

ON THE "IN VITRO" DECOMPOSITION OF TOCOPHEROLS*

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The efficiency of tocopherols "in vitro" and "in vivo" is in close connection with the transformation products due to their various functions. This fact explains for the increasing concentration of recent tocopherol research on the chemistry of decomposition products of tocopherols especially on those of "in vitro" decomposition.

Experimental conditions are too varied and ramified to permit a complete critical review of all work done in this field. In food chemistry and technology, however, undoubtedly the oxidative changes are of utmost importance which directly influence the composition and biological value of food containing tocopherols. In our present paper, therefore, we shall give a short account only of the oxidative decomposition products of tocopherols.

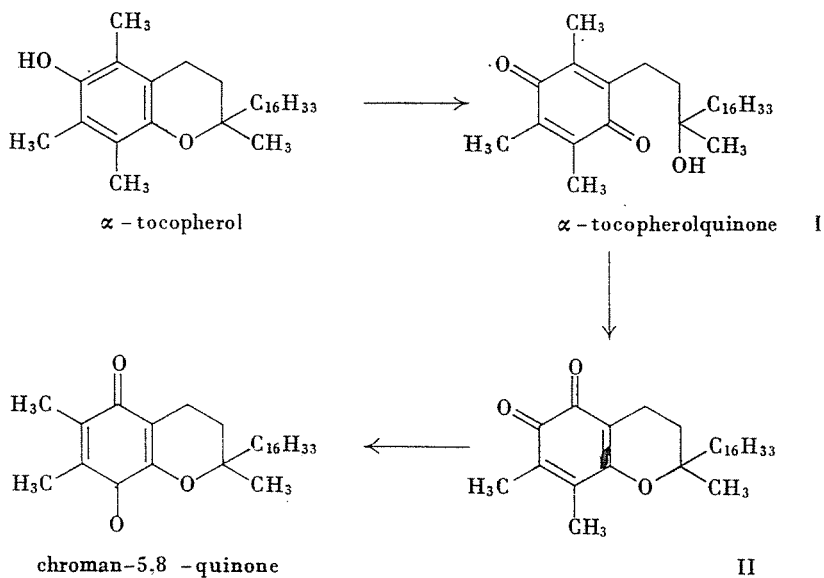
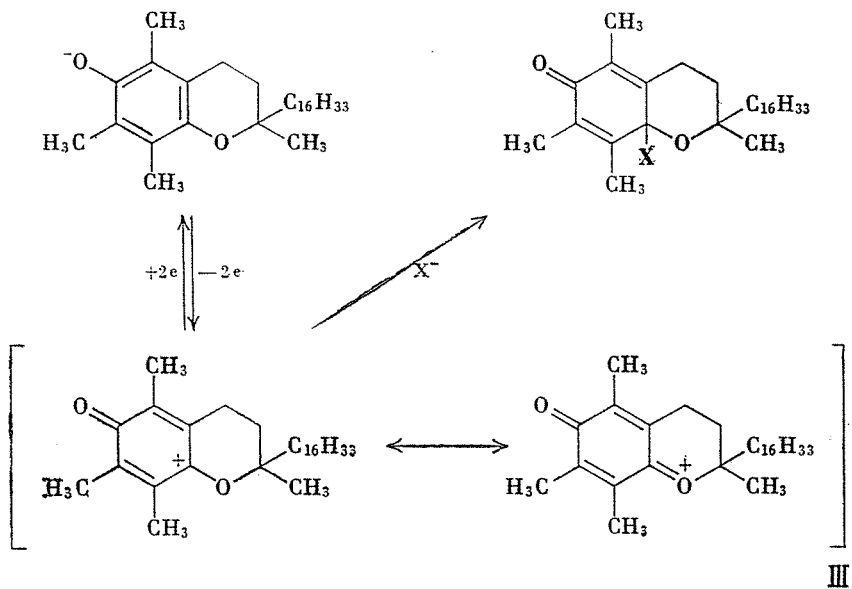
The first identified oxidation product of α -tocopherol was the α -tocopherylquinone (I) produced simply with ferric chloride [1, 2]. A prolonged oxidation — especially at elevated temperatures — facilitates recyculation to give the chroman-5,6-quinone (II). This compound known also as α -toco-red has been isolated from natural sources, from vegetable oils, too. Under acid conditions α -toco-red isomerizes to chroman-5,8-quinone.

