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In the past, the role of tocopherols and tocopheryl hydroquinones as antioxidants in

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mitochondria has been examined. However, structural properties of tocopherols and tocopheryl quinones (arrangement of polar/apolar moieties) have also been recognized as being crucial for the selective transport of RRR- α -congeners compared with other tocopherols in the cell, suggesting that these properties might be generally important for the binding of vitamin Erelated compounds to proteins and enzymes in mitochondria. Therefore, direct modulation of mitochondrial activities, such as bioenergetics, production of reactive oxygen species and apoptosis, not exclusively related to the redox activity of these compounds is increasingly studied. This overview focuses on the influence of α -/ γ -tocopheryl quinones and their parent α -/ γ -tocopherols on mitochondrial functions, including formation of tocopheryl quinones, their analytical aspects, their potential as alternative substrates and their inhibitory activity for some mitochondrial functions. It is shown that the understanding of how tocopheryl quinones and tocopherols interfere with mitochondrial functions on the molecular level is still incomplete and that a better comprehension requires further research activities.