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COPPER (II) COMPLEXES OF VITAMIN D₃ AND 24R,25 DIHYDROXY-VITAMIN D₃.

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In our investigations on complexing properties of vitamin D₃ and/or its hydroxylated derivatives, we describe here some results obtained with copper (II) and vitamin D₃ and 24R,25-dihydroxy vitamin D₃.

We have previously demonstrated that CoCl₂ could lead to the following species in aqueous 9 g.L⁻¹ NaCl (1, 2) : [CoCl₂(vitD)] (vitD is vitamin D₃, 25-hydroxyvitamin D₃, 1 α ,25-dihydroxyvitamin D₃ or 24R,25-dihydroxyvitamin D₃), [CoCl₂(vitD)₄]. The latter complex shows biological effects, depending upon the season (3). The aim of the present work was to determine the chelating properties of vitamin D₃ and 24R,25-dihydroxyvitamin D₃ towards copper (II) in two solvents : methanol (MeOH) and aqueous NaCl.

Experimental

As vit. D₃ and its analogues are not very stable in solution, all reagents were always prepared just before their use. The concentrations were, in MeOH 2.10⁻⁴ mol.L⁻¹ and 2.10⁻⁵ mol.L⁻¹ in water. The copper solutions (Cu(ClO₄)₂ in MeOH and CuCl₂ in H₂O) were prepared in order to obtain the same molarity for the two solutions. The spectra were recorded at 25 °C (298 K) with a Hitachi U 2000 spectrophotometer.

Results and discussion

Composition of the complexes

The continuous variations curves were drawn using corrected absorbance at a given wavelength A_{corr} (4, 5) in order to keep only the spectrum of the complex species (m is related to the metal and ν to the cholecalciferol, ϵ is the molar extinction coefficient) :

$$A_{corr} = A_{exp} - (C_m \epsilon_m + C_\nu \epsilon_\nu)$$

As the solutions of the cupric ion showed a very weak absorption in the visible region because of their low molarity, it can be assumed that $\epsilon_m \approx 0$. The curves were obtained by choosing several wavelengths located around the maximum absorption bands of the vitamin D₃ or its derivatives. The figures 1 and 3 are relative to vitamin D₃ in MeOH and H₂O respectively whereas figure 2 was obtained with 24R,25-dihydroxyvitamin D₃ in aqueous NaCl.

The curves demonstrate the presence of the complex [Cu(vitD)₄]²⁺ in MeOH and [CuCl₂(vitD)] and [CuCl₂(24,25(OH)₂vitD)] in aqueous NaCl.

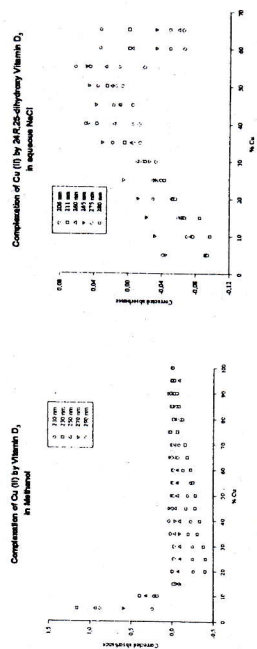


Figure 1

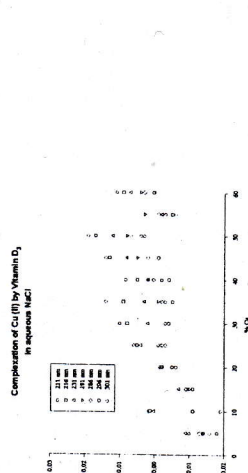


Figure 2

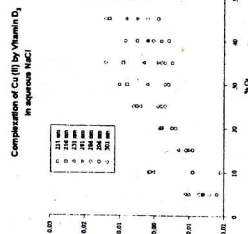


Figure 3

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