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Review

Recent advances in the bioaccessibility and bioavailability of carotenoids and effects of other dietary lipophiles

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ABSTRACT

This article aims to highlight discoveries during the past 5 years regarding aspects of the bioaccessibility of carotenoids and apo-carotenoids, their uptake by intestinal cells, and their absorption that have received less attention in other recent reviews. New discoveries on the impact of various types of lipid on carotenoid bioavailability, their liberation from plant chromoplasts, and the effects of components such as pectin in the food matrix are discussed. Comparison of thermal and non-thermal processing techniques, as well as various styles of food preparation, also are considered. Finally, present knowledge of the impact of dietary lipids, including omega-3 fatty acids, fat soluble vitamins, phytosterols, and minerals, as well as novel excipient foods on carotenoid bioaccessibility and bioavailability, are considered.

1. Absorption of carotenoids and their products

1.1. Background

Carotenoids are a family of fat soluble pigments present in plants, photosynthetic microorganisms and some fungi that participate in the light harvesting processes required for photosynthesis, confer photoprotection, and possess anti-oxidant activity. Approximately 40 carotenoids are present in the human food supply (Wang, 2014). Carotenoids are further classified based upon chemical structure as carotenes (highly conjugated C40 hydrocarbon chains; e.g., lycopene, β-carotene and α-carotene), xanthophylls (oxygenated carotenes; e.g., lutein, zeaxanthin, and β-cryptoxanthin), apo-carotenoids (shortened carotenes and xanthophylls resulting from carotenoid metabolism (e.g., bixin, citral and abscisic acid) and C30 carotenoids (found in bacteria, e.g., 4, 4′-diapolycopene) (Britton et al., 2004). Examples of the chemical structures of these compounds are presented in Fig. 1. Provitamin A carotenoids contain at least one unsubstituted β-ionone ring (e.g., β-carotene, α-carotene, β-cryptoxanthin) and can be enzymatically cleaved to produce vitamin A, an essential micronutrient for human beings (Raghuvanshi et al., 2015). The potential biological functions of non-provitamin A carotenoids and their metabolites in mammals continue to be investigated. *In vitro* and *in vivo* studies have suggested numerous activities for ingested carotenoids and/or their metabolites. These include antioxidant (Stahl and Sies, 2003), anti-inflammatory and neuro-protective (Johnson et al., 2013; Mohammadzadeh Honarvar et al., 2017), anti-cancer (Giovannucci et al., 2002), cardio-protective (Sesso and Gaziano, 2004), vision protecting (Sabour-Pickett et al., 2012), lipid deposing and storage-modulating (Ip et al., 2015; Pickworth et al., 2012), photo-protective (Aust et al., 2005; Kopec et al., 2015), and immune-modulating (Chew and Park, 2004) activities. In order to mediate such activities, these compounds must be delivered to target tissues following ingestion.

1.2. The absorption process

The absorption and tissue distribution of carotenoids occurs by processes similar to that for other dietary fat soluble compounds (Fig. 2). Absorption requires that the carotenoids are first liberated from the food matrix and solubilized in oil droplets. Carotenoids are then transferred to bile salt mixed micelles that are generated during digestion of triglycerides (TAG), phospholipids and cholesterol esters to

Abbreviations: ABCA1, ATP-binding cassette transporter ABCA1 (member 1 of human transporter sub-family ABCA; BA, bioaccessibility; BCO1, β-carotene 15, 15′-dioxygenase; BCO2, β-carotene-9,10′-dioxygenase; CCE, carotenoid cleavage enzyme; CD-36, cluster determinant 36; CM, chylomicrons; FA, fatty acids; HDL, high density lipoprotein; HIPEF, high intensity pulsed electric field; HPH, high pressure homogenization; HPP, high pressure processing; LDL, low density lipoprotein; LRAT, lecithin-retinol acyltransferase; NPC1L1, Niemann-Pick C1 Like1; OFSP, orange fleshed sweet potato; RDH, retinol dehydrogenase; SR-B1, scavenger receptor class B type I; TAG, triacylglyceride; US, ultrasonication; VLDL, very low density lipoprotein

