

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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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 Mo_5O_{14} 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 $\text{MoO}_{2.80}$, and this was confirmed by a subsequent crystal structure determination² which demonstrated the formula to be Mo_5O_{14} . The synthesis was performed by mixing appropriate amounts of MoO_2 (or Mo) and MoO_3 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 Mo_5O_{14} is tetragonal and its unit cell dimensions are given in Table 1. It is composed of MoO_6

Table 1. Unit cell dimensions for Mo_5O_{14} type phases. a' refers to the subcell related to the superstructure cell by $a=2a'$.

Composition	a'	c
$(\text{V}_{0.08}\text{Mo}_{0.92})_5\text{O}_{14}$	22.85 Å	3.989 Å
Mo_5O_{14}	23.00	3.937
$(\text{W}_{0.25}\text{Mo}_{0.75})_5\text{O}_{14}$	23.09	3.905

octahedra and MoO_7 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

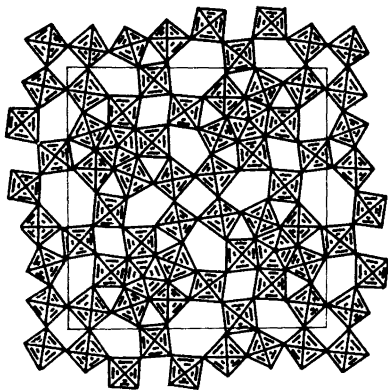


Fig. 1. The structure of Mo_5O_{14} depicted as linked MoO_6 octahedra and MoO_7 pentagonal bipyramids, viewed along the tetragonal axis. The extension of the subcell ($a' = \frac{1}{2} a$) is indicated.

$\text{W}_{18}\text{O}_{49}$ ⁴ and $\text{Mo}_{17}\text{O}_{47}$.⁵ Although all the polyhedra are at the same level there are no mirror planes perpendicular to the tetragonal axis, and the metal atoms are slightly displaced from the planes $z = \frac{1}{2}$ which gives rise to a superstructure with $a = 2 a'$. This superstructure could not be determined, however, probably because of twinning associated with an observed two-dimensional disorder, which caused the superstructure-reflections to be diffuse.

The V—Mo—O system has recently been investigated by heating mixtures of V_2O_5 , MoO_3 , and MoO_2 or V_2O_3 in evacuated silica or platinum tubes and analyzing the products by recording their X-ray powder patterns. In these studies it has been observed that apparently pure θ -phase forms quite reproducibly at a composition close to $\text{V}_{0.08}\text{Mo}_{0.92}\text{O}_{2.80}$ and temperatures in the range 550–650°C. The cell dimensions of this vanadium containing phase are given in Table 1. It is seen that the a axis is somewhat shorter than in Mo_5O_{14} while the tetragonal axis is longer. The density, determined by weighing in air and chloroform, has been found to be 4.39 ± 0.02 g/cm³, in good agreement with the value 4.374 g/cm³ calculated for $(\text{V}_{0.08}\text{Mo}_{0.92})_5\text{O}_{14}$, and thus indicates that vanadium is substituted

for molybdenum. Single crystal patterns have been recorded from a tiny needle by taking oscillation and Weissenberg photographs. A visual comparison with the corresponding films for Mo_5O_{14} revealed no noticeable difference in the intensity distribution, and even the diffuse superstructure-reflections were similar. There is thus no positive evidence for an ordered distribution of the vanadium atoms among the metal atom sites.

By heating MoO_3 , MoO_2 , and WO_3 at 630–740°C a corresponding wolfram substituted Mo_5O_{14} phase could be prepared, which appeared pure at a higher degree of substitution than the vanadium phase, namely around the composition $(\text{W}_{0.25}\text{Mo}_{0.75})_5\text{O}_{14}$. As is evident from Table 1 this substitution increases the a axis and decreases the c axis, in contrast to the above case.

A niobium containing phase which is similar to the vanadium phase both with respect to composition and unit cell dimensions has also been prepared. Recent experiments have shown that titanium also stabilizes the Mo_5O_{14} structure.⁶

The results briefly reported above raise quite interesting questions concerning the conditions governing the stability of this and other tunnel structures, for example $\text{W}_{18}\text{O}_{49}$ and $\text{Mo}_{17}\text{O}_{47}$. A research program has been initiated at this Institute aiming at a detailed study of the composition ranges of these phases in various ternary systems and an investigation of their structural and physical properties.

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