According to numerous observations, the α -tocopherylquinone might play some specific role in biochemical systems, therefore the circumstances of the formation of such quinonoid metabolites have been thoroughly investigated. It was found that α -tocopherylquinones can be formed on various ways: through the very unstable " α -tocopheroxide", or through some other 9-substituted α -tocopherones (III) by oxidation in ethanolic acetic acid solution [3], or in the presence of benzoyl peroxide [4].

The last mechanism is of special importance, since it shows that α -tocopherylquinone can be formed also *indirectly* by a monovalent oxidation of α -tocopherol (IV), whereas by *direct* monovalent oxidation mainly dimer structures are produced. Bivalent oxidation does not lead to dimeric substances.

In the course of the ferricyanide oxidation of α -tocopherols, simultaneously with the formation of α -tocopherylquinone, dimerization takes place [5], due to which di- α -tocopherone (V) is produced. This compound has cis

* Dedicated to Prof. Z. Csűrös on the occasion of his 70th birthday.

Fig. 1. α -tocopherylquinone; Chroman-5,6-quinoneFig. 2. Formation of α -tocopherylquinone through 9-substituted α -tocopherones

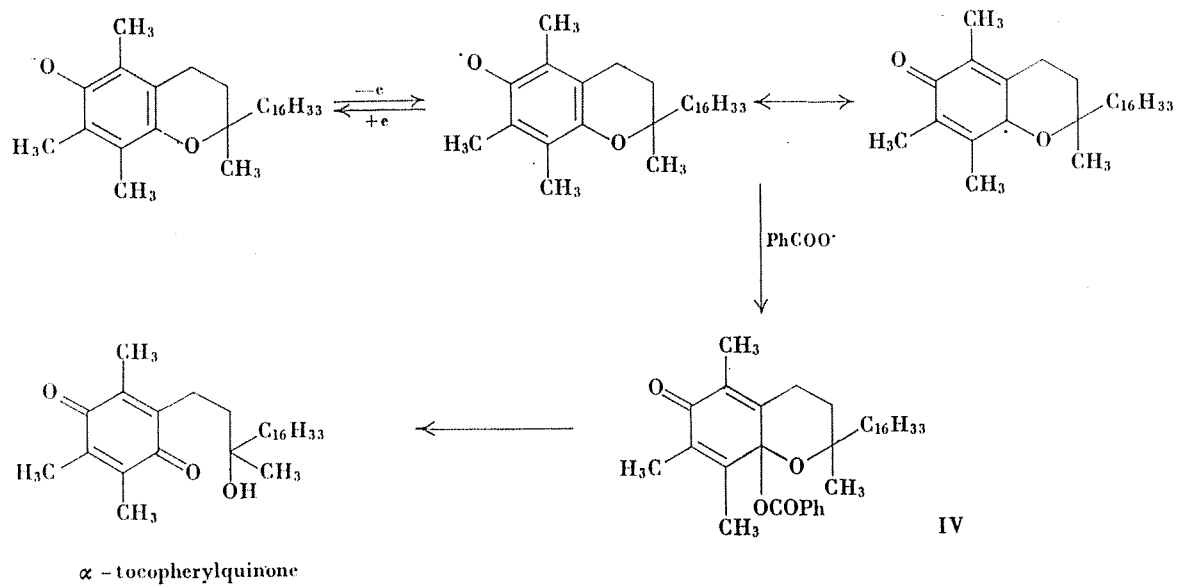


Fig. 3. Monovalent oxidation of α -tocopherol

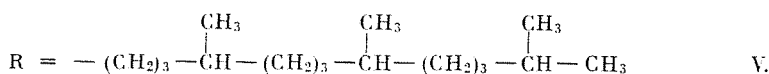
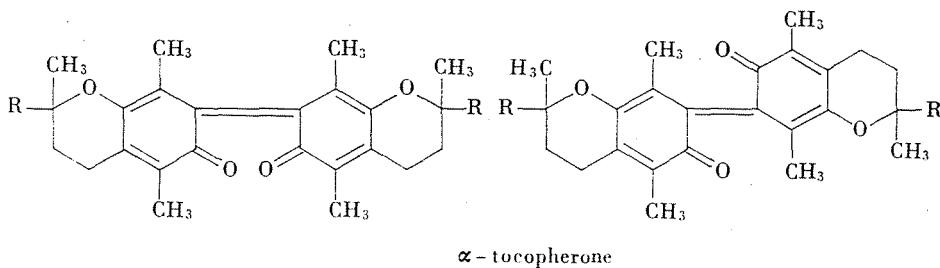


Fig. 4. Production of di- α -tocopherone by dimerization

and trans isomers, with very different physical characteristics (e.g. solubility) among each other, both qualitatively and quantitatively.

