Chemical Conversion of C_{20} Gibberellins into C_{19} Gibberellins

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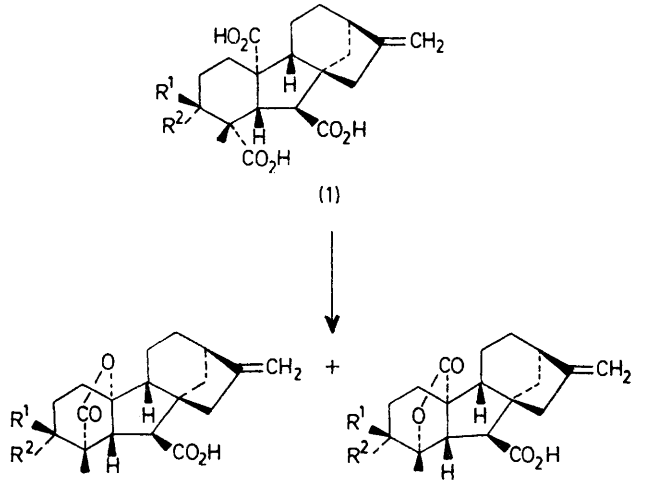
Summary Oxidative decarboxylation of *ent*-gibberellane-19,20-dioic acids with lead tetra-acetate yields mixtures of 19,10- and 20,4-lactones thereby providing a chemical correlation between C_{20} and C_{19} gibberellins.

The gibberellin (GA) family of plant hormones are subdivided into the C_{20} GAs [*e.g.*, (**1a,b**)] which retain the full diterpenoid complement of carbon atoms and the C_{19} GAs [*e.g.*, (**2a,b**)] which have lost C-20 and feature the 19,10-lactone bridge. The two groups have been correlated biosynthetically,[1] certain of the C_{20} GAs serving as precursors of the C_{19} GAs. We now report the first chemical correlation.

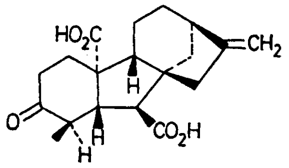


(1)

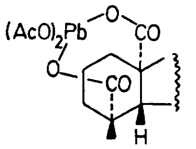
(2) (3)

a; R¹ = OH, R² = H
b; R¹ = R² = H
c; R¹, R² = O
d; R¹ = OAc, R² = H

Oxidative decarboxylation of 1,3- and 1,4-dioic acids has been shown[2] to give γ- and δ-lactones respectively. GA_{13} (**1a**), when treated with $Pb(OAc)_4$–dimethylformamide (DMF) at 18 °C, afforded a mixture (60:40) of the known GA_4 (**2a**), identified by g.l.c.–mass spectrometry of the Me ester, and the new, isomeric lactone (**3a**); minor amounts of the corresponding 3-ketones (**2c**) and (**3c**) were also formed. The structure (**3a**) for the isomeric lactone was established by oxidation (8 N CrO_3 in Me_2CO) of the mixture of lactones (**2a**) and (**3a**) to the corresponding ketones (**2c**) and (**3c**). Reduction [$Cr(OAc)_2$–tetrahydrofuran] of the mixture of ketones gave unchanged GA_4-ketone (**2c**) and the ketone (**4**) which was identical (g.l.c.–mass spectrometry of Me ester) to that obtained by thermal decarboxylation[3] of GA_{13}-ketone (**1c**). The mixture of lactones (**2a**) and (**3a**) could be resolved by g.l.c. but not by t.l.c. A pure sample of the lactone (**3a**) was prepared by treatment of the mixture of (**2a**) and (**3a**) with 0·1 N aqueous NaOH at 85 °C for 0·5 h, separation of the mixture of (**2a**) and (**3a**), enriched in the lactone (**3a**), from the 3-epimer[4] of GA_4 (**2a**) by t.l.c., and repetition of the process. The lactone (**3a**) did not induce α-amylase synthesis in barley endosperm nor did it inhibit the activity of GA_4 (**2a**) in this bio-assay.



(4)



(5)

The rate of the $Pb(OAc)_4$ reaction was faster in DMF or Me_2SO than in Et_2O or $(MeOCH_2CH_2)_2O$. Changes in the 3-substituent had little effect on the ratios of the isomeric lactones. When GA_{25} (**1b**), GA_{13}-ketone (**1c**), and GA_{13}-acetate (**1d**) were treated with $Pb(OAc)_4$–DMF at 18 °C, the pairs of lactones (**2b**) and (**3b**), (**2c**) and (**3c**), and (**2d**) and (**3d**) were formed in the ratios (g.l.c. of Me esters) of *ca.* 50:50, 63:37, and 82:18 respectively. It was shown that the 3-ketolactone (**3c**) was not formed by $Pb(OAc)_4$ treatment of (**4**) and therefore not through thermal decomposition of (**1c**).

The observed product ratios from (**1a**—**d**) suggest that carbonium ions are not involved in the decomposition of the probable intermediate (**5**).[2b]

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[1] B. E. Cross, K. Norton, and J. C. Stewart, *J. Chem. Soc.* (*C*), 1968, 1054; J. R. Bearder, J. MacMillan, and B. O. Phinney, *J.C.S. Perkin I*, 1975, 721.

[2] (a) L. L. McCoy and A. Zagalo, *J. Org. Chem.* 1960, **25**, 824; M. Fétizon and N. Moreat, *Bull. Soc. chim. France*, 1969, 4385; (b) L. R. C. Barclay, C. E. Milligan, and N. D. Hall *Conad. J. Chem.*, 1962, **40**, 1664.

[3] R. H. B. Galt, *J. Chem. Soc.*, 1965, 3143.

[4] D. C. Aldridge, J. R. Hanson, and T. P. C. Mulholland, *J. Chem. Soc.*, 1965, 3539.