture was cooled, diluted with water (300 ml.), and acidified to pH 2—3 with concentrated hydrochloric acid, giving a precipitate which was filtered off. The filtrate (A) was retained. The precipitate (7·6 g.) was washed with a large volume of water, then crystallised from methanol, giving

prisms (4·62 g.), m. p. >230°, and a residue (B). Recrystallisation of the prisms gave *epiallogibberic acid* (4·50 g., 28%), m. p. 244°, $[\alpha]_D^{24}$ +87° (*c* 0·99) (Found: C, 75·9; H, 7·2%; equiv., 284. $C_{18}H_{20}O_3$ requires C, 76·0; H, 7·1%; *M*, 284), $\nu_{max.}$ 3400, ~2625 (broad), 1690, 1599 cm.$^{-1}$, $\lambda_{max.}$ ~261, 266, ~274 (log ε 2·40, 2·50, 2·37) in MeOH.

The *methyl ester*, prepared with diazomethane, was a gum, $[\alpha]_D^{19}$ +60° (*c* 1·05 in N-methanolic sodium hydroxide) unchanged after 90 hr. at room temperature (Found: OMe, 11·1. $C_{19}H_{22}O_3$ requires OMe, 10·4%).

The residue (B) was fractionally crystallised from benzene–methanol and dilute methanol, giving a solid (1·51 g.) which crystallised from benzene in plates (1·24 g., 8%) of allogibberic acid, m. p. 196—198° (decomp.), $[\alpha]_D^{28}$ −83° (*c* 1·02), identified by mixed m. p. and the infrared spectrum.

The filtrate (A) was kept at 0° for 7 days, then extracted with ethyl acetate. The gum (0·8 g.) recovered from the extract gave epiallogibberic acid (13 mg.) on crystallisation.

(ii) Gibberellic acid (26·99 g.) was boiled with 100% hydrazine hydrate (54 ml.) for 6 hr. Dilution with water (350 ml.) and acidification to pH 3 as described above gave crude epiallogibberic acid (6·10 g.) which crystallised from methanol as prisms (2·89 g.), m. p. 244° (decomp.).

The aqueous filtrate was treated with more hydrochloric acid (pH 1—2) and kept at 0° for 18 hr. A mixed fraction (0·3 g.) separated and was removed. The mother-liquor was extracted with ethyl acetate (C) and kept at 0° for 5 days. Allogibberic acid (1·04 g.) which separated crystallised from ethyl acetate–light petroleum in needles, m. p. 193° (decomp.).

Recovery from the extract (C) gave a solid (3 g.) which crystallised from ethyl acetate, giving materials (*a*) (2·19 g.), m. p. 187° (decomp.), (*b*) (502 mg.), m. p. 192—194° (decomp.), $E_{1\,cm.}^{1\%}$ 528 at 253 mμ, and (*c*) (25 mg.), m. p. 184—186° (decomp.). Recrystallisation of fraction (*a*) gave 2,7-dihydroxy-1-methyl-8-methylene-10aξ-gibba-3,4a(4b)-diene-1,10-dicarboxylic acid (II) as needles (2·14 g.), m. p. 191—194° (decomp.), $E_{1\,cm.}^{1\%}$ 579 at 253 mμ, identified by the infrared spectrum [Found: C, 66·2; H, 6·5%; equiv., 174. Calc. for $C_{19}H_{22}O_6$: C, 65·9; H, 6·4%; equiv. (dibasic), 173]. A purer preparation [6] had m. p. 190—192° (decomp.), $E_{1\,cm.}^{1\%}$ 640.

(iii) Gibberellic acid (250 mg.) and 100% hydrazine hydrate (0·5 ml.) were boiled for 30 min. The mixture was cooled, diluted with water (4 ml.), and acidified to pH 2 at 0°, giving a precipitate (41 mg.). The filtrate was extracted with ethyl acetate. Recovery from the extract gave the acid (II) (93 mg.), $E_{1\,cm.}^{1\%}$ 364, m. p. 158—160° (decomp.) raised to 186—194° (decomp.) by recrystallisation.