Again with ferricyanide but under different experimental conditions a dimer of different structure has been isolated: the spirodienone-ether (VI). The formation of this compound can be explained by the monovalent oxidation of α -tocopherol. The resulting radicals dimerize to tocopherylethane, which then undergoes further oxidation to form a new ring characterized as spirodienone-ether [6].

Between the two groups of investigators an interesting discussion on the real structure of the dimer formed by ferricyanide-oxidation arose; we shall explain our opinion about the problem on hand of our own experimental data.

Much work was done on the oxidation effects of irradiation. It was observed that ultraviolet light produced semi-quinone radicals [7]; γ -radiation produced mainly the quinone-methide (VII), or α -tocopherylquinone, when α -tocopherol was irradiated in peroxidizing lipid [8], whereas CSALLÁNY et DRAPER [9] isolated α -tocopherylquinone together with the dimer: di- α -tocopherone. All that points out that the α -tocopherol is very sensitive to the actual circumstances of oxidation and that the many controversial data on the subject published in the literature are due to the differences in experimental conditions.

Relatively few studied oxidation products of the β - and γ -tocopherols, although recent observations showed that these quinonoid products might have biochemical importance too, in the protection of isolated chloroplasts against reduction [10]. With β -tocopherol, ferric chloride oxidation gives

