

Mass Spectra of Chromanols Related to Tocopherols*

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To study the fragmentation pattern of the chroman moiety of various tocopherols, mass spectra for the 6-chromanols 1–8 have been recorded. The data are

summarized in Table I and the fragmental structures are depicted in Scheme 1.

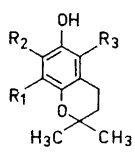
The naturally occurring tocopherols (vitamin E) are all derivatives of 6-chromanol with an isoprenoid side chain in position 2. We have recently investigated the oxidation of the tocopherols and of their model compounds¹ in which the side chain has been replaced by a methyl group. In connection with this work we have recorded the mass spectra presented here.

Mass spectra of tocopherols have so far been little studied. Mayer *et al.*² have

* Tocopherols XIII. Paper XII in this series, see Ref. 1.

Table I. Relative intensities (%) of the principal peaks in the mass spectra of chromanols 1–8. Compounds

<i>m/e</i>	1	2	3	4	5	6	7	8
221	13							
220	81 M ⁺							
207		9	11	10				
206		50 M ⁺	73 M ⁺	70 M ⁺				
205	5		3					
193					12	8	12	
192					90 M ⁺	57 M ⁺	90 M ⁺	
191		4	8	6				
179								10
178								80 M ⁺
177	5	3	3	2	12	12	12	
165	92							
164	100							
163		6	4	5	3	3	5	22
152		6		10				
151		57	100	100				
150		100	77	43	8	3		
149		4				11	12	11
138					8	10	11	
137	4				83	100	100	
136	10				100	25	83	7
135	5			3				9
124								9
123								100
122		9	9	8				42
121	10	6	5		5	4	6	
108					13	9	14	
107	3	7	7	6	15	4	9	8
94								14
91	7	5	6	4	5	5	6	4
79	3	3	5	4	6	4	6	3
77	5	6	7	5	6	4	9	6
67	3	3	4	4	6	3	2	6
65	2	2	3	3	3	—	4	6
55	3	3	5	5	5	3	6	8
53	5	4	5	5	5	3	6	5
43	5	5	6	6	5	4	6	6
41	5	6	7	7	8	6	5	9
39	4	5	6	6	8	9	5	11

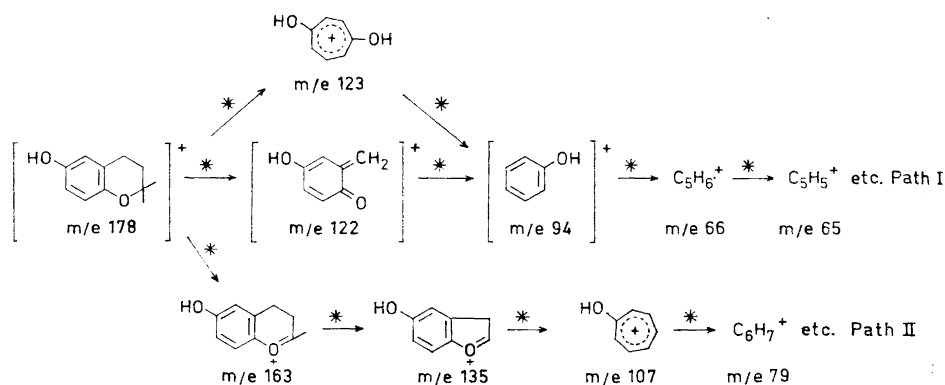
	R ₁	R ₂	R ₃		
	1	CH ₃	CH ₃	CH ₃	5,7,8-Trimethyltolcol model, α-model
	2	CH ₃	H	CH ₃	5,8-Dimethyltolcol model, β-model
	3	CH ₃	CH ₃	H	7,8-Dimethyltolcol model, γ-model
	4	H	CH ₃	CH ₃	5,7-Dimethyltolcol model,
	5	CH ₃	H	H	8-Methyltolcol model, δ-model
	6	H	CH ₃	H	7-Methyltolcol model
	7	H	H	CH ₃	5-Methyltolcol model
	8	H	H	H	Tocol model

published the spectra of γ -tocotrienol and of some chromanols related to plastoquinones. In a paper on the structure elucidation of tocopherol dimers isolated from corn oil, we have reported some details of the fragmentation of γ -tocopherol.³ The mass spectra of a number of cyclic aromatic ethers including chroman, 6-chromanol, and 2,2-dimethylchroman have been described by Willhalm *et al.*⁴

The spectra of all the chromanols studied here show three main peaks, one of which is due to the molecular ion (M^+) while the two other are due to ions formed by loss of a C_4 -fragment from the heterocyclic ring. This reaction occurs with or without hydrogen transfer and the peaks appear at M-55 and M-56. These fragments from the tocol model (8) are depicted in Scheme 1 as tropylium (m/e 123) and quinone methide (m/e 122) ions, respectively (Path I). Willhalm *et al.*⁴ found similar fragmentation from 2,2-dimethylchroman, but in this case always with hydrogen transfer to form the fragment M-55.

