

Distribution of Carotenoids in Foods

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For more than two decades epidemiological studies have associated the high consumption of carotenoid-rich fruits and vegetables to a lower risk for human cancers [1]. The consumption of fruits and vegetables rich in specific carotenoids such as lutein, lycopene, α -carotene, and β -carotene in a human intervention study has been shown to significantly reduce the oxidative DNA base damage as was detected in the peripheral blood lymphocytes [2]. For a review of the case-controlled epidemiological studies and the role of carotenoids in disease prevention in humans see the publications by van Poppel [3] and Mayne [4]. Dietary intakes of carotenoids from fruits and vegetables as well as of individual carotenoids have been inversely associated with the risk of stomach, lung, breast, and prostate cancers [5-8]. For example, the evidence from one epidemiological study indicates that pre-menopausal breast cancer risk is inversely associated with intake of fruits and vegetables and specifically greens such as spinach that contains lutein, zeaxanthin, and β -carotene [9]. In another study, a strong association has been observed between carotenoid intake, plasma lutein and estrogen receptor status, linking a lutein-rich diet with improved prognosis after diagnosis of breast cancer [10]. Much has changed since these studies were first reported. In addition to β -carotene, other dietary carotenoids such as lutein, zeaxanthin, astaxanthin, lycopene, and α -carotene have also become commercially available. This has led to numerous studies that have investigated the role of a wide range of dietary carotenoids in the prevention of chronic diseases such as cancer [3, 11], cardiovascular

disease [12, 13], and age-related macular degeneration (AMD) [14-21]. Recent advances in understanding of the distribution, absorption, metabolism, and chemopreventive properties of dietary carotenoids and their metabolites has provided researchers with a unique opportunity to further investigate these essential nutrients. The ability to establish a statistically sound relationship between dietary intake of carotenoids and the incidence of chronic disease requires detailed understanding of qualitative and quantitative distribution of these compounds in food supply as well as in human plasma, major organs, and tissues. In the past two decades, technological advances in high performance liquid chromatography (HPLC) have provided analysts with powerful new tools to separate and quantify carotenoids and low levels of their metabolites in foods and biological samples from humans and animals. The following is a review of the qualitative distribution of carotenoids in foods.

Classification of Carotenoid Containing Foods and Major Dietary Sources of Carotenoids

1. Greens

The major carotenoids in green fruits and vegetables can be classified as: hydroxycarotenoids, epoxy-carotenoids, and hydrocarbon carotenoids. In addition, these foods also contain substantial amounts of chlorophylls *a* and *b* and their derivatives pheophytin *a* and *b*. The qualitative distribution of carotenoids in most fruits and vegetables, for the most part, remains nearly the same while the quantitative distribution of individual carotenoids varies depending on the nature of the food. Other green fruits and vegetables have very similar carotenoid profiles [22, 23]. The chemical structures of some of the abundant xanthophylls in green vegetables are shown in Figure 2.

