

THE ROLE OF GIBBERELLINS A<sub>13</sub> AND A<sub>14</sub> IN THE  
BIOSYNTHESIS OF GIBBERELIC ACID

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(Received 21 September 1966)

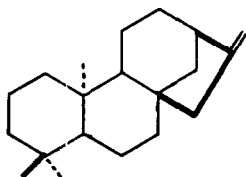
The reaction sequence (-)-kaurene (I) → gibberellin A<sub>12</sub> (II) → gibberellin A<sub>14</sub> (III) → gibberellin A<sub>13</sub> (VI) → gibberellic acid (IX) has been proposed (1) as a possible biosynthetic route to gibberellic acid; it was based on the structures of gibberellins A<sub>12</sub> (2), A<sub>13</sub> (3), and A<sub>14</sub> (4) and on the incorporation (5) of (-)-kaurene into gibberellic acid. Recently Cross and Norton (6) provided evidence in support of this proposal, when they showed that both gibberellin A<sub>12</sub> and the corresponding diol (X),<sup>\*\*\*</sup> were transformed into gibberellic acid by Gibberella fujikuroi with incorporations of 0.7 and 7.5% respectively. Both substrates also acted as precursors

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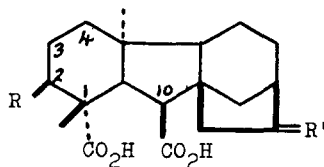
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It is unlikely that the diol (X) is an intermediate between kaurene and gibberellic acid, since contraction of ring B of kaurene would be expected to extrude an aldehyde or carboxyl group. However, the diol was used because it was readily accessible.

of gibberellin  $A_{13}$ . We now report our work on the role of gibberellins  $A_{13}$  and  $A_{14}$  in the biosynthesis of gibberellic acid.



I

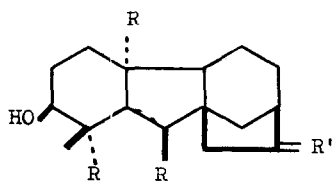


II R = H, R' = CH<sub>2</sub>

III R = OH, R' = CH<sub>2</sub>

IV R = OH, R' = O

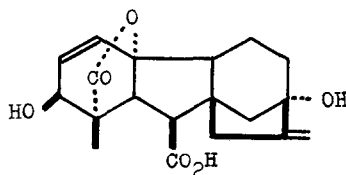
V R = OH, R' = <sup>14</sup>CH<sub>2</sub>



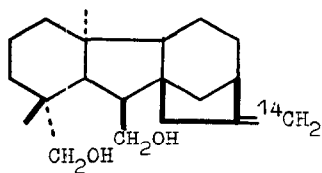
VI R = CO<sub>2</sub>H, R' = CH<sub>2</sub>

VII R = CO<sub>2</sub>H, R' = <sup>14</sup>CH<sub>2</sub>

VIII R = CH<sub>2</sub>OH, R' = <sup>14</sup>CH<sub>2</sub>



IX



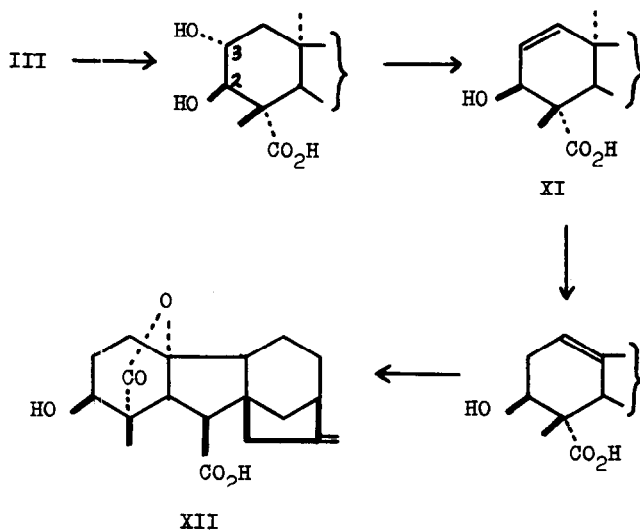
X

Gibberellin A<sub>14</sub> nor-ketone (IV) was prepared by oxidation of gibberellin A<sub>14</sub> with periodate in the presence of a catalytic amount of osmium tetroxide (7). It reacted with the Wittig reagent <sup>14</sup>CH<sub>2</sub>=PPh<sub>3</sub> to give [<sup>14</sup>C]gibberellin A<sub>14</sub> (V) which was added to a fermentation of G. fujikuroi. After the fermentation had run for a further 3 days, the gibberellic acid and gibberellin A<sub>13</sub> were isolated and found to be labelled with incorporations of 4.7 and 0.9% respectively.

[<sup>14</sup>C]Gibberellin A<sub>13</sub> (VII) was prepared in a similar manner to [<sup>14</sup>C]gibberellin A<sub>14</sub>, and part of it was methylated and then reduced with lithium aluminium hydride to the [<sup>14</sup>C]tetraol (VIII). (VII) and (VIII) were not incorporated into gibberellic acid by G. fujikuroi, nor was the tetraol transformed into gibberellin A<sub>13</sub>. Recovery of part of the tetraol from the fermentation showed that cyclic ether formation was not responsible for the resistance of the tetraol to enzymic attack.

It would appear that gibberellin A<sub>13</sub> is not a precursor of gibberellic acid, but that it is formed by the irreversible oxidation of such a precursor. This conclusion is in agreement with the observation (8) that gibberellin A<sub>13</sub> occurs in fermentation broths at higher concentrations than gibberellins A<sub>12</sub> and A<sub>14</sub>.

The role of gibberellin  $A_{14}$  is more interesting. The high incorporations of gibberellin  $A_{14}$  (4.7%) and the diol (X) (7.5%) compared with that of gibberellin  $A_{12}$  (0.7%), suggests that hydroxylation at C-2 takes place before the  $1\alpha$ - and  $10$ -substituents have both been oxidised to carboxyl groups. The formation of the  $\gamma$ -lactone ring of the  $C_{19}$  gibberellins is open to



speculation. It is tempting to propose that gibberellin  $A_{14}$  is converted into a  $2\beta,3\alpha$ -diol, which by elimination of water and oxidation of the angular methyl group affords

the  $\beta$ -unsaturated acid (XI). Decarboxylation followed by lactonisation would then give gibberellin A<sub>4</sub> (XII). Further modifications would yield the other fungal gibberellins.

We thank the Science Research Council for a Research Studentship (to K.N.) and Imperial Chemical Industries Ltd. (Pharmaceuticals Division) for carrying out the fermentations.

#### REFERENCES

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