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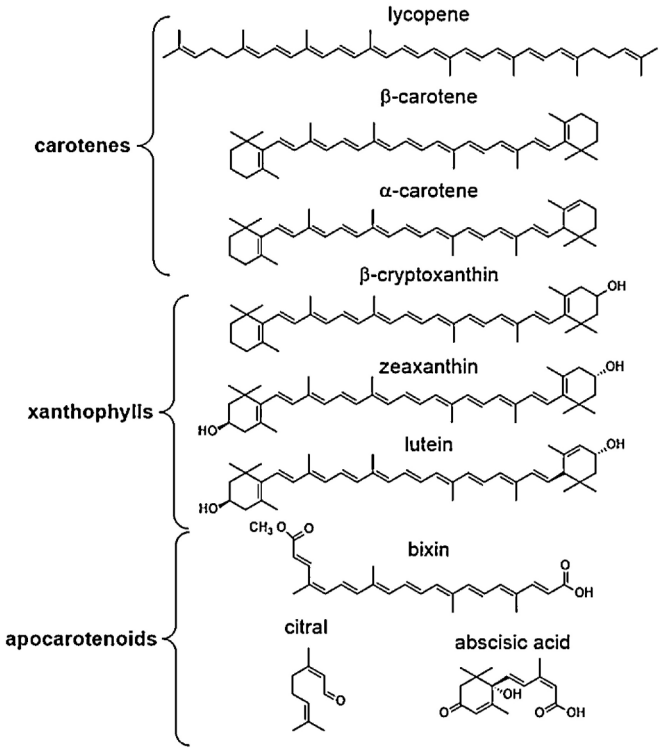

Fig. 1. Structures of common carotenoids.

form free fatty acids, mono- and di-acylglycerides, lyso-phospholipids, and free cholesterol (Harrison, 2012). The mean diameter of mixed micelles is less than that of the pores in the network of mucin glycoproteins (100–300 nm) that separate the intestinal mucosa from the lumen (Bajka et al., 2015). Therefore, the generated micelles diffuse through the mucin layer to the apical cell surface of the absorptive epithelial cells that line the luminal border of the gastrointestinal tract. Carotenoids and other fat soluble compounds interact with brush border proteins for transfer to the cell interior, bile salts in the micelles dissociate and are re-absorbed primarily in the ileum. Delivery across the apical membrane is facilitated via scavenger receptor class B type I (SR-B1), cluster determinant 36 (CD36), and possibly Niemann-Pick C1 Like1 (NPC1L1). It is unclear whether these proteins directly transfer carotenoids from the extracellular space to the cell interior, or whether they are components of membrane complexes responsible for internalization of the carotenoids (Reboul, 2013). Because these proteins also mediate the transport of other fat soluble dietary compounds and products of lipid digestion, they may compete with carotenoids for binding and cellular uptake. Passive diffusion of carotenoids across the brush border membrane of absorptive epithelial cells is also believed to occur at supra-physiologic concentrations.

Once within the cell, a portion of provitamin A carotenoids may be cleaved to retinal by cytoplasmic β-carotene 15, 15′-dioxygenase (BCO1). This is followed by reduction of retinal to retinol by retinol dehydrogenase (RDH) and esterification by lecithin-retinol acyltransferase (LRAT) to produce retinyl esters. Mitochondrial β,β-carotene-9,10′-dioxygenase (BCO2) is also expressed in the mucosal epithelium (Raghuvanshi et al., 2015) where it is localized in the inner mitochondrial membrane (Palczewski et al., 2014). Mechanisms remain undefined for the delivery of carotenoids to the cleavage enzymes, but this process likely involves cytosolic or fatty acid binding proteins (Reboul, 2013). BCO2 has been shown to catalyze the eccentric cleavage of both provitamin A and non-provitamin A carotenoids generating compounds such as β-apo-8′, 10′ and 12′-carotenals, β-ionone, 3-hydroxy-β-apo-10-carotenal and 3-hyroxy-α-apo-ionone (Keifer et al., 2001; Mein et al., 2011), and is upregulated during conditions of oxidative stress (Amengual et al., 2011; Babino et al., 2015). Indeed, minor amounts of β-apo-carotenals have been observed in homogenates of rat intestine after consuming a meal containing β-carotene (Barua and Olson, 2000) and in homogenate from human gastric mucosa briefly incubated with β-carotene *ex vivo* (Yeum et al., 1995). However, it should be noted that many enzymes are active in a tissue homogenate, and the specific influence of intestinal BCO2 was not determined as the enzyme had not yet been identified when these experiments were conducted. Furthermore, apo-carotenyl esters, the anticipated product for transport in the chylomicron fraction, have not been reported.