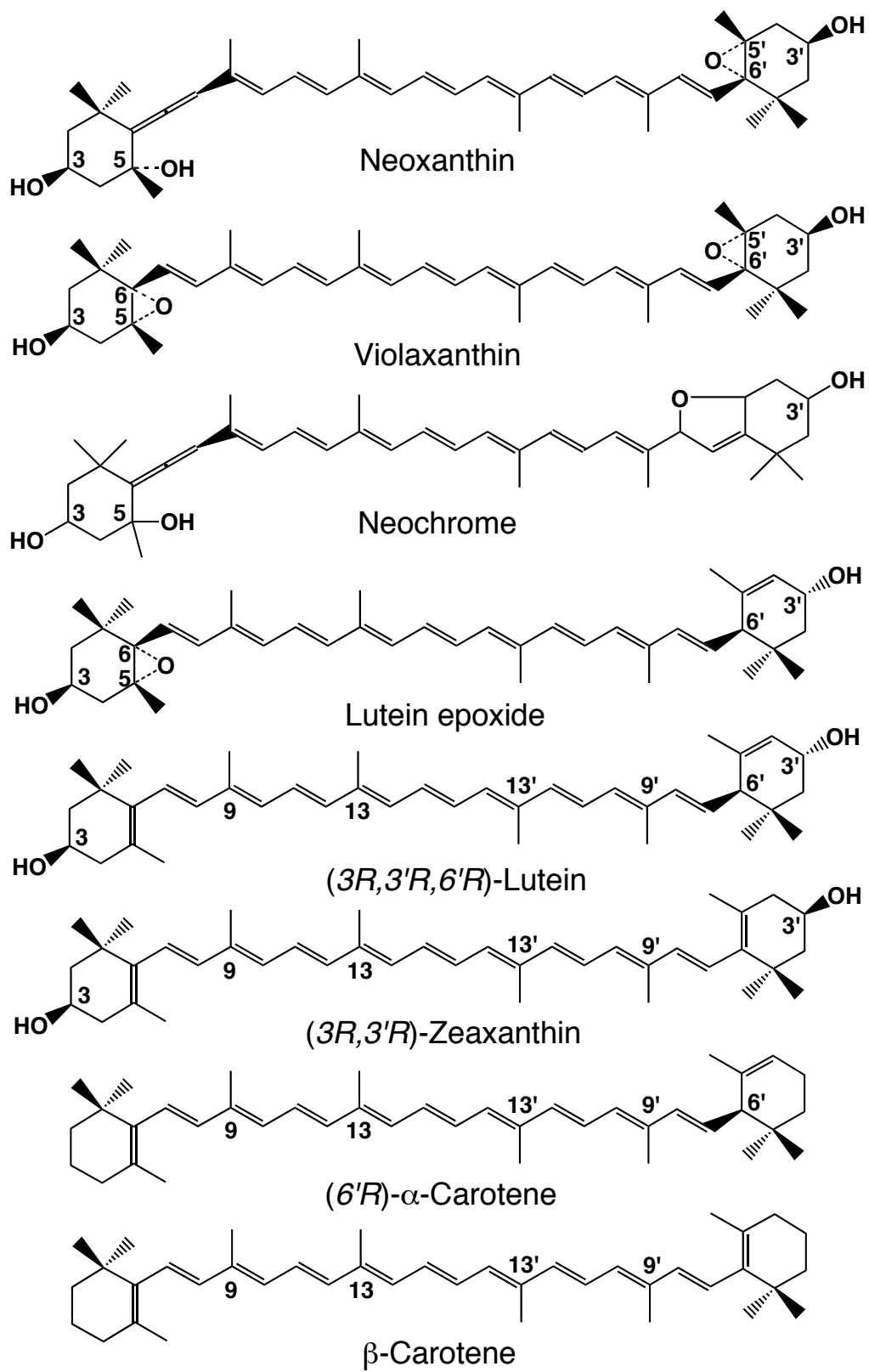


Fig. 1. Chemical structures of major xanthophylls in green vegetables.

2. Yellow/Red

The yellow/red fruits and vegetables contain mostly hydrocarbon carotenoids (carotenes). The common yellow ones are apricot, cantaloupe, carrot, pumpkin, and sweet potato that are the primary sources of α -carotene and β -carotene and several other hydrocarbon carotenoids [24, 25].

The typical red fruits, i.e. tomato, pink grapefruit, and watermelon are major dietary sources of carotenoids such as lycopene, ζ -carotene, phytofluene, phytoene and to a lesser extent also contain neurosporene, γ -carotene, and β -carotene [25-27]. All of the hydrocarbon carotenoids of the yellow/red fruits and vegetables are absorbed by humans [6, 7]. However, lycopene is one of the most important carotenoids in this group since tomatoes and tomato-based food products, which are the main source of this compound, constitute a large proportion of fruit consumed in the Western diet [27]. Consequently, a high concentration of lycopene is normally found in human serum. In a study by Giovannucci et al., a high intake of foods rich in lycopene has been inversely correlated with a lower risk for the incidence of prostate cancer [8]. In addition to lycopene, tomatoes and tomato-based food products are the major sources of other carotenoids such as phytoene, phytofluene, ζ -carotene, γ -carotene, β -carotene, neurosporene [23, 26-28]. The chemical structures of these carotenoids are shown in Figure 2.