(iv) The acid (II) (0·5 g.) was boiled with 100% hydrazine hydrate (1·5 ml.) for 24 hr. Recovery as in (i) gave a solid (339 mg.) from which were isolated epiallogibberic acid (59 mg.), m. p. 242—243°, and allogibberic acid (107 mg.), m. p. 189—192°, raised to 193—196° by recrystallisation.

(v) The acid (II) (52 mg.) was boiled with water (25 ml.) for 3 hr. The mixture was cooled and filtered, giving allogibberic acid hydrate as needles (35 mg.), softening at *ca.* 120° and melting at 190—194° (decomp.), not depressed on admixture with an authentic specimen.

(vi) The acid (II) (27 mg.) was dissolved in water (16 ml.) at 30—40° and then cooled to 20°, 3N-hydrochloric acid (8 ml.) was added. On storage at room temperature for 2 days allogibberic acid hydrate (18 mg.; m. p. 182—188°) separated. Recrystallisation from benzene gave the solvent-free acid, m. p. and mixed m. p. 191—195°.

(vii) Gibberellic acid (52 mg.) was boiled with water for 12·5 hr. Allogibberic acid hydrate (16 mg.) separated; it had m. p. 120—125° with softening and remelting 179—182°, raised to 188—192° by recrystallisation from benzene.

Action of Hydrochloric Acid on Epiallogibberic Acid.—Powdered epiallogibberic acid (38 mg.) was boiled with hydrochloric acid (5 ml.; 1 vol. of concentrated acid + 5 vol. of water) for 8 hr. The solid product (34 mg.) crystallised from ethanol, giving epigibberic acid (21 mg.), double m. p. 226°, 254°, identified by the infrared spectrum.

Hydrolysis of Methyl Epiallogibberate.—The ester (51 mg.) was boiled with 2N-sodium hydroxide (5 ml.) for 2 hr. Acidification gave a precipitate (41 mg.), m. p. 247° (decomp.), which, crystallised from methanol, yielded epiallogibberic acid as prisms (31 mg.), m. p. 238—240° (decomp.), $[\alpha]_D^{23}$ +88° (*c* 1·06), identified by the infrared spectrum. Epiallogibberic acid was stable to boiling 2N-sodium hydroxide for 2 hr.

Hydrogenation of Epiallogibberic Acid.—(i) The acid (284 mg.) in acetic acid (30 ml.) was

shaken with hydrogen at room temperature and pressure in the presence of Adams catalyst (60 mg.) (uptake 1·0 mol. in 20 min.). Recovery gave a solid which was separated by crystallisation from toluene–acetone into (*a*) crystals (246 mg.; m. p. 200—205°, softening at 180°) and (*b*) a more soluble residue (31 mg.), m. p. 150—175°.

Crystallisation of product (*a*) from toluene, then from dilute methanol, gave prisms (61 mg.) of *dihydroepiallogibberic acid*, m. p. 234—236°, $[\alpha]_D^{23}$ +90° (*c* 1·16) (Found: C, 75·6; H, 7·8%; equiv., 291. $C_{18}H_{22}O_3$ requires C, 75·5; H, 7·7%; *M*, 286), $\nu_{max.}$ 3430, ~2400, 1693 cm.$^{-1}$.

Crystallisation of product (*b*) and material from the toluene mother-liquor from product (*a*), from benzene and benzene–light petroleum (b. p. 60—80°), gave the epimeric *dihydroepiallogibberic acid* as needles (40 mg.), double m. p. 60—70° (loss of solvent), 178—180°, $[\alpha]_D^{23}$ +42° (*c* 0·80) (Found: C, 75·6; H, 7·7%; equiv., 277), $\nu_{max.}$ 3465, 3280, 1706, 1684 cm.$^{-1}$.

(ii) The acid (284 mg.) in ethyl acetate (100 ml.) was hydrogenated in the presence of 10% palladium–carbon (250 mg.) (absorption 1·1 mol. in 4·5 hr.). The recovered product crystallised from ethyl acetate–light petroleum in prisms (263 mg.) of the dihydroepiallogibberic acid, m. p. 230—233°.