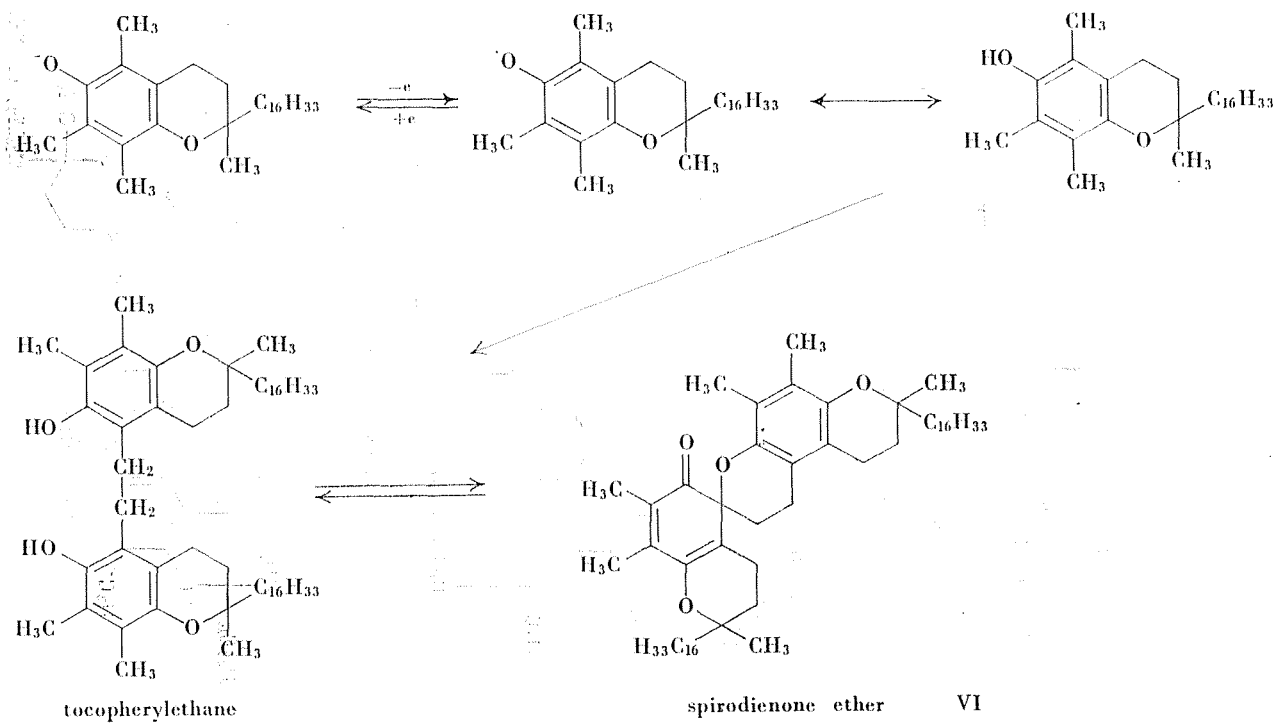


Fig. 5. Spirodienone-ether

β -tocopherylquinone; in the case of γ -tocopherol, however, two quinones are formed; γ -tocopherylquinone and chroman-5,8-quinone, the isomer of α -tocopherol. The position of the aromatic methyl groups in the tocopherols seems to play an important role in affecting the course of these and other oxidation reactions.

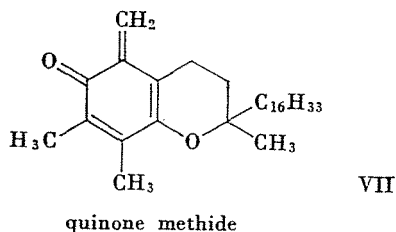


Fig. 6. Quinone-methide

Under entirely laboratory conditions and special circumstances, from the ferricyanide oxidation products of α -tocopherol a *trimer* (VIII) could also be isolated [11, 12].

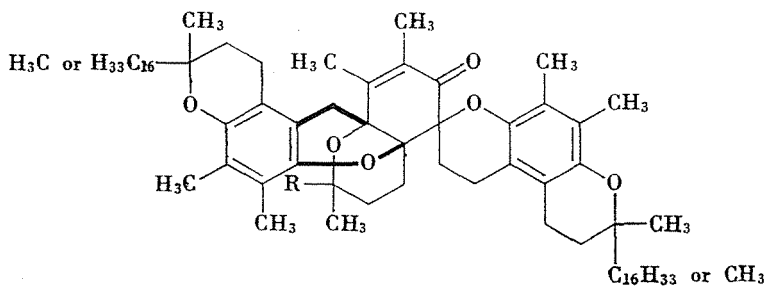
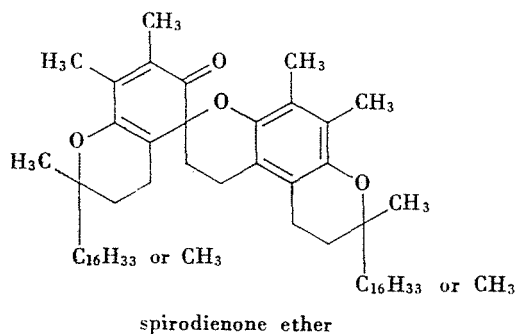


Fig. 7. Trimer oxidation product of α -tocopherol

In the first part of our own experimental work, we produced and isolated various oxidation products of α -tocopherol, in order to have sufficient etalons of known parameters for the check and identification of decomposition products obtained by simple and complicated oxidation mechanisms.

Thus, ferric chloride and ferricyanide oxidation products have been prepared. For isolation of the products thin layer-chromatography, for their

