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(-)-PIMARADIENE: A NEW PRECURSOR OF THE GIBBERELLINS

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Birch et al.[1] proposed that gibberellic acid (I) is biosynthesised via a tricyclic intermediate, which in the light of subsequent developments[2] in this field would be expected to be (-)-pimaradiene (III)[3] or the related carbonium ion (X). Cyclisation[4] of this intermediate would yield (-)-kaurene (XI), a known[2] precursor of some of the gibberellins. The discovery of (-)-pimaradienoic acid (IV) has made it possible to test this hypothesis.

With 1 mol. of osmium tetroxide methyl (-)-pimaradienoate* (V) afforded the diol (XII) which was oxidised with $NaIO_4$ to give the aldehyde (XIII), whose NMR spectrum (in $CDCl_3$) showed only one olefinic proton (broadened singlet at τ 4.78, 14-H) and an aldehydic proton as a singlet at τ 0.49. Reaction of the aldehyde with the Wittig reagent $^{14}CH_2{=}PPh_3$ gave the labelled ester (VI), identified by its IR spectrum. The ester (VI) was reduced to the alcohol[3] (VII), oxidised to the aldehyde[5] (VIII), and finally reduced[5] (Wolff-Kishner) to the labelled (-)-pimaradiene (IX) which was identified by its IR and NMR spectra.

Addition of (-)-pimaradiene (IX) to a fermentation[6] of Gibberella fujikuroi, and isolation[6] of the metabolites produced, gave labelled methyl gibberellate (II) (incorporation 0.05%) and labelled 7-hydroxykaurenolide.[7] Thus (-)-pimaradiene acts as a precursor of gibberellic acid and presumably also of the other gibberellins.[2] The very low incorporation[8] (cf. ref. 2) is consistent with the formation of the kaurene nucleus from a bicyclic precursor[1,2] by a concerted process, i.e. the tricyclic "intermediate" is probably the carbonium ion (X).

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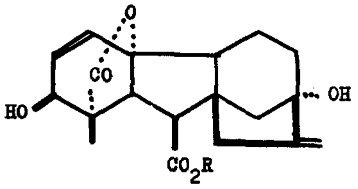
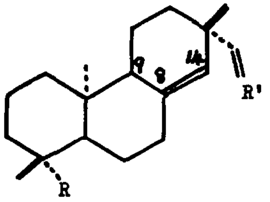
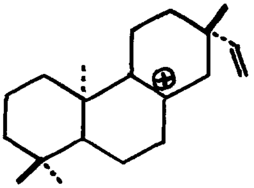


I R = H

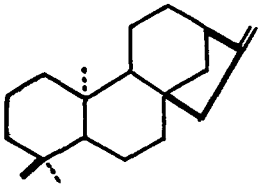
II R = Me



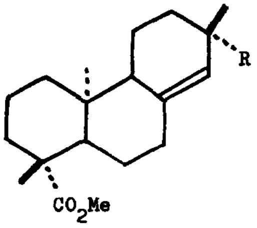
	R	R'
III	Me	CH_2
IV	CO_2H	CH_2
V	CO_2Me	CH_2
VI	CO_2Me	$^{14}CH_2$
VII	CH_2OH	$^{14}CH_2$
VIII	CHO	$^{14}CH_2$
IX	Me	$^{14}CH_2$



X



XI



XII R = $CHOH.CH_2OH$

XIII R = CHO

References

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8. Dr. J. R. Hansonhas also obtained a very low incorporation of (-)-pimaradiene into gibberellic acid, personal communication.