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Vitamin A and the provitamin A carotenoids

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3.1 INTRODUCTION

In 1915 McCollum and Davis isolated from animal fats and fish oils a ‘fat-soluble A’ that was essential to rats for growth and also cured eye disorders. In 1921 Bloch reported that a diet containing full milk and cod-liver oil cured xerophthalmia in infants and concluded that the eye affliction was due to the absence of the fat-soluble A in the diet. In the meantime it was discovered that green vegetables also possess fat-soluble A activity and in 1930 Moore provided evidence that carotene was converted to vitamin A in the body. The biochemical function of vitamin A in vision was established by Wald in 1935.
Vitamin A-active compounds are represented by retinoids (preformed vitamin A) and provitamin A carotenoids. The retinoids, as defined by Sporn, Roberts and Goodman (1984), comprise retinol, retinaldehyde and retinoic acid, together with their naturally occurring and synthetic analogues. Carotenoids are yellow, orange, red or violet pigments that are responsible for the colour of many vegetables and fruits. Certain almost colourless carotenoids also exist, such as phytofluene, which fluoresces intensely under ultraviolet (UV) irradiation. In nature, the carotenoids are synthesized exclusively by higher plants and photosynthetic microorganisms, in which they play fundamental roles in metabolism. Although animals are unable to synthesize carotenoids de novo, they can assimilate them through their diet.

3.2 CHEMICAL STRUCTURE AND NOMENCLATURE

**Vitamin A**

The structures of retinoids found in foods and fish-liver oils are shown in Figure 3.1. The parent vitamin A compound, retinol, has the empirical formula C_{20}H_{30}O and a molecular weight (MW) of 286.44. It is systematically named 9,13-dimethyl-7-(1,1,5-trimethyl-6-cyclohexen-5-yl)-7,9,11,13-nonatetraen-15-01 (Harris, 1967) and comprises a β-ionone (cyclohexenyl) ring attached at the carbon-6 position to a side chain composed of four isoprene units. The four double bonds in the polyene side chain give rise to cis–trans (Z-E) isomerism. Theory predicts the existence of a possible 16 isomers of retinol, but most of these exhibit steric hindrance, and some are too labile to exist (Schwieter and Isler, 1967). The predominant isomer, all-trans-retinol, possesses maximal (100%) vitamin A activity and is frequently accompanied in foodstuffs by smaller amounts of 13-cis-retinol. 9-Cis- and 9,13-di-cis-retinol occur in small amounts in fish-liver oils. 3-Dehydroretinol (vitamin A$_{2}$) represents the major form of vitamin A in the liver and flesh of freshwater fish.

Retinyl acetate (C$_{22}$H$_{32}$O$_{2}$; MW = 328.5) and retinyl palmitate (C$_{36}$H$_{60}$O$_{2}$; MW = 524) are used commercially in synthetic form to supplement the vitamin A content of foodstuffs. Current industrial processes for synthesizing retinyl acetate start from acetone and proceed through the key intermediate, β-ionone (O'Leary, 1993).

**Provitamin A carotenoids**

Carotenoids are classified chemically as carotenes, which are hydrocarbons, and xanthophylls, which have an oxygen group either on the ring or in the chain. These oxygen-containing groups include hydroxyl, carbonyl, carboxylic acid, ester, epoxide, glycoside and ether (Simpson