Reaction of Methyl Gibberellate with Triphenylphosphine and Carbon Tetrachloride

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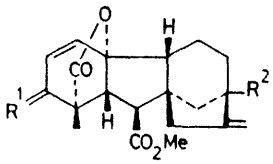
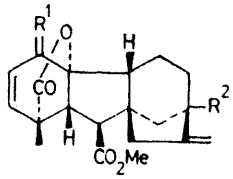
Treatment of methyl gibberellate and its 3-epimer with triphenylphosphine and carbon tetrachloride containing acetone or pyridine, gave the 1β-chloro- and 1β,13-dichloro-Δ^2-derivatives respectively as the major products. The 3-chloro-compounds were obtained as minor products. The 1-bromo-compounds were obtained with carbon tetrabromide. The structures of these compounds were established by location of the label in the products from methyl 3-*epi*-[3β-^{2}H]gibberellate.

TRIPHENYLPHOSPHINE–CARBON TETRACHLORIDE [1] has been recommended as a mild reagent for the conversion of allylic alcohols into their chlorides without allylic rearrangement.[2] We have used this reagent with success in the kaurenolide series.[3] Ring A of methyl gibberellate (1) is sensitive to attack by acidic reagents.[4] Consequently in connection with the partial synthesis of gibberellins from methyl gibberellate,[5,6] we have contrasted the displacement of the axial C-3 hydroxy-group of methyl gibberellate (1) with that of its equatorial epimer (2) and examined various reactions for differentiating between the 3- and 13-hydroxy-groups. The results, some of which have been reported in a lecture,[5] form the subject of this paper.

The allylic displacement of the axial 3-hydroxy-group of methyl gibberellate (1) with the consequent introduction of a 1β-halogen, has been noted [7,8] on a number of occasions. These reactions have played an important role in the total and partial synthesis of gibberellins.[3,5,9]





(1) R^1 = α-H, β-OH; R^2 = OH
(2) R^1 = α-OH, β-H; R^2 = OH
(4) R^1 = α-Cl, β-H; R^2 = OH
(7) R^1 = α-Cl, β-H; R^2 = Cl
(10) R^1 = α-OH, β-H; R^2 = OH
(11) R^1 = O; R^2 = OH
(12) R^1 = α-H, β-Cl; R^2 = Cl
(13) R^1 = α-OH, β = ^{2}H; R^2 = OH

(3) R^1 = α-H, β-Cl; R^2 = OH
(5) R^1 = α-H, β-Br; R^2 = OH
(6) R^1 = α-H, β-Cl; R^2 = Cl
(8) R^1 = α-Cl, β-H; R^2 = Cl
(9) R^1 = α-H, β-Br; R^2 = Br
(14) R^1 = H_2; R^2 = OH

Treatment of methyl gibberellate with triphenylphosphine in carbon tetrachloride with acetone as a co-solvent gave predominantly 1β-chloro-gibberellin A_5 methyl ester (3).[8,9] The crude material contained a small amount of the unrearranged 3α-chloride (4) which could be separated chromatographically. The 1β-bromide (5) was obtained when carbon tetrabromide was used but the 3α-isomer was not detected. Although the 13-hydroxy-group is at a bridgehead, it is nevertheless quite reactive.[6,8] The rates of triphenylphosphine–carbon tetrachloride reactions show a marked solvent dependance.[1] When the reaction was carried out in the presence of pyridine, the corresponding 1β, 13- (6) and 3α,13-dichlorides (7) were obtained. Treatment of the 1β-chlorogibberellin A_5 methyl ester (3) with triphenylphosphine–carbon tetrachloride in pyridine also gave the 1β,13-dichloride (6). When the reaction was prolonged, a small amount of the 1α,13-dichloride (8) was formed which was detected by n.m.r. spectroscopy. This could be obtained by treatment of the 1β,13-dichloride (6) with triphenyl phosphine–carbon tetrachloride–pyridine and presumably arises by chloride ion displacement. On the other hand the 3,13-dichloride (7) was recovered unchanged. Cross has described [8] the 1β,13-dichloride as a glass with the 5-H proton resonance as an unexplained doublet of doublets (J 3 and 10 Hz). In our hands the dichloride was crystalline and the 5-H proton resonance, even at 220 MHz, remained a doublet. Hence we suspect that the earlier material was contaminated possibly with the 1α-epimer. When carbon tetrabromide in pyridine was used, the 1β,13-dibromide (9) was obtained. Again the 3α-isomer was not detected. Hexachloroacetone has been recommended [10] as an alternative to carbon tetrachloride for the generation of unrearranged chlorides. However treatment of methyl gibberellate with triphenyl phosphine–hexachloroacetone gave a separable mixture (2 : 1) of the 1β,13- and 3α,13-dichlorides (6) and (7). However in this instance, it was a less satisfactory system because of the separation problems posed by the reagent.

