

spectroscopic properties indicative of structure III (λ_{\max} 215, 282 $m\mu$; ν_{\max} 3450 (OH and overtone of C=O), 1955 ($-\text{C}=\text{C}=\text{C}-$), 1730 (ester C=O), 1675 (conj. C=O), 1605 ($-\text{C}=\text{C}-\text{C}=\text{O}$), 1455 (CH_2), 1365 (broad $-\text{CH}_3 >\text{C}(\text{CH}_3)_2$), 1240 (ester $-\text{C}-\text{O}-\text{C}-$), 1160 (tert. OH), 1070 ($-\text{C}=\text{C}=\text{C}-$), 1025 ($-\text{C}-\text{O}-\text{C}-$ in carotenoid acetates), 850 ($>\text{C}=\text{CH}-\text{C}-$) and 820 cm^{-1} ($>\text{C}(\text{CH}_3)_2$); τ -values 8.85 (3H), 8.58 (6H), 7.97 (3H), 7.91 (3H) and 4.29 (1H)). The above data rule out the presence of any aromatic ester in product III, and show that the acetoxy function and the allene group of fucoxanthin belong to the same end of the molecule. The acetoxy group therefore seems to be located in the 3-position rather than in the 3'-position, and fucoxanthin should probably be represented by structure Ia. It should be mentioned that the choice of the 3,3'-positions for the acetoxy and the secondary hydroxy group is based on the substitution pattern commonly found in algal carotenoids, and is in accordance with the results of the oxidative degradation of fucoxanthin.⁷

The observation of Stene Sørensen reported by Liaaen and Sørensen² that fucoxanthin, upon treatment with weak base, gave, among several products, a pigment with $\lambda_{\max} = 425 m\mu$ which had lost the infrared absorption band at 1660 but retained the one at 1735 cm^{-1} , may be explained by assuming a semi-acetal formation (II).

The characteristic blue colour-reaction given by fucoxanthin with strong hydrochloric acid may be explained by rearrangement of Ia to produce furanoid rings at one or both ends.

According to the structure given in Ia, the fucoxanthols obtained by reduction of fucoxanthin with lithium aluminium hydride must be C_8' epimers (IV).

The structure Ia corresponds to $\text{C}_{42}\text{H}_{58}\text{O}_6$ which requires C 76.55; H 8.88 and O 14.57%. Willstätter and Page¹⁰ reported C 76.39 and H 8.77% (C 76.17–76.55 and H 8.61–9.03) for highly purified samples. Torto and Weedon³ obtained 14.9% oxygen by direct determination. The revised formula Ia is therefore in good agreement with analytical data obtained for fucoxanthin. In fact, all the data presented above are in full accord with the structure (Ia) suggested for the pigment. The unequivocal proof has, however, still to be presented.

A detailed report on this work will be published elsewhere. Further studies on the structure and stereochemistry of fucoxanthin are in progress in our laboratory.

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On the Structural Relation between Niobium- and Tantalum-Wolfram Oxides and the Tetragonal Potassium Wolfram

Bronze

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The existence of a phase in the $\text{Ta}_2\text{O}_5-\text{WO}_3$ system structurally similar to the tetragonal wolfram bronzes of the K_xWO_3 type¹ was first pointed out by Banks and Noval.² They stated that the phase has a range of homogeneity, while Kovba and Trunov³ reported it to have the stoichiometric composition $\text{Ta}_2\text{O}_5 \cdot 3\text{WO}_3$. Goldschmidt⁴ found the phase $\text{Nb}_2\text{O}_5 \cdot 3\text{WO}_3$, and Mohanty and Fiegel⁵ indicated that this is also structurally related to tetragonal K_xWO_3 .

In the present study 99.9 % wolfram metal and spectroscopically pure niobium and tantalum were used as starting materials. These powders were intimately mixed in correct proportions and oxidized in air at 500°C in alumina crucibles. The resulting mixture of oxides was then sealed in a platinum tube and heated at temperatures from 1200° to 1400°C for one to three days. In general the products were characterized by their X-ray powder patterns as registered by a Guinier camera with strictly monochromatic $\text{CuK}\alpha_1$ radiation and using potassium chloride ($a = 6.2919 \text{ \AA}$ at 20°) as an internal standard.

