

SYNTHESIS AND STUDY BY IR AND UV METHODS OF SPECTRAL ANALYSIS OF A COMPLEX OF Mo(VI) WITH QUERCETIN

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A complex of Mo(VI) with quercetin has been obtained. A hypothetical structure of the complex is proposed on the basis of IR and UV spectral investigations and elementary analysis.

The creation of drugs stimulating hematopoietic processes in cases of radiation disease is an urgent problem. It is known that in various biological systems molybdenum plays a large role in regulating the physical processes occurring under the influence of ionizing radiations. It has been established experimentally that, on irradiation, the molybdenum content of tissues decreases by a factor of almost five [1], and the molybdenum deficiency that develops in radiation disease therefore requires therapeutic correction. However, as has been shown previously [2], the use of molybdenum salts has proved undesirable because of their high toxicity. In view of this, it appeared of interest to investigate coordination compounds of Mo(VI) and, in particular, its complex with quercetin, which is a biologically active ligand. While having a low toxicity, it possesses radioprotector activity [3].

An investigation of the structure and properties of the complex (1) of molybdenum with quercetin has been performed with the use of methods of IR and UV spectroscopy.

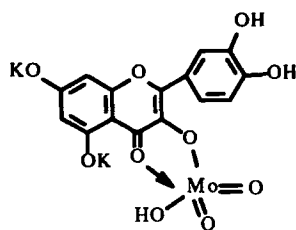
In the electronic spectrum of the complex (1) we observed a bathochromic shift of the maximum of the band corresponding to a $\pi-\pi^*$ electronic transition by 50 nm relative to λ_{\max} of the band observed in the UV spectrum of quercetin (λ_{\max} 375 nm). This experimental fact probably witnesses the presence of a charge-transfer complex (CTC) produced through the formation of a coordination bond between the unshared electron pair of the oxygen atom of the C=O group of quercetin and the *d*-orbital of Mo(VI).

The degree of oxidation of the molybdenum in the complex obtained and the state of molybdates at pH 9 also show the possible formation of bonds between the metal atom and the OH groups [4].

In the IR spectrum of the complex of Mo(VI) with quercetin that had been obtained (1), the presence of bands at 830 and 860 cm^{-1} corresponding the symmetrical and asymmetrical stretching vibrations of the dioxo group MoO_2^{+2} obviously characterizes not only the presence of the MoO_2^{+2} group but also its *cis*- structure. Moreover, a lowering of the frequency of the band at 1660 cm^{-1} connected with the stretching vibration of the γ -pyrone (chromone) C=O of quercetin by 25 cm^{-1} , a decrease in the intensity of the band characterizing the presence of the C—O bond of a phenol, and, together with this, the presence of a band at 1270 cm^{-1} probably connected with the formation of phenolate ion [5, 6] were observed.

On the basis of the above-given changes of the absorption band maxima in the UV spectra and of the characteristic frequencies in the IR spectra, it may be assumed that, in the complex, quercetin was coordinated in bidentate fashion through the oxygen atoms of the γ -pyrone ring [5, 6]. Furthermore, it may be observed that the oxygen atoms of the γ -pyrone ring are also the most effective coordination center in the case of other quercetin derivatives [4].

Thus, on the basis of IR and UV spectral investigations, and literature information, we propose the following most probable structure of the complex.



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EXPERIMENTAL

Preparation of the Complex Compound of Molybdenum(VI) with Quercetin. With stirring, 0.70 g of caustic potash in 20 ml of water was added to a reaction mixture consisting of a suspension of 4 g of quercetin in a solution of 2.79 g of potassium molybdate dihydrate in 20 ml of water, and stirring was continued for 25—30 min. The final product was precipitated by the addition of 300 ml of methyl ethyl ketone, and the precipitate formed was separated off and was washed with methyl ethyl ketone and with ethyl acetate. The yield of the complex was 6.60 g (80%), mp 215—220°C (decomp.). Readily soluble in water, insoluble in ether, acetone, and chloroform.

Results of the elementary analysis of compound (1): found, %: Mo 15.06; 14.90; C 30.25; 30.0; H₂ 3.08; 2.98; O₂ 39.18; 41.0; K 12.16; 12.05; H₂O 14.04; 14.21; calculated, MoC₁₅H₁₈O₁₀K₂ %: Mo 15.28; C 28.66; H₂ 2.869; O₂ 40.76; K 12.42.

Investigations of the thermal decomposition of complex compound (1) were made on a TG-200 derivatograph using the Paulik—Paulik—Erdey system in an atmosphere of air with a 300-mg sample and with Al₂O₃ as standard. As the sample support we used a DTA-1/5 platinum crucible; the rate of heating was 5 deg/min.

On the derivatogram of the compound studied we observed exo-effects at 142, 290, 427, and 665°C and 225, 395, and 800°C. The temperature interval of 70—130°C corresponds to the melting of the complex. An endo-effect at 290°C is connected with the beginning of the decomposition of the coordinated quercetin.

IR spectra were recorded on a Specord 75 IR spectrometer (Germany). The samples were prepared by molding with KBr.

UV spectra were recorded on a Specord UV-VIS spectrometer (Germany) in 96% ethanol solution.

REFERENCES

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