The Ring Contraction Stage in Gibberellin Biosynthesis

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Summary Evidence presented suggests that the ring contraction of a kauranoid diterpene to a gibbane is accompanied by a hydrogen migration from C-6 to C-7.

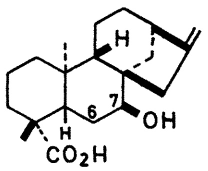
A UNIQUE feature of the gibberellin plant growth hormones is their five-membered ring B which is formed by rearrangement of a six-membered ring. There has been biogenetic speculation on the nature of this step. It has been shown[1] that 7β-hydroxy-(—)-kaur-16-en-19-oic acid (I) is converted into the aldehyde (II), gibberellin A_{12} (III), and gibberellic acid (IV). Furthermore in the overall conversion into gibberellic acid, we showed that the kauranoid C-6-equatorial hydrogen atom was lost and that the axial atom was retained.[2] The next logical precursor to prepare was 6β,7β-dihydroxy-(—)kaur-16-en-19-oic acid. However, this was only converted into fujenal (0·01%). There was no detectable conversion into gibberellic acid. At this stage in our work, Cross reported[3] the same negative result. An alternative which we have considered,[2] is that the ring contraction may be initiated by the abstraction of the 6β-hydrogen itself. We now present evidence for the fate of this hydrogen atom.

TABLE

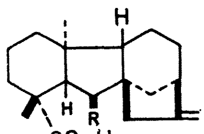
	$^3H:^{14}C$	No. of ^3H
Geraniol	10 : 1	2
(—)-Kaurene	9·1 : 1	1·8 (2)
7-Hydroxykaurenolide	6·0 : 1	1·2 (1)
Gibbane aldehyde (II)[a]	9·7 : 1	1·9 (2)
Gibberellic acid (IV)[b]	5·7 : 1	1·1 (1)

[a] As its methyl ester semicarbazone.
[b] As its methyl ester.

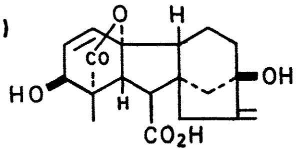
[1-$^3H_2$,1-^{14}C]Geraniol was fed, as its pyrophosphate, to *Gibberella fujikuroi* and the metabolites were isolated. The $^3H:^{14}C$ ratios are tabulated. The gibbane aldehyde was then oxidized to gibberellin A_{12} monomethyl ester with the loss of one tritium atom ($^3H:^{14}C$, 4·9 : 1). The remaining label has already been located in gibberellic acid.[2] Consequently, we suggest that the ring contraction occurs by oxidation at C-7 and a hydride shift from C-6 to C-7 as the C-7,C-8 bond migrates. Further confirmatory studies utilizing kauranoid and gibbane derivatives are in hand. The formation of both 6α- and 6β- alcohols may therefore represent divergent pathways.[4]



(I)



(II) R = CHO
(III) R = CO₂H



(IV)

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[4] P. R. Jefferies, J. R. Knox, and T. Ratajczak, *Tetrahedron Letters*, 1970, 3229.