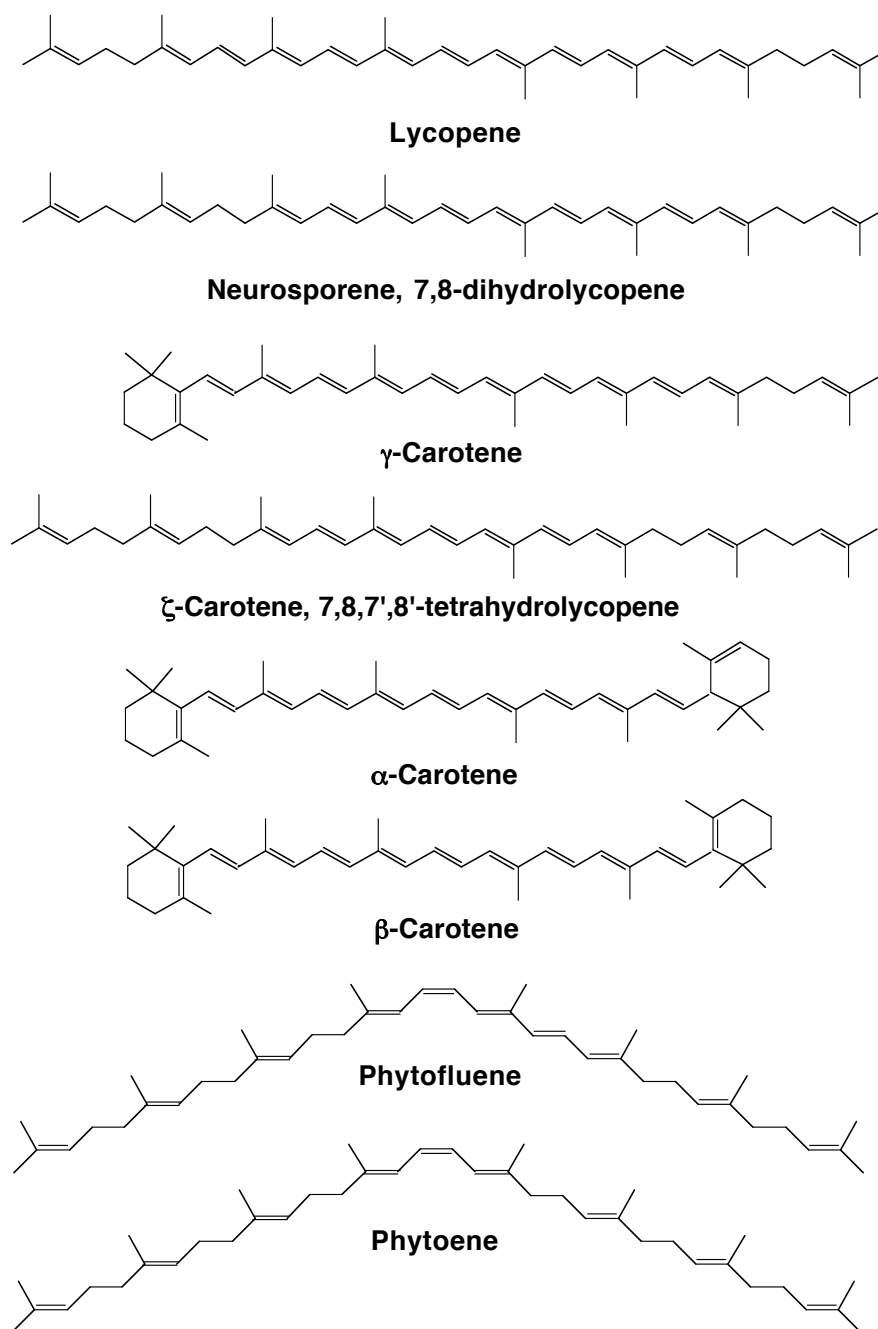


Fig. 2. Chemical structures of carotenoids in tomatoes and tomato-based food products.

Other commonly consumed fruits in the U.S. that contain lycopene are pink grapefruit and papaya. Apricots (fresh, canned, dried) also contain low concentration of lycopene and related carotenoids [25]. Among the yellow/red fruits and vegetables which are the major source of hydrocarbon carotenoids, only β -carotene, α -carotene, and γ -carotene are precursors of

vitamin A. Other tomato-based food products have similar carotenoid profile although depending on the nature of the foods, the concentrations of individual carotenoids vary.

Because the reduced risk of prostate cancer has been specifically correlated with the high consumption of tomato-based food products, this protective effect has been largely attributed to lycopene [8, 29-31]. Although lycopene is the major carotenoid in these foods, the presence of a wide range of other carotenoids in tomato-based food products cannot be overlooked [32]. It is quite likely that lycopene in combination with other related tomato carotenoids mentioned above, might be responsible for the observed biological activity. In 1995, Tonucci et al. reported on the qualitative and quantitative distribution of carotenoids in name brand and store-brand tomato-based food products purchased in three major U.S. cities [27]. While lycopene has, to some extent, been investigated for its biological properties in the prevention of carcinogenesis, other major tomato carotenoids have not received much attention. Therefore, the contribution of other related tomato carotenoids besides lycopene to the chemoprevention of prostate cancer remains unclear. The qualitative and quantitative distributions of the major carotenoids in some of the most commonly consumed yellow/red fruits and vegetables have been published in several articles [23, 24-28, 33].