Another fragmentation route of the tocopherol models occurs *via* the loss of one of the geminal methyl groups (m/e 163; Path II in the Scheme). This reaction would be equivalent to the loss of the side chain which occurs in the fragmentation of γ -tocotrienol.² The further degradation after the methyl elimination occurs by ring contraction *via* the loss of a C_2 -fragment (m/e 135). Similar fragmentation is found in 2,2-dimethylchroman.⁴

The original motive for this work was to study the fragmentation pattern of the chromanol moiety of the various tocopherols by recording the mass spectra of their model compounds. The naturally occurring tocopherols differ only in the number and position of the aromatic methyl groups. We were therefore interested to see if the fragmentation pattern of the chroman structure, as previously¹ oxidation reactions, would be dependent on the positions of the aromatic methyl groups. This could then form the basis for a simple identification procedure of the



Scheme 1

tocopherols. However, all the compounds I-8 fragmented as shown in the Scheme with path I as the dominating route. In addition, peaks of uncertain origin with low intensity appear at M-29 and M-42 in the spectra of compounds 5-8 *i.e.* the chromanols with one or no aromatic methyl groups.

Experimental. Mass spectra were recorded using an LKB 9000 apparatus, electron energy level 70 eV. The tocol model compounds I-8 were prepared as previously described.⁵

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2. Mayer, H., Metzger J. and Isler, O. *Helv. Chim. Acta* **50** (1967) 1376.
3. Nilsson, J. L. G., Daves, Jr., G. D. and Folkers, K. *Acta Chem. Scand.* **22** (1968) 207.
4. Willhalm, B., Thomas, A. F. and Gautchi, F. *Tetrahedron* **20** (1964) 1185.
5. Nilsson, J. L. G., Sievertsson, H. and Selander, H. *Acta Chem. Scand.* **22** (1968) 3160.

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Correction to "Mass Spectrometric Studies on Carotenoids

2. A Survey of Fragmentation Reactions**

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On p. 794, line 6 from below, the *m/e*-values for the M-16 ion of lycoranthin should read: found 536.438, required 536.4375.

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Stabilization of the Tunnel Structure of Mo₅O₁₄ by Partial Metal Atom Substitution

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In the course of a study of the molybdenum-oxygen system¹ a phase designated θ -molybdenum oxide was observed. Its composition was found to be close to MoO_{2.80}, and this was confirmed by a subsequent crystal structure determination² which demonstrated the formula to be Mo₅O₁₄. The synthesis was performed by mixing appropriate amounts of MoO₂ (or Mo) and MoO₃ and heating the samples in evacuated silica tubes. The θ -phase was obtained in the small temperature interval 500-520°C. It seemed to form in a metastable state, however, since it could not be reproducibly prepared and was found to decompose by prolonged heat treatment.

The crystal structure of Mo₅O₁₄ is tetragonal and its unit cell dimensions are given in Table 1. It is composed of MoO₆

Table 1. Unit cell dimensions for Mo₅O₁₄ type phases. *a'* refers to the subcell related to the superstructure cell by *a* = 2 *a'*.

Composition	<i>a'</i>	<i>c</i>
(V _{0.08} Mo _{0.92}) ₅ O ₁₄	22.85 Å	3.989 Å
Mo ₅ O ₁₄	23.00	3.937
(W _{0.25} Mo _{0.75}) ₅ O ₁₄	23.09	3.905

octahedra and MoO₇ pentagonal bipyramids which, perpendicular to the unique axis, are coupled together by edge- and corner-sharing in a rather complicated way as shown in Fig. 1. Parallel to that axis the polyhedra share corners with identical ones above and below. Rings of 5 and 6 octahedra can be distinguished as seen in Fig. 1, giving rise to tunnels running parallel to the tetragonal axis. It may thus be characterized as a tunnel structure according to Wadsley,³ and bears striking similarities to the structures of