

# Systematics of *in-vivo* Hydrogen Isotope Fractionations, Basis of the Deuterium Patterns of Natural Plant Compounds

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The primary source of any organically bound hydrogen in natural plant matter is leaf water; therefore the bulk  $\delta^2\text{H}$ -values of the biomass are mainly depending on local climatic conditions and the water households of the plants. Within this given frame, the average and positional  $^2\text{H}$ -abundances of individual compounds are determined by the mechanisms of and the kinetic isotope effects on the hydrogen transfer reactions during their biosyntheses. The  $^2\text{H}$ -patterns of many aroma and flavour compounds, measured by quantitative NMR in context with origin and authenticity determinations, are available in the literature; their comparison revealed a systematic and logic for their origin. The photosynthetic formed  $\text{H}^-$  has probably a  $\delta^2\text{H}$ -value of  $\sim -600\text{‰}$ , yet due to isotope effects on its consumption, the pool of the  $\text{H}^-$  in NADPH attains obviously a steady state at  $\sim -250\text{‰}$ . NADPH produced by the oxidative PPC is at a somewhat more positive level. C-bound H-atoms originating from a direct  $\text{H}^-$ -transfer from NADPH are depleted to  $\sim -350\text{‰}$ ; by secondary hydrogen exchange with water carbohydrates are relatively more enriched in  $^2\text{H}$ . On the other hand, when the hydrogen transfer from NADPH is catalysed by flavoproteins, the acceptor positions are depleted in  $^2\text{H}$  up to  $-600$  to  $-750\text{‰}$ . The consequent application of this fundamental finding to the corresponding biosyntheses and the mechanisms of the involved enzyme catalysed reactions led to astonishingly correct agreements between prediction and experimental data of  $^2\text{H}$ -patterns. This will be demonstrated for the alternating  $^2\text{H}$ -abundance in the hydrocarbon chains of fatty acids, for the assignment of isoprenoids to the different pathways of their biosynthesis on the basis of their  $^2\text{H}$ -patterns, for the understanding of the complex  $^2\text{H}$ -pattern of phenylpropanoids and their descendents, and for the explanation of the general-ly observed extreme  $^2\text{H}$ -depletion of the O- and N-methyl groups in natural compounds.

## References

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