Attempted Oxidation of Dihydroepiallogibberic Acid, m. p. 234°.—A solution of the compound (51 mg.) in sodium hydrogen carbonate solution (0·6 ml.) and water (0·16 ml.) was treated portionwise with 1% potassium permanganate solution (2·5 ml.) at 0—5° during 60 min. After 15 min. at 0° sulphur dioxide was passed into the mixture. Acidification of the solution with hydrochloric acid precipitated starting material (38 mg.; m. p. 220—227°) which crystallised from ethyl acetate—light petroleum in prisms, m. p. 222—226°.

Epigibberic acid was also stable to oxidation under these conditions.

Ozonolysis of Epiallogibberic Acid.—(i) The compound (500 mg.) in acetic acid (20 ml.) was ozonised (uptake 1·5 mol.) at 20° for 30 min. The solution was diluted with water (20 ml.), kept at room temperature for 30 min., and steam-distilled. With saturated aqueous dimedone the distillate gave the methone of formaldehyde (230 mg., 0·45 mol.), m. p. and mixed m. p. 187—188°.

The gum (0·5 g.) recovered in ether from the involatile fraction was intractable. Methylation with diazomethane followed by crystallisation from methanol and chromatography gave needles (52 mg. of m. p. 163—164°; 22 mg. of m. p. 155—158°) of an ester (XXIV) (see ii, below).

(ii) The compound (2·0 g.) in acetic acid (120 ml.) was ozonised as described above (uptake 0·9 mol.), and the solution was kept with 20% hydrogen peroxide (20 ml.) for 88 hr. Recovery from the extract, after removal of peroxides (see above), gave a gum (1·77 g.). The solid (810 mg.; m. p. 188—196°) obtained by trituration of the gum with ethyl acetate crystallised in prisms (603 mg.) of 9β-*carboxy*-4bβ,5,6,7,8,8a-*hexahydro*-1-*methyl*-7-*oxofluoren*-8aβ-*ylacetic acid* (XIX), m. p. 196—200°, raised to 206—207° by recrystallisation from ethyl methyl ketone–light petroleum, $[\alpha]_D^{24}$ +77° (*c* 1·09), $[\alpha]_D^{24}$ +46° (*c* 1·05 in 1·94N-NaOH) [Found: C, 67·75; H, 6·15%; equiv., 155. $C_{17}H_{18}O_5$ requires C, 67·5; H, 6·0%; equiv. (dibasic), 151]. The infrared spectrum ($\nu_{max.}$ ~3050, ~2570, 1717, 1701 cm.$^{-1}$) was identical with that of the antipode (XVII) prepared from allogibberic acid (above).

The acid was stable to boiling 2N-sodium hydroxide for 2 hr.

The *dimethyl ester* (XXIV), prepared with diazomethane, crystallised from methanol in needles and prisms, m. p. 168—169°, $[\alpha]_D^{24}$ +80° (*c* 0·40), +79° (*c* 0·56 in $COMe_2$) (Found: C, 69·3; H, 7·0; OMe, 18·7. $C_{19}H_{22}O_5$ requires C, 69·1; H, 6·7; 2OMe, 18·8%). The infrared spectrum [$\nu_{max.}$ in Nujol 1735 (broad), 1696 cm.$^{-1}$ (OH absent); in CCl_4 1741, 1719 cm.$^{-1}$] was identical with that of the ester prepared as in (i) above and with the antipodal ester from the acid (XVII).

Action of Sodium Methoxide on the Ester (XXIV).—The ester (72 mg.) and sodium (7·5 mg., 1·5 g.-atom) in methanol (1·0 ml.) were heated under reflux for 1 hr. The solid dissolved slowly. On cooling, starting material (42 mg.) separated having m. p. 167—169°, $[\alpha]_D^{26}$ +76° (*c* 0·84 in $COMe_2$).

The residue obtained by evaporation of the mother-liquor *in vacuo* was dissolved in water (2 ml.), and the solution was acidified. Ether-extraction gave an intractable gum (24 mg.), $\nu_{max.}$ 1725 (broad) cm.$^{-1}$ (some carboxylic hydroxyl, but no alcoholic hydroxyl).