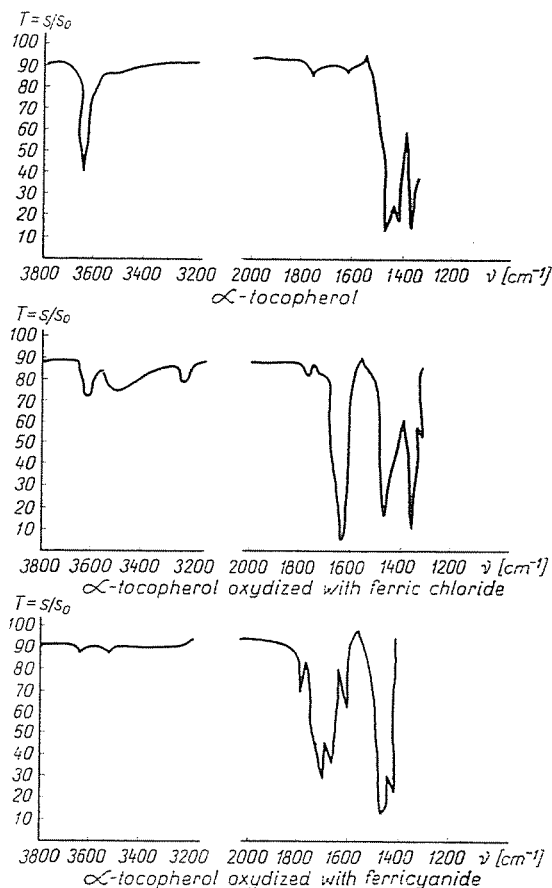


Fig. 8. IR absorption spectra of the oxidation products of α -tocopherols

identification IR absorption spectrophotometry was used. From our data it is clear that α -tocopherol oxidized with ferric chloride yielded almost entirely quinone, with ferricyanide quinone and the dimer: di- α -tocopherone.

In the second part of our work the effects of UV irradiation have been investigated by methods published previously [13]. After 5 hours of irradiation no effects could be detected. A longer treatment, however, led to oxida-

tion products: dimer and a small quantity of quinone were identified; furthermore a new band appeared produced by the hydrogen bonds formed between the tocopherol-hydroxyls and some groups of the dimer. To ease comparison, the spectrograms of the tocopherol and its irradiation products are shown on one diagram.

It is noteworthy that in the detection of the oxidation products, TLC was a much more sensitive method than was IR absorption, since minor

