Endogenous biosynthetic precursors of (+)-abscisic acid. VII. The 1′,4′-trans-diol is formed from ABA, it is not a precursor

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Abstract

[^{14}C]ABA fed to avocado fruit is known to be converted into the 1′,4′-*trans*-diol and [^{14}C]1′,4′-*trans*-diol has been shown to be converted into ABA by several plant tissues. As a 'cold trap'of *trans*-diol becomes labelled with ^{14}C when [^{14}C]mevalonate is converted into ABA, the trans-diol has been suggested to be the immediate precursor of ABA. This proposal has now been tested by feeding [5-^{14}C,5-$^{3}H_2$]mevalonolactone to unripe avocado fruit and measuring the ^{3}H :^{14}C ratio in the ABA and in the 1′,4′-*trans*-diol isolated from the fruit after 16 h. Little labelled diol was present unless a 'cold trap' of unlabelled 1,4-*trans*-diol was added with the mevalonate. One ^{3}H atom, derived from those at C-5 of mevalonate, would be expected at C-4′ of the diol, adjacent to the hydroxyl group, and another at C-5 of the side chain of the diol if the diol were a precursor of ABA (^{3}H:^{14}C ratio of 2:3). However, if the 4′-hydroxyl group had been oxidised to a ketone to form ABA, then the ^{3}H atom at C-4′ of the diol would have been lost and the ^{3}H:^{14}C ratio would be expected to be 1:3. The normalised ^{3}H : ^{14}C ratios of ABA and 1′,4′-*trans*-diol biosynthesised from [^{14}C,5-$^{3}H_2$]mevalonate were 0.915:3 and 0.844:3 respectively and after oxidation of the diol to ABA with MnO_2 the ratio was 0.869:3 i.e. there was no ^{3}H at C-4′ of the diol. These ratios are as expected for the *trans*-diol if it had been formed by reduction of ABA. This, and the absence of labelled diol in the fruit unless a 'cold trap'was added, establishes that the 1′,4′-*trans*-diol is formed from ABA and it is not a precursor. The formation of the diols from newly synthesised labelled ABA in cell-free systems can be attributed to the addition to the homogenate of compounds with strong reducing potential. $NADPH_2^+$ (8.4 nmol) added to a mung bean seedling homogenate caused the reduction of (±)-[^{14}C]ABA (0.37 nmol, 22.5 μCi/mol) to *trans*-diol (1189 dpm) whereas with $NADP^+$ only 338 dpm were present in *trans*-diol. Glutathione (46 nmol) caused the formation of 1214 dpm while oxidised glutathione produced 638 dpm. Less 1′,4′-*cis*-diol was formed.

Keywords: ABA, 1′ ,4′ -trans-diol, [5-3H2] mevalonate, biosynthesis, avocado, glutathione reductase, NADPH.

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