Action of Aqueous Alkali on the Ester (XXIV).—The ester (500 mg.) was boiled with 2N-sodium hydroxide (100 ml.) for 2·5 hr. The acidic gum (0·45 g.) recovered as described above for the ester (XIII) crystallised from ether, yielding prisms (201 mg.) of 9α-*carboxy*-4bβ,5,6,7,8,8a-*hexahydro*-1-*methyl*-7-*oxofluoren*-8aβ-*ylacetic acid* (XXVI), m. p. 218—220° (from ethyl

methyl ketone–light petroleum), $[\alpha]_D^{24}$ −25° (*c* 1·09), $[\alpha]_D^{22}$ −48° (*c* 0·75 in 1·9N-NaOH), unchanged after 24 hr. at room temperature [Found: C, 67·6; H, 6·25%; equiv., 145. $C_{17}H_{18}O_5$ requires C, 67·5; H, 6·0%; equiv. (dibasic), 151].

The *dimethyl ester* (XXVII), prepared with diazomethane, was a gum, $[\alpha]_D^{26}$ −57° (*c* 1·10) (Found: OMe, 18·1. $C_{19}H_{22}O_5$ requires OMe, 18·8%).

The infrared spectra of the acid, and its dimethyl ester in CCl_4 were identical with those of the respective antipodes derived from allogibberic acid.

A portion (0·2 g.) of the gum recovered from the ethereal mother-liquor (above) crystallised from ethyl acetate, giving prisms (85 mg.), m. p. 188—196°. Recrystallisation from ethyl acetate and from ethyl methyl ketone–light petroleum gave prisms (36 mg.), m. p. 205—207° (yellow at the m. p.), $[\alpha]_D^{24}$ +78° (*c* 0·87), identified as the acid (XIX) by the infrared spectrum, mixed m. p., and formation of the dimethyl ester (XXIV), m. p. 168°, $[\alpha]_D$ +79°.

Reduction of the Ester (XXIV).—(a) *With sodium borohydride.* Reduction of the ester (100 mg.) with sodium borohydride (50 mg.) as for the dimethyl ester of the acid (IX) gave a gum (99 mg.). This was chromatographed in ether on alumina (13 × 1·5 cm.), and the column was eluted with 10 ml. portions of ether.

Fraction (ii) (45 mg.) crystallised from ether–light petroleum, giving prisms (35 mg.) of alcohol C, *methyl* 4bβ,5,6,7,8,8a-*hexahydro*-7ξ-*hydroxy*-9β-*methoxycarbonyl*-1-*methylfluoren*-8aβ-*ylacetate*, m. p. 95—96° (Found: C, 68·8; H, 7·3; OMe, 18·2. $C_{19}H_{24}O_5$ requires C, 68·65; H, 7·3; 2OMe, 18·7%), $\nu_{max.}$ 3570, 1724, 1708, 1598 cm.$^{-1}$ (in CCl_4 3520, 1735 cm.$^{-1}$).

Fractions (iv—vii) (25 mg.) crystallised from ethyl acetate–light petroleum in needles (16 mg.), m. p. 134°, $[\alpha]_D^{23}$ +107° (*c* 0·57), of alcohol D, the 7-*epimer* (Found: C, 68·3; H, 7·2; OMe, 18·8%), $\nu_{max.}$ 3390, 1732, 1598 cm.$^{-1}$.

(b) *Catalytic hydrogenation.* The ester (252 mg.) in acetic acid (25 ml.) was shaken with hydrogen at room temperature and pressure in the presence of Adams catalyst (100 mg.) (absorption *ca.* 2 mol. in 24 hr.). Recovery gave a gum (0·25 g.). This (0·22 g.) was chromatographed in ether on alumina (15 × 1·2 cm.) and was eluted with 10 ml. portions of ether.

Products (ii—iii) (25 mg.) crystallised from ether–light petroleum, giving prisms (15 mg.) of *methyl* 4bβ,5,6,7,8,8a-*hexahydro*-9β-*methoxycarbonyl*-1-*methylfluoren*-8aβ-*ylacetate* (XXVIII), m. p. 121—125° (Found: C, 71·85; H, 7·7; OMe, 19·2. $C_{19}H_{24}O_4$ requires C, 72·1; H, 7·65; 2OMe, 19·6%), $\nu_{max.}$ 1727, 1595 cm.$^{-1}$ (OH absent).

