PREFACE

VITAMINS: A PLANT AFFAIR

All organisms need to synthesize, transform and interconvert a myriad of molecules to enable them to grow and reproduce. All these reactions are catalysed by enzymes (the living tools) which facilitate chemical modifications of substrates owing to their specific binding properties. In many cases, suitable coenzymes (nicotinamide adenine dinucleotide [NAD^+], nicotinamide adenine dinucleotide phosphate [$NADP^+$], flavin adenine dinucleotide [FAD], flavin mononucleotide [FMN], pyridoxal 5′-phosphate, biotin, coenzyme A, etc.) may assist in biochemical transformations. Some of these coenzymes may be more or less tightly bound to enzymes as part of prosthetic groups (biotin, FMN, etc.). Coenzymes may also be loosely bound to enzymes as detachable molecules. In that case, they are acting as substrates, being often recycled through other set of reactions ($NAD(P)^+$, folates, ascorbate, etc.).

Vitamin (a combination word from *vita* and *amine*) are by definition dietary substances required for good health and normal development that are only synthesized by microorganisms and plants. During the course of animal evolution, the ability to biosynthesize these compounds has been lost and, instead, elaborate uptake mechanisms have been developed. There are 13 recognized vitamins, involved in various catalytic functions. The largest number of vitamins serve as precursors to coenzymes (vitamins B_1 [thiamine], B_2 [riboflavin], B_3 [niacin], B_5 [pantothenic acid], B_6 [pyridoxine], B_9 [folic acid]) or as coenzymes themselves (vitamins B_8 [biotin], B_{12} [cobalamin], C [ascorbic acid], K [phylloquinone, menaquinone]). Some of these vitamins, especially the hydrophobic (vitamins A [retinol, pro-vitamin A carotenoids], E [tocopherols, tocotrienols] and D [ergocalciferol, cholecalciferol]), cannot be truly considered as coenzymes: vitamins A and D display hormonal effects in the human body, and vitamin E has a protective role in membranes by scavenging free radicals. Vitamins are involved in almost all important cellular functions, displaying protective (antioxidant) functions or participating to numerous metabolisms, including the energetic metabolism (respiration, photosynthesis) and the metabolisms of sugars, amino acids, fatty acids and nucleic acids. The daily amount of vitamins required for a good health depends on the considered vitamin and fluctuates widely, from a few micrograms (B_{12}, D, K) to several milligrams (B_3, B_5, C). Vitamin deficiencies are quite common in low-resource countries but also occur in developed countries due to bad food habits. Well-known vitamin-related diseases include, among others, blindness (vitamin A), beriberi (vitamin B_1), pellagra (vitamin B_3), anaemia (vitamins B_6 and B_9), scurvy (vitamin C), rickets (vitamin D) or neural tube defects (vitamin B_9). In addition, antioxidant vitamins (such as A, C, E and B_6) have protective roles as efficient quenchers of reactive oxygen species.

Plants synthesize an impressive diverse array of natural products including vitamins, and plants are considered as a major nutritional source for these essential molecules. Plants are able to synthesize 12 out of the 13 vitamins. Indeed, plants have no cobalamin-dependent proteins and use for methionine synthesis an alternate catalytic mechanism that does not need vitamin B_{12}. Vitamin B_{12} is only synthesized in prokaryotes, and humans primarily obtained it from animal food, thanks to the intestine flora of herbivores. Two of the vitamins (vitamins A and D) have 'hormonal' functions in animals, which functions do not exist in plants. Plants do not synthesize vitamin A, but carotenoids. Some of these carotenoids are pro-vitamin A, which are transformed in retinol once assimilated by animals. Vitamin D (D_2 and D_3) is formed from the precursors ergosterol (mainly present in fungal cells) and cholesterol (mainly present in mammalian cells) following sun exposure (UV radiation). Although vitamins D_2 and D_3 can be found in low amounts in the membranes of some *Solanaceous* plants, higher plants are not considered as a source of vitamin D and plant food cannot compensate insufficient synthesis in the human body. Thus, the plant kingdom is a recognized dietary source for 11 out of the 13 vitamins.

As many vitamins are only required in trace quantities, their biosynthesis is normally strictly controlled and the involved enzymes are generally produced in very small amounts. This is why it has been extremely difficult to elucidate their complete biosynthetic pathways, and it still remains the case that several steps within the biosynthesis of vitamins are poorly understood (e.g. thiazole ring scaffolding). However, the advent of modern recombinant DNA techniques, coupled with the completion of many genome projects, made possible to decipher pathways in plants, thus allowing now a more complete understanding of how these molecules are made. The general picture emerging from these recent data indicates that the metabolic web represented by these molecules is of a rare complexity. Indeed, not only may the synthesis of vitamins require some 10 enzymatic steps but also several of these metabolic routes are split between various compartments of the plant cell, adding a further level of complexity when compared to prokaryotes. Since all cell compartments need their vitamins, this situation implies transport and trafficking of intermediates and end products of the pathways. Today, there is no explanation for such compartmentalization.

The actual understanding of how these biosynthetic pathways operate can be exploited for health and wealth creation. Vitamin synthesis is largely restricted to plants and microorganisms, a biochemical feature that can be harnessed for the development of specific pesticides (bactericides, herbicides, fungicides, etc.). Taking into account the health problems related to vitamin deficiencies, together with an increase in the use of vitamin supplements for human and animal nutrition, there is also a requirement, from a nutritional and commercial standpoint, to enhance the production of many of these vitamins. Overproduction of the vitamins can be achieved in a number of ways, by removing transcriptional controls, overproduction of key enzymes that represent bottlenecks in the pathways of biosynthesis, suppression of metabolic feedbacks, limitation of the catabolism and increase of the storage. It is clear that the 'optimization' of these systems requires a complete understanding of (i) their endogenous regulation and (ii) their integration within the metabolism as a whole.

This book includes comprehensive and authoritative reviews from leading experts on vitamins in plants, and we are thankful for their time and effort. The aim of this book is to collect and interpret the rapid growing experimental information on vitamins in plants, especially in the challenging area of their biosynthesis. We also hope that this book may be useful as a starting point for those graduates and undergraduate students and researchers wishing to pursue special studies in this field.

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