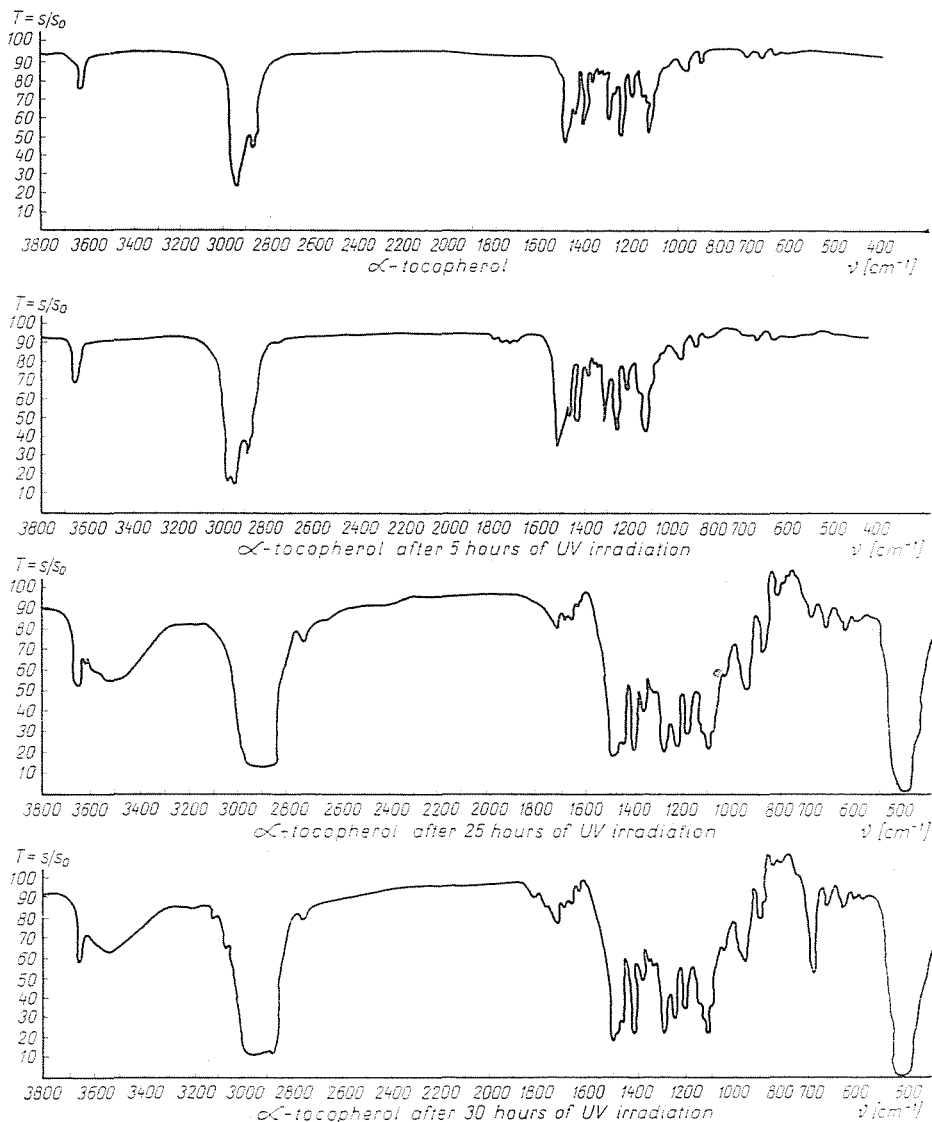


Fig. 9. IR absorption spectra of UV irradiation products of α -tocopherols

changes after 10 hours of irradiation could be detected only by the former method.

In the third part of our experimental work using the *Activated Oxygen Method* (AOM), that is a continuous air current at 120° C for oxidation the α -tocopherol decomposed to the dimer. That is clearly demonstrated by a comparison of the compound so formed with the IR spectrogram of the ferricyanide oxidation product.

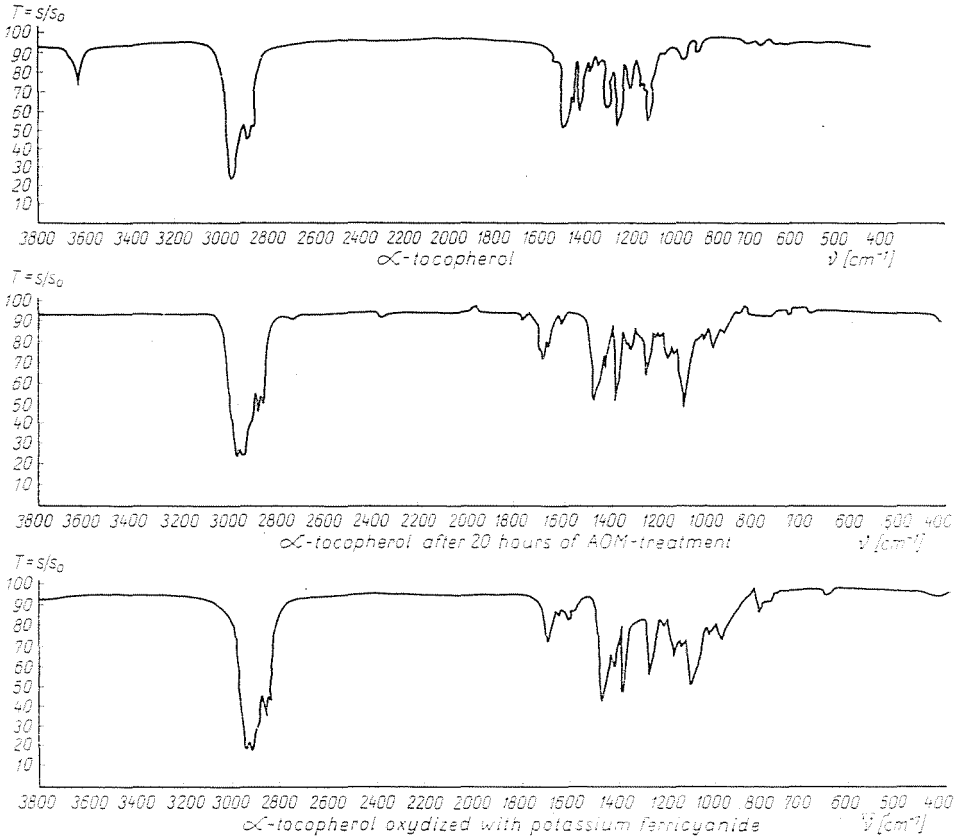


Fig. 10. IR absorption spectra of α -tocopherols after AOM-oxidation

Summarizing the results, our experimental data on the "in vitro" decomposition of tocopherols clearly show that the oxidation mechanism of α -tocopherol is of great variety depending on the conditions of the oxidation. These variations lead to the formation of different products which seem to represent types of decompositions. Such types are the quinone formed with ferric chloride, the dimer produced with ferricyanide, which can be found also