Products (iv—vi) (144 mg.) crystallised from ether–light petroleum, giving prisms (115 mg.), m. p. 96°, identical with alcohol C obtained as in (a) above.

Products (viii—xii) (21 mg.) crystallised from ether–light petroleum in needles (5 mg.) of alcohol D, m. p. 133—135°.

Reduction of the Ester (XXVII).—The ester (212 mg.) was reduced with sodium borohydride (111 mg.) as described above, giving a gum (204 mg.) which was chromatographed in ether on alumina (28 × 1·2 cm.). The column was eluted with 10 ml. portions of solvent, and similar fractions were combined, giving the following main fractions (eluants in parentheses): (i—iv) (ether) a gum (1·6 mg.); (v—ix) an unidentified solid, m. p. 99—116° (2·5 mg.); (x—xvi) (ether–methanol, 50 : 1), no product; (xvii—xxi) a gum (0·10 g.); (xxii), a gum (13 mg.); (xxiii—xxvi), a gum (44 mg.).

The product from fractions (xvii—xxi) did not crystallise and consisted essentially of alcohol E, *methyl* 4bβ,5,6,7,8,8a-*hexahydro*-7ξ-*hydroxy*-9α-*methoxycarbonyl*-1-*methylfluoren*-8aβ-*ylacetate*, $[\alpha]_D^{19}$ −39° (*c* 1·06) (Found: C, 68·1; H, 7·3; OMe, 18·0. $C_{19}H_{24}O_5$ requires C, 68·65; H, 7·3; 2OMe, 18·7%), $\nu_{max.}$ 3435, 1731, 1599 cm.$^{-1}$.

The gummy product from fractions (xxiii—xxvi), $[\alpha]_D^{19}$ +8° (*c* 0·60), is considered to consist essentially of the 7-*epimer* (F) (Found: OMe, 18·3%). The infrared spectrum ($\nu_{max.}$ 3410, 1735, 1595 cm.$^{-1}$) was distinct from that of alcohol (E).

Dehydration of the Acids (XIX) *and* (XXVI).—(*a*) The acid (XIX) (99 mg.) and acetic anhydride (1·8 ml.) were boiled for 1 hr. Evaporation *in vacuo* gave a solid which crystallised from ethyl methyl ketone–light petroleum as prisms (70 mg.) of the *anhydride* (XXIII), m. p. 154—155°, $[\alpha]_D^{24}$ −191° (*c* 0·87 in $COMe_2$) (Found: C, 72·1; H, 5·7. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·7%). The infrared spectrum in $CHCl_3$ was identical with that of its antipode (XIV) obtained by degrading allogibberic acid. The compound was dimorphic; in Nujol mull some specimens had $\nu_{max.}$ identical with that of the antipode (see above); in others the spectrum was distinct ($\nu_{max.}$ 1817, 1768, 1718 cm.$^{-1}$).

(*b*) The acid (XXVI) (42 mg.) was boiled with acetic anhydride for 1 hr. as described above. Crystallisation of the product (m. p. 143—149°) gave prisms (30 mg.) of the anhydride (XXIII), m. p. 154—155°, $[\alpha]_D^{24}$ −189° (*c* 0·42 in $COMe_2$).

Hydrolysis of the Anhydride (XXIII).—(*a*) The anhydride (37 mg.) was warmed at 50—60° with 2N-sodium hydroxide (1·0 ml.) until it dissolved (*ca.* 1 min.). Acidification and recovery of the product gave a solid (36 mg.), m. p. 196—202°, $[\alpha]_D^{24}$ +73° (*c* 1·02), which crystallised from ethyl methyl ketone–light petroleum in prisms (26 mg.) of the acid (XIX), m. p. 203—205°, $[\alpha]_D^{23}$ +76° (*c* 1·40).

(*b*) The anhydride (20 mg.) was boiled with water (2 ml.) for 1 hr. Recovery in ether gave the acid (XIX), m. p. 200—203°, $[\alpha]_D^{25}$ +74° (*c* 1·02).