In both of the ternary systems, phases bearing structural resemblance to tetragonal K_xWO_3 were observed in samples heated at 1200°C within the approximate region $0.3 \text{ NbO}_{2.5}(\text{TaO}_{2.5}) \cdot 0.7 \text{ WO}_3 - 0.5 \text{ NbO}_{2.5}(\text{TaO}_{2.5}) \cdot 0.5 \text{ WO}_3$ and at 1400°C in the region $0.2 \text{ NbO}_{2.5}(\text{TaO}_{2.5}) \cdot 0.8 \text{ WO}_3 - 0.5 \text{ NbO}_{2.5}(\text{TaO}_{2.5}) \cdot 0.5 \text{ WO}_3$. However, these wide ranges of composition can, by details in the powder patterns, be divided into at least two, and possibly three, sub-regions. In both systems there is at least one tetragonal phase having approximately the cell dimensions of K_xWO_3 and existing over a range of composition rich in WO_3 . Also in each system there is an orthorhombic phase (poorer in WO_3) which is likewise related to K_xWO_3 but has a superstructure requiring that the b axis be tripled. This phase also clearly exists over a range of composition. The type of multiple cell has been confirmed in both systems by single-crystal Weissenberg photographs.

Single crystals of the composition $0.4 \text{ NbO}_{2.5} \cdot 0.6 \text{ WO}_3$ have been studied in some detail. The unit cell is orthorhombic with $a = 12.250 \text{ \AA}$, $b = 36.616 \text{ \AA}$ and $c = 3.9439 \text{ \AA}$. The space group is $P2_12_12$. The close agreement of the intensity data with those given by a crystal from the sample $0.4 \text{ TaO}_{2.5} \cdot 0.6 \text{ WO}_3$ indicates that there is no ordering among the niobium and wolfram atoms. Therefore, Nb and W were assumed to be randomly distributed at the metal sites.

The high density of the compound, 5.95, indicates that the stoichiometric deviation of the phase from the metal to oxygen ratio 1:3 is due not to the presence of oxygen vacancies but to atoms occupying interstitial positions in the WO_3 framework of the K_xWO_3 structure. Such holes, which in the bronze are partially occupied by potassium atoms,

exist in "cages" within the perovskite-like regions of the structure and in "tunnels" running parallel to the c axis. Filling the cages seemed unlikely, but a probable way of filling the tunnels would be to place oxygen atoms in potassium positions of the bronze and to introduce metal atoms in the resulting pentagonal bipyramids. Such a model results in an arrangement of atoms similar to those present in $\text{W}_{18}\text{O}_{49}$,⁶ Mo_5O_{14} ,⁷ and $\text{Mo}_{17}\text{O}_{47}$.⁸

Using this model there would at the composition $0.4 \text{ NbO}_{2.5} \cdot 0.6 \text{ WO}_3$ be 3.33 MeO available for filling the twelve tunnels of the unit cell. The range of this phase ends at about $0.5 \text{ NbO}_{2.5} \cdot 0.5 \text{ WO}_3$ which would correspond roughly to 4 MeO per unit cell in the tunnel positions. It therefore seemed likely that the interpolating atoms are filling one out of three tunnels in an ordered way. A trial structure based on this model refined very quickly. A discrepancy index, R , of 0.080 was obtained for the $hk0$ data. The density calculated for this model, 6.015, is in good agreement with the observed density.

If an alternative model in which the metal atoms occupy the potassium positions (no oxygens in the tunnels) is considered, there would be 2.14 metal atoms per unit cell available for filling the tunnels. This model is clearly not in good agreement with the X-ray data. Furthermore, the density calculated for this model, 5.801, is not in such good accord with the observed density.

The structure of $0.4 \text{ NbO}_{2.5} \cdot 0.6 \text{ WO}_3$ is being refined further and will be published in detail later.

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