CHOLESTEROL OXIDATION PRODUCTS

Their Occurrence and Detection in Our Foodstuffs

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1. ABSTRACT

The structural similarity of cholesterol oxidation products (COP) to native cholesterol and their xenobiotic effects prompt researchers to study the long-term effects of the assimilation of these compounds into our tissues. COP are present in our food system. The level of exposure changes as our food products and our food choices alter. Therefore, the presence of COP in our food system has to be carefully monitored and their presence in processed foods minimized by optimizing processing and storage conditions. This review will briefly discuss the chemistry of some commonly-occurring COP and their biological significance. A more in-depth survey of the literature on the pitfalls of COP determination is included. It is the intention of the author to impress the readers that 'exogenous' COP can easily form during sample preparation. These artifacts will hinder our understanding of factors that promote COP formation in foods. The effects of heating, dehydrating, packaging and the presence of highly unsaturated lipids on the levels of COP in cholesterol-containing foods are evaluated to gauge the levels of exposure to different consumer groups.

2. CHOLESTEROL AUTOXIDATION

Cholesterol, with its double bond between the C-5 and C-6 of the B-ring (Figure 1), readily undergoes oxidation via the free radical mechanism to form some 66 cholesterol oxidation products (COP). Research in this area is explored extensively in a monograph (1981) and in several reviews by Dr. Leland Smith (Smith, 1987; Smith, 1991). Readers are asked to seek out any one of these works for detailed reactions of cholesterol autoxidation.
Figure 1. Cholesterol molecule with ring labeling and carbon numbering. Cholesteryl ester molecule depicting the fatty acid portion esterified to the cholesterol portion. From Paniangvait et al. (1995).

At low temperatures, as protons in the allylic C-7 and the tertiary C-25 positions of the cholesterol molecules are abstracted, their respective free radicals are formed. Both of these radicals react with oxygen to give the corresponding peroxyl radicals. However, only the C-7 peroxyl radical survives at room temperature and this becomes the first detectible COP, the epimeric 7-hydroperoxides (Figure 2). These hydroperoxides undergo thermal decomposition to form the epimeric cholest-5-ene-3β-7-diols (7-hydroxycholesterols) and 3β-hydroxycholest-5-en-7-one (7-ketocholesterol). Further decomposition of the latter compound forms cholesta-3,5-dien-7-one. Detection of this compound indicates degradation of 7-ketocholesterol by harsh sample preparation procedures.

Epoxidation of the Δ5-double bond may occur by the attack of 7-hydroperoxides already present and yields the isomeric 5,6-epoxycholestan-3β-ol (epoxycholestanol). The β-isomer usually predominates because of its more sterically hindered epoxide. Both isomers can further degrade into cholestane-3β,5α,6β-triol (cholestanetriol) by hydration.