3. Yellow/Orange

The yellow/orange fruits and vegetables, e.g. mango, papaya, peaches, prunes, acorn and winter squash, and oranges, each have unique and complex carotenoid profiles [23, 25, 28, 34, 35]. This is because these foods, in addition to the carotenoids found in green and yellow/red fruits and vegetables described above, contain a number of hydroxycarotenoids and epoxides which are esterified with straight chain fatty acid esters such as lauric, myristic, and palmitic acids [23, 25, 28, 34, 35]. These esterified hydroxycarotenoids and carotenoid epoxides have not

been detected in human serum whereas the parent hydroxycarotenoids, i.e. α -cryptoxanthin (3-hydroxy- α -carotene), β -cryptoxanthin, lutein, and zeaxanthin, are present [23, 36-38]. These findings suggest that this class of carotenol esters undergo hydrolysis in the presence of pancreatic secretions to regenerate the free hydroxycarotenoids that are then absorbed into the bloodstream. The dietary importance of this class of fruits and vegetables should not be overlooked since these foods are sources of a variety of carotenoids that are absorbed, utilized, and metabolized by humans [36-39]. The structure of some of the most common carotenoid acyl esters in yellow/orange fruits and vegetables are shown in Figure 3.

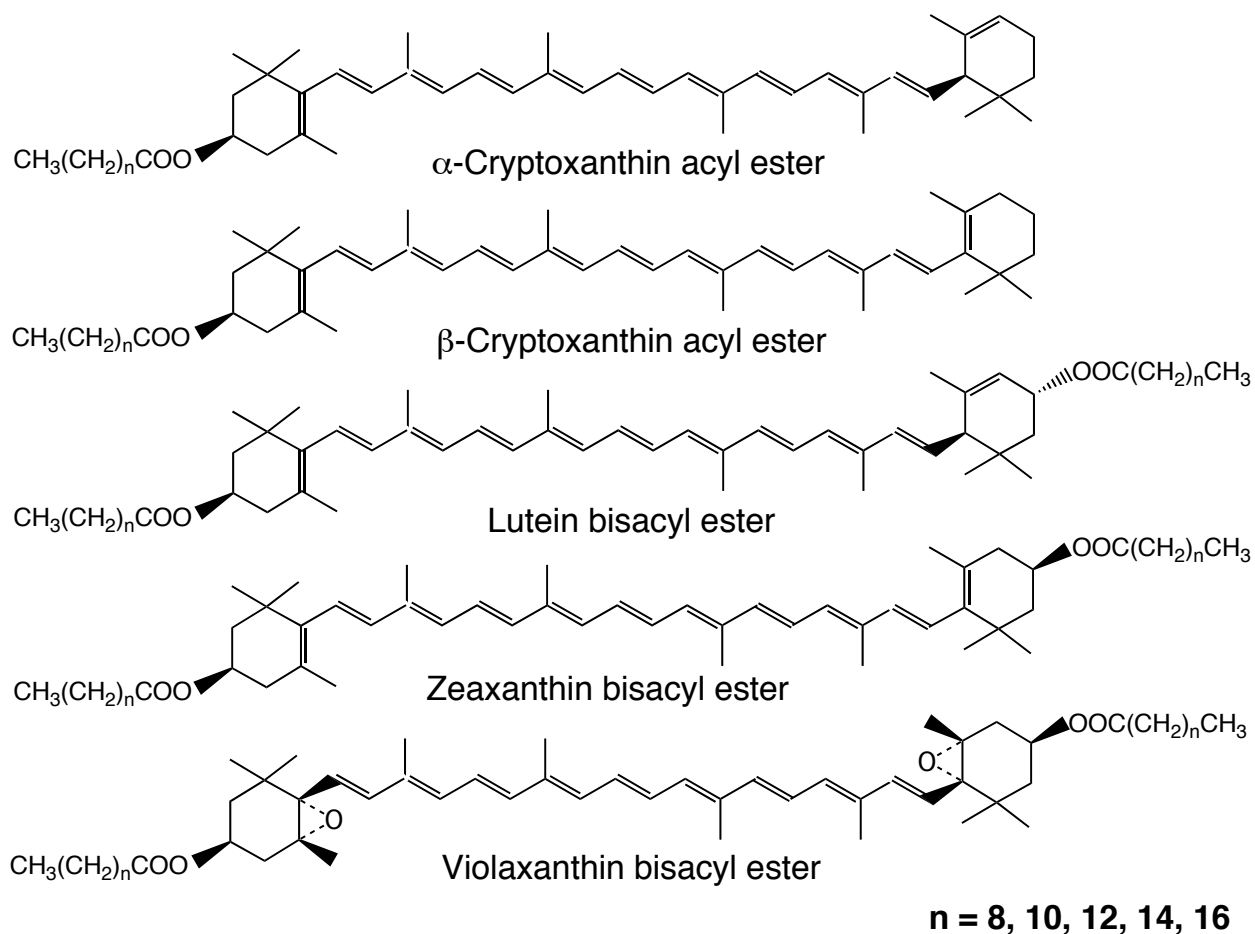


Fig. 3. Chemical structures of carotenoids in yellow/orange fruits and vegetables.

4. Wheat and Pasta Products

The major carotenoids of interest in wheat and pasta products are lutein and zeaxanthin since the high consumption of foods that contain these carotenoids has been associated with a reduced risk of age-related macular degeneration [14]. The origin of lutein and zeaxanthin in pasta products that are considered as basic foods in Western diets is due to the presence of these carotenoids in egg yolk. As an example, the distribution of lutein and zeaxanthin in two types of pasta products (Lasagne and egg noodles) and three varieties of wheat that have been measured and reported [40].

The carotenoid profiles of pasta products are similar to that of wheat and consist of mainly lutein, zeaxanthin and their stereoisomers.

The Effect of Cooking and Processing on Qualitative and Quantitative Distribution of Carotenoids in Foods

Owing to the sensitivity of carotenoids to heat, light, and oxygen, in generation of analytical data on carotenoid-containing foods, one has to be concerned about the effect of cooking and processing on qualitative and quantitative distribution of these pigments. As a result of heat treatment, carotenoids may undergo oxidative degradation, structural transformation, and/or stereoisomerization. It is reasonable to assume that food carotenoids that have been classified into various groups according to their chemical structures (i.e., hydroxycarotenoids, epoxy-carotenoids, hydrocarbons, etc.) would be expected to exhibit different stability towards heat treatment. In fact, most of the existing data to date is in agreement with such an assumption. For example, a study of the effects of cooking and processing on a number of yellow-orange vegetables (carrot, sweet potato, pumpkin) has demonstrated that the destruction of the