Methyl 3-*epi*-gibberellate (10) [11] was prepared by the sodium borohydride–cerium(III) chloride reduction [12] of the αβ-unsaturated ketone (11). Previous preparations using sodium borohydride alone [11] gave mixtures containing 3-*epi*-gibberellin A_1 methyl ester. The formation of the latter is favoured by the use of sodium borohydride–copper(I) chloride.[6] In accordance with the 3α-stereochemistry for the alcohol (10), the 5β-proton resonance was at higher field than in methyl gibberellate.[12] This method of preparation permitted deuteriation at C-3 by using sodium borodeuteride as the reductant. Treatment of methyl 3-*epi*-gibberellate (10) with triphenylphosphine–carbon tetrachloride in pyridine gave an inseparable mixture of methyl 1β,13- and 3β,13-

dichlorogibberellate, (6) and (12), (2 : 1 n.m.r. assay) together with a small amount of the 3α,13-dichlorogibberellate (7). When triphenylphosphine–carbon tetrabromide in pyridine was used as the reagent, the 1β,13-dibromide (9) was the sole product.

The structure of the 1β-chlorides (3) and (6), were originally established from their ^{1}H n.m.r. spectrum.[8,9] The closeness of the olefinic proton multiplet resonances is normally characteristic [8,13] of C-2(3)-double bonds in contrast to C-1(2)-double bonds where the signals are distinct. In the case of the 1-chloro-compounds, although the 2- and 3-H proton resonances almost overlap at 60 MHz, at 220 MHz they are cleanly resolved (δ 5.95, 2-H; 5.86, 3-H). Examination of the n.m.r. spectrum of the corresponding 1β-bromo-compounds (5) and (9) where the signals are well-separated (δ 6.00 dd, *J* 3 and 9 Hz, 2-H; 5.66, d, *J* 9 Hz, 3-H), showed that the closeness of the olefinic proton resonances is not an unambiguous criterion of a 2,3-double bond. Hence we sought a better proof for its location. Methyl [3-^{2}H]-3-*epi*-gibberellate (13) was used as the substrate for the reactions in pyridine. In the rearrangement products an olefinic C-H (δ 5.86 in the 1β-chloro- and 6.00 in the 1β-bromo-compounds) was absent whilst in the 3-chloro-compound, the C*H*Cl signal was absent. The stereochemistry at C-1 was assigned since in the case of the 1β-halides, the 5β-proton resonance was deshielded when compared with the 1α-epimer (8) (Δδ 0.12 p.p.m.). In this connection it is interesting to note that even in the 1α-chloro-epimer, the 5β-proton resonance is at lower field than that in gibberellin A_5 methyl ester (Δδ 0.20) emphasizing the importance of comparing epimers in this series. The 3α-chloro-stereochemistry was assigned on the basis of the magnitude of the $J_{2,3}$ (3 Hz) and $J_{1,3}$ (1 Hz) coupling constants (*cf.* methyl 3-*epi*-gibberellate, $J_{2,3}$ 3 Hz, $J_{1,3}$ 1 Hz) and the lack of deshielding of the 5β-proton compared with the 3β-epimer (Δδ 0.35 p.p.m.). In the 1α-chloro-compound the 2-H resonance (δ 5.84, dd, *J* 3.5 and 9 Hz) is at higher field than the 3- resonance (δ 5.96, *J* 9 Hz) whereas in the 1β-chloro-compound the reverse is true (δ 5.95 dd, *J* 9 and 3.3 Hz, 2-H; δ 5.86, d, *J* 9 Hz, 3-H).