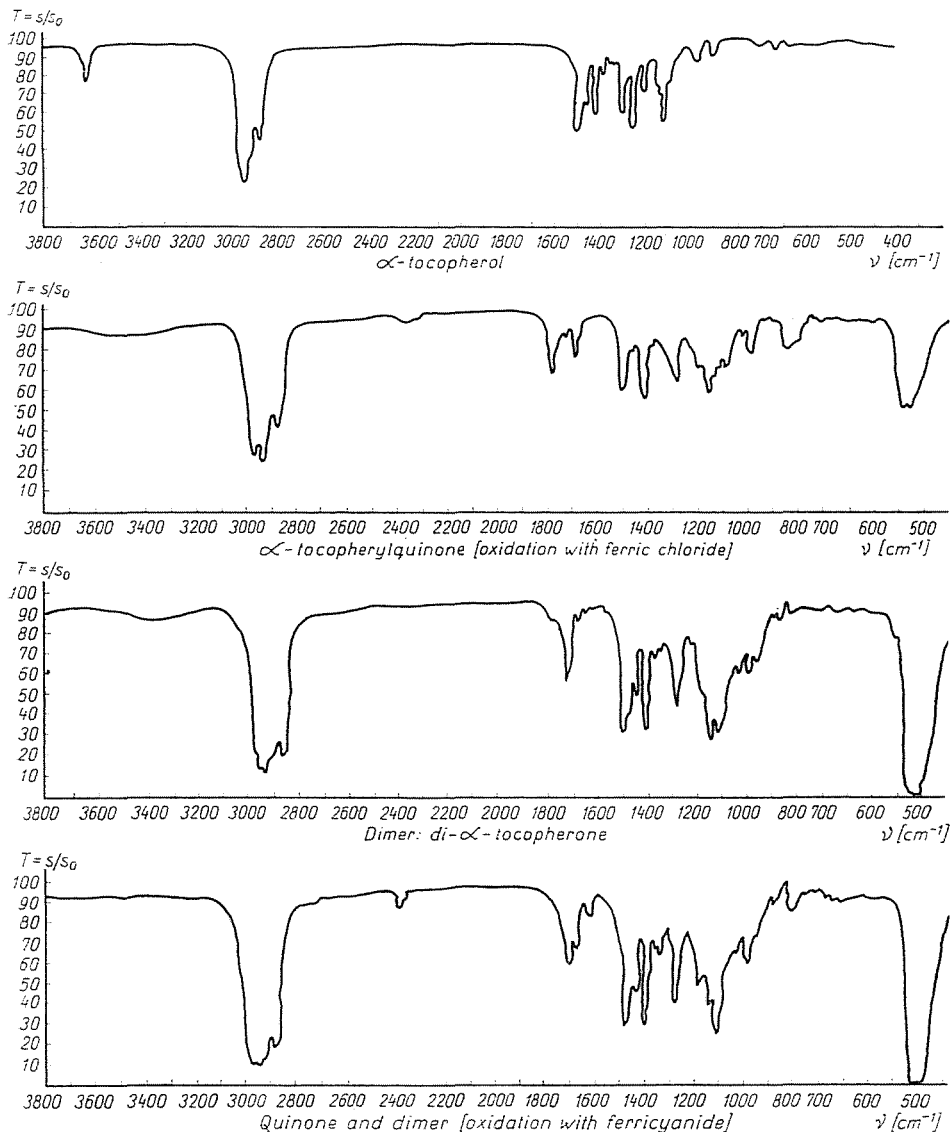


Fig. 11. Comparison of products of various types of oxidation mechanism

as a product of methods simulating natural circumstances as AOM or UV irradiation.

A repetition of the same experiments with α -tocopherols solved in vegetable oil gave similar results. The α -tocopherol acting as antioxidant was converted — to a greater extent — into the dimeric product, and — to a smaller extent — into quinone. Thus the circumstances of one type of the “in vitro”

decomposition mechanisms have been elucidated, and the dimer formed as "di- α -tocopherone" identified. Investigations dealing with other types of oxidation mechanisms are going on.

Summary

The "in vitro" transformation and decomposition of tocopherols are of special importance for the food industries because the exact pathways of the decomposition of these powerful antioxidants under technological circumstances are rather unknown. Accordingly, various oxidation products have been prepared and isolated by means of which the derivatives produced during technological influences could be identified.

On the basis of derivatograms and IR absorption spectra of the oxidation products it was tried to elucidate the probable mechanisms of decomposition of tocopherols under practical "in vitro" conditions.

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