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BIOSYNTHESIS OF GIBBERELLIC ACID. A CORRECTION

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We recently reported[1] that a fermentation of Gibberella fujikuroi gave a low (0.05%) incorporation of (-)-[^{14}C]pimaradiene (I) into gibberellic acid (VII). Subsequently we have obtained an apparent incorporation (0.1%) of [^{14}C]pimaradienol[1,2] (II) into gibberellic acid.

Degradation of the methyl gibberellate derived from these two fermentations has shown that the label is not in the 11-position as expected[3] if the dienes (I) and (II) had acted as precursors. Thus for the methyl gibberellate from the dienol fermentation 91% of the label was in the terminal methylene group and no activity was found in the carbon dioxide (see below), one third of which was derived from C-11. Similar results were obtained on degradation of the methyl gibberellate from the pimaradiene fermentation. These results suggested that the labelled methyl gibberellate was derived from a precursor with the kaurene nucleus[3] which was present as an impurity in the original (-)-pimaradienoic acid[2] (III). In support of this view kauren-19-oic acid (V) is known[2] to co-occur with pimaradienoic acid. Such an impurity would become labelled in its terminal methylene group during the preparation[1] of labelled pimaradiene and only ~1% of impurity would be needed[3] to account for the activity incorporated into gibberellic acid. The [^{14}C]pimaradiene[1] was no longer available, but examination of the [^{14}C]-pimaradienol by VPC[7] showed a very weak peak corresponding in retention time to that of kauren-19-ol (IV). Similarly on VPC the original methyl pimaradienoate[1,2] showed two very small impurity peaks one of which corresponded in retention time to that of methyl kaurenoate (VI). Hence there is little doubt that under the conditions of our fermentations pimaradiene does not act as a precursor of gibberellic acid.

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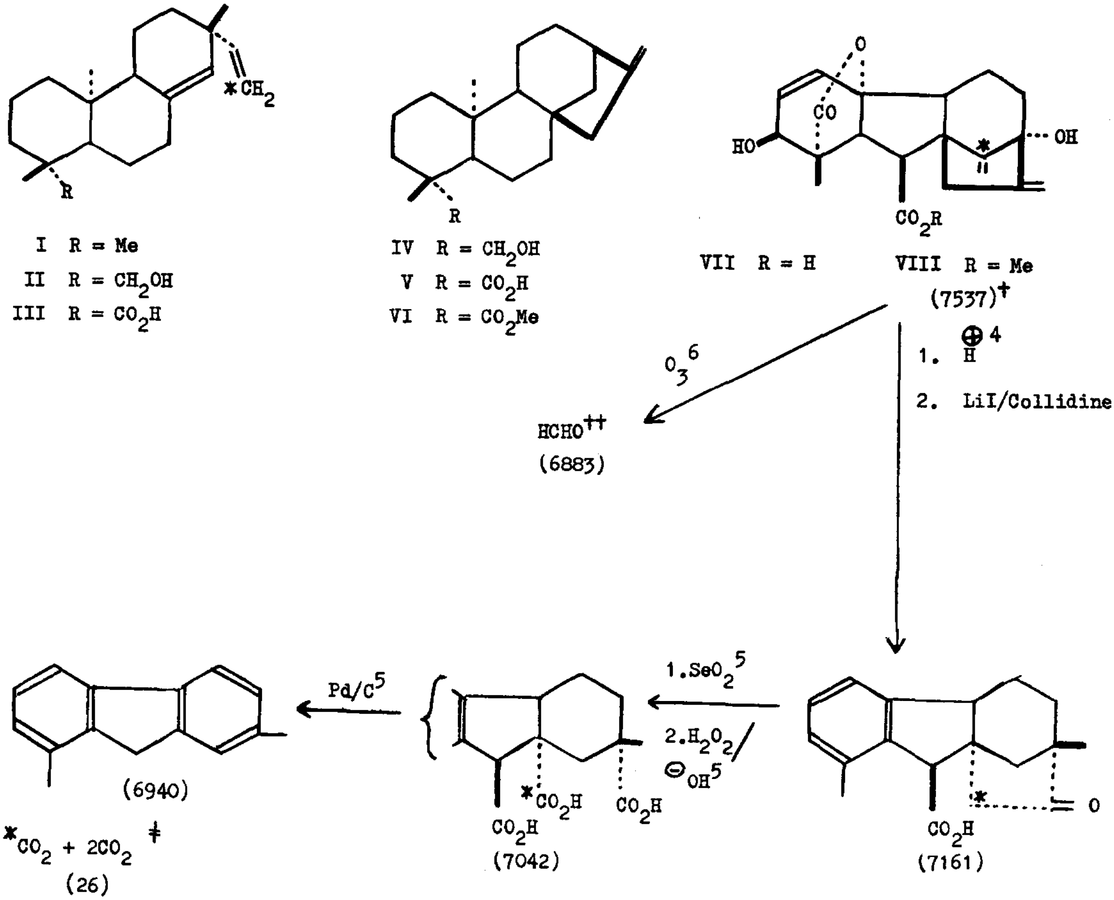

I R = Me
II R = CH$_2$OH
III R = CO$_2$H

IV R = CH$_2$OH
V R = CO$_2$H
VI R = CO$_2$Me

VII R = H
VIII R = Me
(7537)†

HCHO†† (6883)

(7161)

(7042)

(6940)

$^{*}CO_2 + 2CO_2$ ǂ (26)

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* Denotes expected position of ^{14}C derived from dienes (I) and (II).

† Numbers in parentheses are counts/mmole/100sec. in NE213 scintillator and are corrected for quenching. Samples were counted for at least 10^4 counts.

†† Counted as the dimedone derivative.

ǂ Collected as $BaCO_3$ and then liberated by mineral acid and absorbed in Hyamine solution.

Key Words

(-)-[^{14}C]Pimaradiene

(-)-[^{14}C]Pimaradienol