Oxidation of Methyl Epiallogibberate.—(i) *Ozonolysis.* The ester (484 mg.) in acetic acid (20 ml.) was ozonised at 20° as described above. The solution was diluted with water (20 ml.), kept at 0° for 40 min., and steam-distilled. The methone of formaldehyde (226 mg., 0·47 mol.) was obtained by treatment of the distillate with dimedone.

The involatile portion was concentrated *in vacuo* and extracted with ethyl acetate. The extract was washed with sodium carbonate solution (A), 1% sodium hydroxide solution, and water, then dried, and the neutral product (256 mg.) was recovered as an intractable gum.

The solution (A) was acidified. Recovery of the product by extraction with ethyl acetate gave a gum (169 mg.) which was extracted with boiling light petroleum (b. p. 80—100°) and carbon tetrachloride (residue 24 mg.). The material recovered from the extracts was sublimed *in vacuo* and crystallised several times from ether–light petroleum, giving (*a*) semicrystalline gums, (*b*) impure product (6 mg.), m. p. 125—130°, and (*c*) plates and prisms (25 mg.) of 4bβ,5,6,7,8,8a-*hexahydro*-9β-*methoxycarbonyl*-1-*methyl*-7-*oxofluoren*-8aβ-*ylacetic acid* (XXV), m. p. 130—132°, $[\alpha]_D^{21}$ +74° (*c* 0·73) {[*M*]; positive Cotton effect curve (600 mμ), +200°; (307·5, peak) +3350°; (275, trough) +1350°; (262·5) +1950°} (Found: C, 68·4; H, 6·5; OMe, 10·3%; equiv., 323. $C_{18}H_{20}O_5$ requires C, 68·3; H, 6·4; OMe, 9·8%; *M*, 316), $\nu_{max.}$ 3100—2500, 1740, 1725 (sh), 1696 cm.$^{-1}$ (in $CHCl_3$, 1726—1713 cm.$^{-1}$).

Methylation gave the dimethyl ester (XXIV), m. p. 166—168°, $[\alpha]_D$ +79°, identical with material obtained by other methods (above).

(ii) Methyl epiallogibberate (180 mg.) was kept with pyridine (160 mg.) and osmium tetroxide (200 mg.) in benzene (*ca.* 10 ml.) in the dark for 11 days. The black crystalline osmiate was filtered off, washed with benzene, and shaken with a 10% solution of mannitol in 1% aqueous potassium hydroxide (25 ml.) for 25 min. The organic layer was washed with water, dried, and evaporated, giving a gum (150 mg.). Crystallisation from ethyl acetate–light petroleum (b. p. 60—80°) gave prisms (118 mg.) of the *glycol* (XXII), m. p. 79—81°, raised to 84—86° by recrystallisation (Found: C, 64·9; H, 7·3. $C_{19}H_{24}O_5,H_2O$ requires C, 65·1; H, 7·5%), $\nu_{max.}$ 3510, 3330, 1739, 1633 (?H_2O) cm.$^{-1}$.

The glycol (33 mg.), " AnalaR " sodium bismuthate (60 mg.), and acetic acid (1·2 ml.) were shaken together at room temperature until the reagent was consumed. Three more 20 mg. portions of bismuthate were added during *ca.* 20 hr. The mixture was diluted with water and extracted with ether. The extract was washed with water, and the gummy product (30 mg.), recovered in ether, was separated (in ethyl acetate; sodium carbonate extraction) into an intractable neutral fraction (11 mg.) and an acidic fraction (18 mg.).

The acidic fraction was sublimed at 150°/10^{-2} mm. and crystallised from ether–light petroleum in prisms (6 mg.), m. p. 130—132°, identical (mixed m. p. and infrared spectrum) with the acid ester (XXV) obtained as in (i) above.

Alkaline Hydrolysis of the Acid Ester (XXV).—The above acid ester (67 mg.) was heated under reflux with 2N-sodium hydroxide (7 ml.) for 2 hr. The solution was washed with ether and acidified and the product (68 mg.), recovered in ether, was treated with ether, giving gums and prisms (34 mg.) which from ethyl methyl ketone–light petroleum gave the acid (XXVI) (27 mg.), prisms, m. p. 216—217°, $[\alpha]_D^{24}$ −24° (*c* 0·46), identical with material prepared by hydrolysis of the dimethyl ester (XXIV) (above).