hydrocarbon carotenoids such as α - and β -carotene as a result of heat treatment is about 8-10% [24]. It is often very difficult to compare various analytical data with regard to the effects of cooking and processing on carotenoid levels in fruits and vegetables that have been reported by different sources. In most cases, this is owing to the lack of extensive data on the history of the samples (i.e., cultivar, growing season, location), the length of cooking, and the method of preparation (i.e., frying, steaming, boiling, baking, microwave cooking) of cooked foods that can result in variability in analytical data. Examination of the raw and cooked extracts from several green vegetables (kale, Brussels sprouts, broccoli, cabbage, spinach) has demonstrated that some of the major chlorophyll and carotenoid constituents of these vegetables undergo some interesting structural transformation, once subjected to heat [22].

For example, a comparison between the carotenoid profile of raw and cooked Brussels sprouts, has indicated that lutein, zeaxanthin, α -carotene, and β -carotene survive the cooking process while considerable amount of carotenoid epoxides are destroyed as a result of cooking [22]. It must be stressed that the degradation, rearrangement, and stereoisomerization of carotenoids and chlorophylls are expected to be greatly influenced by the severity and the length of cooking as well as the means by which the vegetables were cooked (i.e., frying, steaming, boiling, microwave cooking, etc.). Therefore, these factors would be expected to affect the extent to which the integrity of each carotenoid may be changed in cooked foods.

As a result of various food preparation techniques, food carotenoids, in addition to degradation, may undergo three types of chemical reactions, these are: 1) rearrangement, 2) dehydration, and 3) oxidation. The scope of each of these reactions is dependent on the nature of carotenoids, the food matrix, and the method of preparation. The best examples of the rearrangement reactions of carotenoids is the well known conversion of 5,6- to 5,8-epoxides in

green vegetables which can even take place as a result of mild heat treatment and in the presence of traces of naturally occurring acids [22]. The rearrangement of the carotenoid 5,6-epoxides commonly found in greens to their counterpart 5,8-epoxides, i.e. neoxanthin to neochrome, violaxanthin to auroxanthin, and lutein 5,6-epoxide to lutein 5,8-epoxide is shown in Figure 4.