A number of conclusions may be drawn from this work. First, the reagents based on triphenylphosphine can, contrary to the literature,[2] lead predominantly to allylic rearrangement. Secondly the reaction does not necessarily proceed with a *syn*-stereochemistry. There is some evidence that a $\Delta^{2,3}$-double bond is thermodynamically more stable than the $\Delta^{1,2}$-double bond. A possible rationalization of our results can then be seen in terms of the combination of a simple nucleophilic substitution at C-3 with inversion of configuration and secondly the formation of an allylic carbocation which is discharged by an axial attack of a nucleophile at C-1. Attack on the β-face of ring A will also be favoured by the presence of the lactone ring on the α-face. As the reaction proceeds a third pathway intervenes involving a displacement, with inversion of configuration, of the chloride.

EXPERIMENTAL

General experimental details have been described previously.[14] ^{1}H N.m.r. were determined in deuteriochloroform at 60 MHz (Perkin–Elmer R 12, Varian T 60), at 90 MHz (Perkin–Elmer R 32) or at 220 MHz (PCMU service, R. 34).

Reaction of Methyl gibberellate with Triphenylphosphine–Carbon Tetrachloride.—(*a*) Methyl gibberellate (1)(1 g) was dissolved in acetone (10 ml) and treated with triphenylphosphine (1.5 g) and carbon tetrachloride (10 ml) under reflux for 1 h. The solvents were evaporated and the residue chromatographed on silica to afford *ent*-1α-chloro-10β,13-dihydroxy-7-methoxycarbonyl-20-norgibberella-2,16-dien-19-oic acid 19,10β-lactone (3)[8,9] which crystallized from ethyl acetate–light petroleum as needles, m.p. 120—120.5 °C (lit.,[8] glass; lit.,[9] m.p. 112—114 °C) (Found: C, 63.7; H, 6.0. Calc. for $C_{20}H_{23}ClO_5$: C, 63.4; H, 6.1%), $\nu_{max.}$ 3 490, 1 780, and 1 710 cm^{-1}; δ 1.25 (3H, s, 18-H), 2.64 (1H, d, *J* 10 Hz, 6-H), 3.10 (1H, d, *J* 10 Hz, 5-H), 3.70, (3H, s, OMe), 4.48 (1H, d, *J* 3 Hz, 1-H), 4,95 and 5.24 (1 H each, 17-H) 5.86 (d, *J* 9 Hz, 3-H), 5.95 (1H, dd, *J* 3 and 9 Hz, 2-H). Further purification of the mother liquors afforded a small amount of *ent*-3β-chloro-10β,13-dihydroxy-7-methoxycarbonyl-20-norgibberella-1,16-dien-19-oic acid 19,10-lactone (4) as a gum (M^+ 378.123, $C_{20}H_{23}{}^{35}ClO_5$ requires 378.123), δ 1.30 (3 H 18-H), 2.78 (1 H, d, *J* 10 Hz, 6-H), 3.06 (1 H, d, *J* 10 Hz, 5-H), 3.70 (3 H, s, OMe), 4.59 (1 H, 1- and 3-Hz, 3-H), 4.97 and 5.25 (each 1 H, m, 17-H), 5.90 (1 H, dd, *J* 3 and 9 Hz, 2-H) and 6.25 (1 H, dd, *J* 1 and 9 Hz, 1-H).