Material from the ethereal mother-liquor crystallised from ethyl acetate as prisms (15 mg.), m. p. 180—195°, $[\alpha]_D^{22}$ +46° (*c* 0·82). Recrystallisation from ethyl methyl ketone–light petroleum gave prisms (8 mg.), m. p. 200—203°, $[\alpha]_D^{19}$ +66° (*c* 0·53), consisting essentially of the acid (XIX).

Methylation and crystallisation of the product from methanol gave needles (5 mg.), m. p. 166—168°, $[\alpha]_D^{19}$ +77° (*c* 0·17), identified as the dimethyl ester (XXIV), by mixed m. p. and

infrared spectrum. The specific rotations of the crude crystalline fractions showed that the ratio of the acids (XXVI : XIX) formed was *ca.* 3 : 1.

Action of Alkali on Methyl Gibberate.—(*a*) The ester (53 mg.) was boiled with 2N-sodium hydroxide (5 ml.) for 2 hr. and, after cooling, the solution was washed with ether and acidified. The gummy product (47 mg.), recovered in ether, consisted essentially of the 10α-*isomer* of gibberic acid, $[\alpha]_D^{25}$ −62° (*c* 1·25) (Found: C, 76·1; H, 7·45. $C_{18}H_{20}O_3$ requires C, 76·0; H, 7·1%), $\nu_{max.}$ ~3100 (broad), 1736, 1704 cm.$^{-1}$.

(*b*) The ester {500 mg., $[\alpha]_D^{23}$ −4° (*c* 1·15)} was kept with 0·8N-methanolic sodium hydroxide (40 ml.) for 15 hr., $[\alpha]_D$ being measured at intervals (6 min., −9°; reaching −49° in 210 min.). After dilution with water the neutral product, recovered in ether, was a gum (457 mg.), $[\alpha]_D^{19}$ −54° (*c* 0·99). The gum (0·44 g.) was chromatographed in benzene on alumina (22 × 2·0 cm.) and was eluted with 100 ml. portions of benzene–methanol (50 : 1). Fractions (v—xiii) (190 mg.) were twice distilled (bath 120°, 10^{-4} mm.; and bath 170°/10^{-3} mm.), giving a syrup consisting essentially of the 10α-*isomer* of methyl gibberate, $[\alpha]_D^{19}$ −59° (*c* 0·54) (analyses erratic) (Found: C, 79·6, 74·8, 75·4; H, 7·4, 7·5, 7·5; OMe, 9·85. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·4; OMe, 10·4%), $\nu_{max.}$ 1736 (broad and intense), 1600 cm.$^{-1}$; the spectrum was distinct from that of methyl gibberate. Attempts to prepare a crystalline oxime failed.

Methyl dehydrogibberate, prepared by the action of diazomethane on dehydrogibberic acid,[9] was a gum (Found: OMe, 10·1. $C_{19}H_{22}O_3$ requires OMe, 10·5%).

This ester (80 mg.) was heated under reflux with 2N-sodium hydroxide (7 ml.) for 2 hr. The solution was washed with ether, acidified, and kept at 0°, yielding prisms (50 mg.), which, crystallised from dilute methanol, gave dehydrogibberic acid, m. p. 222° (decomp.), $[\alpha]_D^{20}$ +101° (*c* 0·46), identified by the infrared spectrum.

Hydrolysis of Methyl Epigibberate.—This ester (50 mg.) was boiled with 2N-sodium hydroxide (5 ml.) for 2 hr. The product (42 mg.; m. p. 247—250°) which separated on acidification crystallised from dilute ethanol in prisms (41 mg.) of epigibberic acid, m. p. 249—251°, $[\alpha]_D^{23}$ +127° (*c* 1·16). In N-methanolic sodium hydroxide methyl epigibberate had $[\alpha]_D^{19}$ +122° (*c* 1·05), unchanged after 90 hr. at room temperature. Epigibberic acid was stable to boiling 2N-sodium hydroxide for 2 hr.

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