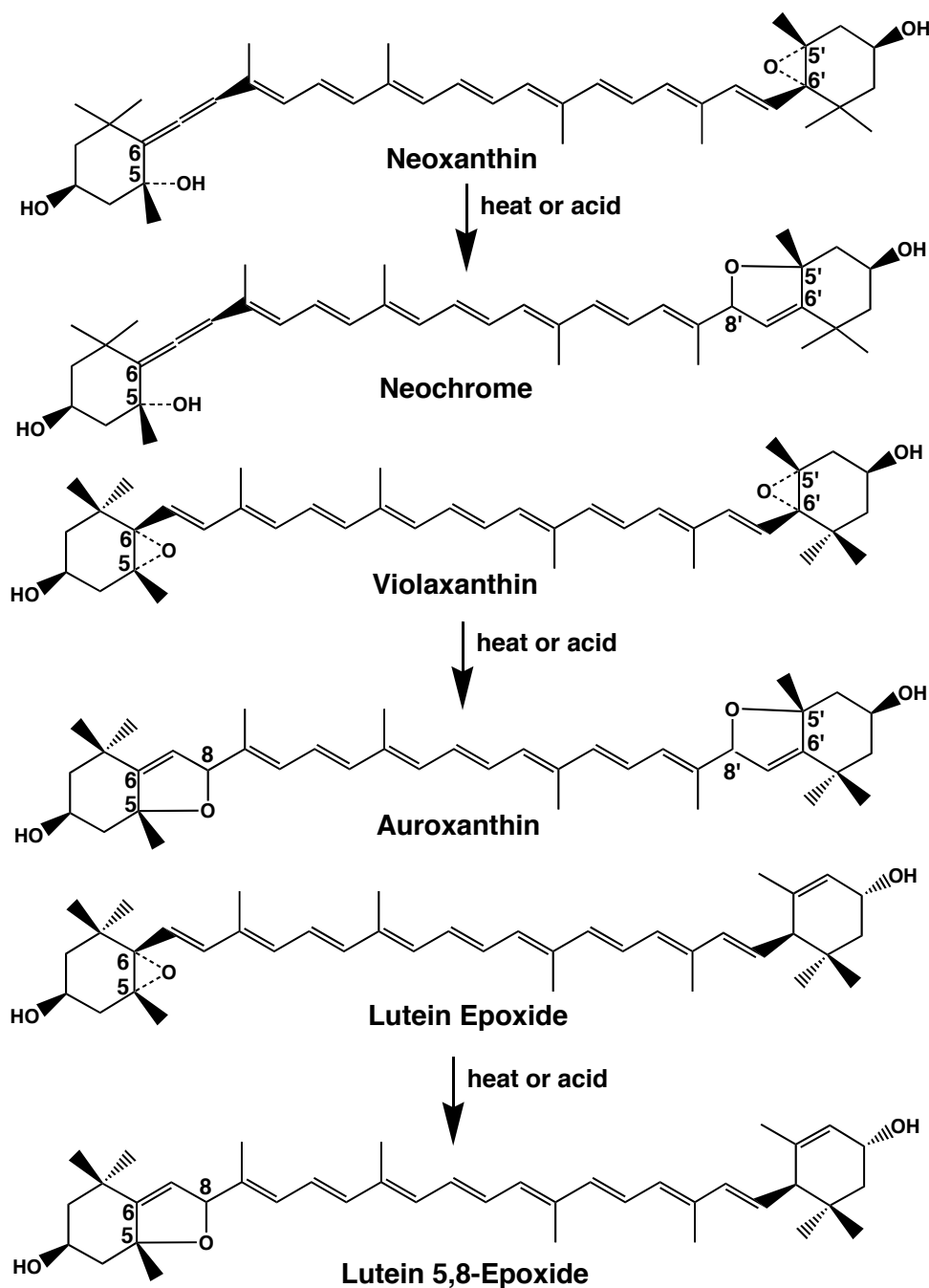


Fig. 4. Chemical transformation of carotenoid epoxides in fruits and vegetables induced by heat and acid.

The quantitative loss and rearrangement of carotenoid 5,6-epoxides in cooked foods should not be of great concern since these compounds and their by-products have not been detected in human serum or plasma [35, 36]. Although the biological activity and the metabolic fate of carotenoid epoxides and their degradation products in humans is not known at present, it appears that this class of carotenoids is either not absorbed or may undergo certain metabolic modifications before they are excreted.

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