(*b*) The methyl ester (1) (4.0 g) was heated under reflux with triphenylphosphine (6 g) and carbon tetrachloride (25 ml) and pyridine (7 ml) for 30 min. The solvents were evaporated under reduced pressure and the residue was chromatographed on silica. Elution with 10% ethyl acetate–light petroleum afforded *ent*-1α,13-dichloro-10β-hydroxy-7-methoxycarbonyl-20-norgibberella-2,16-dien-19-oic acid 19,10β-lactone (6) (2.0 g) which crystallized from light petroleum as needles, m.p. 105—107 °C (lit.,[8] glass), (Found: C, 60.3; H, 5.5. Calc. for $C_{20}H_{22}O_4Cl_2$: C, 60.45; H, 5.5%), $\nu_{max.}$ 1 775, 1 735, and 1 660 cm^{-1}; δ 1.26 (3 H, s, 18-H), 2.65 (1 H, d, *J* 10 Hz, 6-H), 3.10 (1 H, d, *J* 10 Hz, 5-H), 3.75 (3 H, s, OMe), 4.55 (1 H, d, *J* 3 Hz, 1-H), 5.19 (1 H, t, *J* 1.5 Hz) and 5.46 (1 H, t, *J* 2.0 Hz) (each 17-H), 5.86 (1 H, d, *J* 9 Hz, 3-H), and 5.95 (1 H, dd, *J* 3 and 9 Hz, 2-H). Further elution gave ent-3β,13-dichloro-10β-*hydroxy*-7-*methoxycarbonyl*-20-*norgibberella*-1,16-*dien*-19-*oic acid* 19,10β-*lactone* (7) (580 mg) which crystallized from light petroleum as needles, m.p. 145—147 °C (Found: C, 60.4; H, 5.6. $C_{20}H_{22}Cl_2O_4$ requires C, 60.45; H, 5.5%), δ 1.30 (3 H, s, 18-H), 2.70 (1 H, d, *J* 11 Hz, 6-H), 3.05 (1 H, d, *J* 11 Hz, 5-H), 3.65 (3 H, s, OMe), 4.60 (1 H, dd, *J* 1 and 2 Hz, 3-H), 5.2 and 5.5 (1 H each, 17-H), 5.82 (1 H, dd, *J* 2 and 9 Hz, 2-H), and 6.25 (1 H, dd, *J* 1 and 9 Hz, 1-H). Elution with 25% ethyl acetate–light petroleum afforded *ent*-1α-chloro-10β,13-dihydroxy-7-methoxycarbonyl-20-norgibberella-2,16-dien-19-oic acid 19,10β-lactone (3) (640 mg).

(*c*) Methyl gibberellate (800 mg) in pyridine (6 ml) was heated under reflux with triphenylphosphine (1.6 g) and carbon tetrachloride (30 ml) for the following periods:

Time (min.)	Amount of compd. (3) (mg)	Compd. (6) (mg)	Compd. (7) + (8) (mg)
15	360	120	90
45	200	270	90 (5%)
75	—	290	80 (10%)
180	—	290	96 (18%)

The percentage of (8) was based on the ^{1}H n.m.r. spectrum (18-H and CH= signals). Only 1β-chlorogibberellin A_5 methyl ester (400 mg) was obtained pure when the amount of pyridine was reduced to 1 ml in a reflux period of 75 min.

Treatment of 1β-*Chlorogibberellin* A_5 *Methyl Ester with Triphenylphosphine–Carbon Tetrachloride.*—The ester (3) (300 mg) in pyridine (5 ml) was heated under reflux with triphenyl phosphine (600 mg) and carbon tetrachloride (20 ml) for 3 h. The solvent was evaporated and the residue chromatographed on silica. Elution with 7% ethyl acetate–light petroleum gave the 1β,13-dichloro-ester (6) (290 mg) identified by its n.m.r. spectrum.