Within the cell, newly acquired fatty acids and mono-acylglycerols are re-esterified to TAG that are assembled into CM which are TAG-rich particles containing phospholipids, cholesterol, other dietary lipophiles

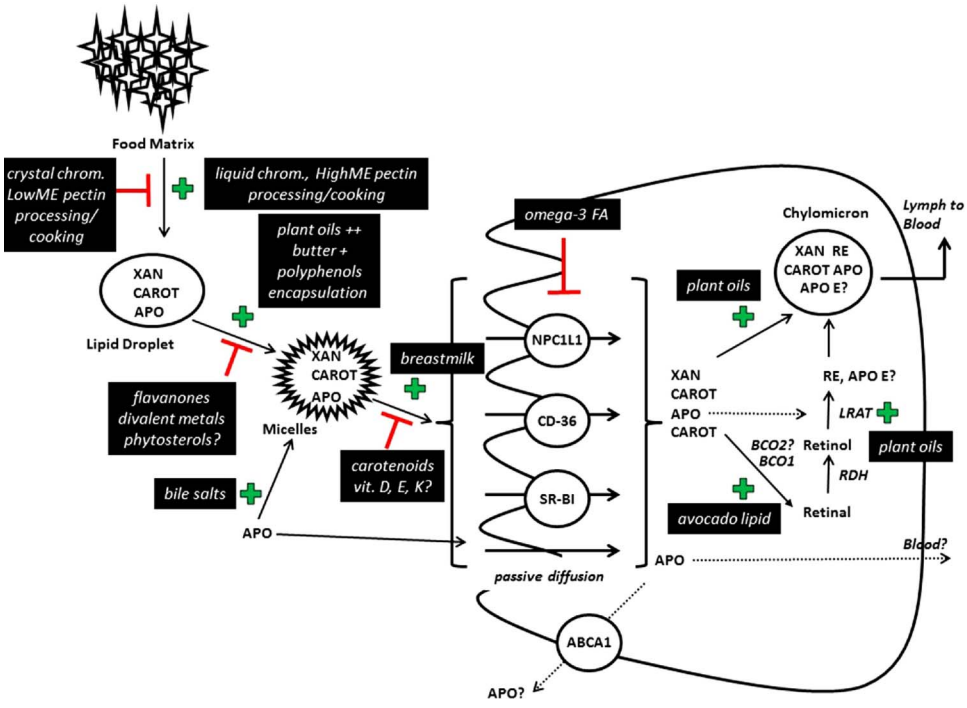

Fig. 2. Overview of the processes required for carotenoid release from the food matrix through their absorption. Factors that enhance (+) and diminish (−) carotenoid transfer at each step are highlighted. XAN = xanthophylls, CAROT = carotenes, APO = apo-carotenoids, RE = retinyl esters, APO E = putative apo-carotenoid esters. NPC1L1 = Niemann-Pick C1 Like1, SR-B1 = scavenger receptor class B type I, CD–36 = cluster determinant 36, LRAT = lecithin retinol acyltransferase, BCO1 = β-carotene oxygenase 1, BCO2 = β-carotene oxygenase 2, ABC1A1 = ATP binding cassette A1, RDH = retinol dehydrogenase, Crystal chrom = crystalline form in chromoplasts, liquid chrom. = carotenoid in liquid form in chromoplasts, LowME pectin = pectin with a low percentage of methylesters, HighME pectin = pectin with a high percentage of methyl esters, FA = fatty acid.

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