Treatment of the 1β,13-*Dichloro-ester* (6) *with Triphenylphosphine–Carbon Tetrachloride.*—The dichloro-ester (6) (500 mg) in pyridine (3 ml) was heated with triphenylphosphine (1 g) and carbon tetrachloride (15 ml) under reflux for 5 h. The solvent was evaporated and the residue chromatographed on silica. Elution with 7% ethyl acetate–light petroleum gave the starting material (250 mg). Elution with 12% ethyl acetate–light petroleum gave ent-1β,13-*dichloro*-10-*hydroxy*-7-*methoxycarbonyl*-20-*norgibberella*-2,16-*dien*-19-*oic acid* 19,10β-*lactone* (200 mg) as a gum (Found: M^+ 396.089. $C_{20}H_{22}O_4{}^{35}Cl_2$ requires M 396.092), δ 1.47 (3 H, s, 18-H), 2.66 (1 H, d, J 9 Hz, 5-H), 2.98 (1 H, d, J 9 Hz, 6-H), 3.76 (3 H, s, OMe), 4.53 (1 H, d, J 3.5 Hz, 1-H), 5.18 (1 H, t, J 1.5 Hz) and 5.45 (1 H, t, J 2 Hz) (each 17-H), 5.84 (1 H, dd, J 3.5 and 9 Hz, 2-H), and 5.96 (1 H, d, J 9 Hz, 3-H).

Treatment of the 3α,13-dichloro-ester (7) under the same conditions gave only the starting material.

Treatment of Methyl Gibberellate with Triphenylphosphine–Hexachloroacetone—The ester (1) (500 mg) in acetone (5 ml) was heated under reflux with triphenylphosphine (1 g) and hexachloroacetone (10 ml) for 2 h. The solvents were evaporated under reduced pressure and the residue was chromatographed on silica. Elution with 10% ethyl acetate–light petroleum gave the 1β,13-dichloro-ester (6) (60 mg) followed by the 3α,13-dichloro-ester (7) (35 mg). Each compound was identified by its n.m.r. spectrum.

Treatment of Methyl Gibberellate with Triphenylphosphine–Carbon Tetrabromide.—The ester (1) (1.5 g) in acetone (10 ml) was heated under reflux with triphenyl phosphine (2.5 g) and carbon tetrabromide (800 mg) for 5 h. The solvent was evaporated and the residue was chromatographed on silica. Elution with 20% ethyl acetate–light petroleum gave *ent*-1α-bromo-10β,13-dihydroxy-7-methoxycarbonyl-20-norgibberella-2,16-dien-19-oic acid 19,10β-lactone (5) (1.2 g) as a gum (lit.,[9] gum) (Found: M^+ 422. Calc. for $C_{20}H_{23}{}^{79}BrO_5$ M 422), $\nu_{max.}$ 3 400, 1 780, 1 730, 1 660 cm^{-1}; δ 1.22 (3 H, s, 18-H), 2.60 (1 H, d, J 10 Hz, 6-H), 3.16 (1 H, d, J 10 Hz, 5-H), 3.78 (3 H, s, OMe), 4.67 (1 H, d, J 3 Hz, 1-H), 4.98 and 5.21 (each 1 H, 17-H), 5.66 (1 H, d, J 9 Hz, 3-H), and 6.00 (1 H, dd, J 3 and 9 Hz, 2-H). When the reaction was repeated in the presence of pyridine, the gummy *ent*-1α,13-dibromo-10β-hydroxy-7-methoxycarbonyl-20-norgibberella-2,16-dien-19-oic acid 19,10β-lactone (9) was the sole product (Found: M^+ 484. $C_{20}H_{22}{}^{79}Br_2O_4$ requires M 484), δ 1.25 (3 H, s, 18-H), 2.60 (1 H, d, J 10 Hz, 6-H), 3.20 (1 H, d, J 10 Hz, 5-H), 3.78 (3 H, s, OMe), 4.7 (1 H, m, 1-H), 5.25 and 5.57 (each 1 H, 17-H), 5.78 (1 H, d, J 9 Hz, 3-H), and 6.06 (1 H, dd, J 3 and 9 Hz, 2-H).

Preparation of Methyl 3-epi-*Gibberellate* (2).—The unsaturated ketone (11)[4] (600 mg) in methanolic 0.4M-cerium-(III) chloride (8 ml) was treated with sodium borohydride (75 mg) for 15 min. at 0 °C. Water was added and the product recovered in ethyl acetate to afford *ent*-3β,10β,13-trihydroxy-7-methoxycarbonyl-20-norgibberella-1,16-dien-19-oic acid 19,10β-lactone (2), (500 mg) which crystallized from acetone–light petroleum as prisms, m.p. 176—177 °C, (lit.,[11] 173—176 °C), $\nu_{max.}$ 3 400, 1 760, 1660 cm^{-1}, δ 1.26 (3 H, s, 18-H), 2.72 (1 H, d, J 10 Hz, 6-H), 2.91 (1 H, d, J 10 Hz, 5-H), 3.70 (3 H, s, OMe), 4.20 (1 H, m, 3-H), 4.94 and 5.25 (1 H each m, 17-H), 5.86 (1 H, dd, J 1 and 9 Hz, 1-H), 6.22 (1 H, dd, J 3 and 9 Hz, 2-H).

Treatment of Methyl 3-epi-*Gibberellate with Triphenylphosphine–Carbon Tetrachloride.*—The ester (2) (300 mg) in pyridine (2 ml) was heated under reflux with triphenylphosphine (500 mg) and carbon tetrachloride (10 ml) for 3 h. The solvents were evaporated and the residue was chromatographed on silica. Elution with 5% ethyl acetate–light petroleum gave *ent*-3β,13-dichloro-10β-hydroxy-7-methoxycarbonyl-20-norgibberella-1,16-dien-19-oic acid 19,10-lactone (7) (30 mg). Further elution gave a mixture of *ent*-1α,13-dichloro-10β-hydroxy-7-methoxycarbonyl-20-norgibberella-2,16-dien-19-oic acid 19,10β-lactone (6) and *ent*-3α,13-dichloro-10-hydroxy-7-methoxycarbonyl-20-norgibberella-1,16-dien-19-oic acid 19,10β-lactone (12) (120 mg) (*ca.* 2 : 1 by n.m.r.). The mixture crystallized as needles, m.p. 96—98 °C, δ (for 12) 1.30 (s, 18-H), 2.60 (d, J 10 Hz, 6-H), 3.35 (d, J 10 Hz, 5-H), 3.71 (s, OMe) 4.50 (m 3-H), 5.14 and 5.40 (17-H), 5.90 (dd, J 3 and 9 Hz, 2-H), 6.25 (d, J 1 and 9 Hz, 1-H). Repetition of the experiment with methyl 3-*epi*-[3-^{2}H]gibberellate gave the same products but the 3-H signal at δ 4.50 was missing in the *ent*-3α,13-dichloride. In the 1β,13-dichloride the 3-H signal at δ 5.86 was missing.

Treatment of Methyl 3-epi-*Gibberellate with Triphenylphosphine–Carbon Tetrabromide.*—The ester (2) (150 mg) in pyridine (6 ml) was treated with triphenylphosphine (800 mg) and carbon tetrabromide (200 mg) under reflux for 3 h. The reaction was worked up as above and the product chromatographed to afford *ent*-1α,13-dibromo-10β-hydroxy-7-methoxycarbonyl-20-norgibberella-2,16-dien-19-oic acid 19,10β-lactone (9) as a gum (70 mg) identified by its n.m.r. spectrum. When the reaction was repeated with methyl 3-*epi*-[3-^{2}H]gibberellate, the dibromide (9) was obtained lacking an olefinic proton resonance at δ 5.78.

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