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ORIENTAL JOURNAL OF CHEMISTRY
An International Open Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2021, Vol. 37, No.(1):
Pg. 80-83

Antioxidant Studies of Some Lanthanide Complexes Derived from Curcuminoid Analogues

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http://dx.doi.org/10.13005/ojc/370110

(Received: November 30, 2020; Accepted: February 16, 2021)

ABSTRACT

Antioxidant activities of the Pr(III), Nd(III), Sm(III), Dy(III), Er(III) and Yb(III) complexes of eight curcuminoid analogues (HL^1 to HL^8), derived from acetylacetone and aromatic aldehydes (benzaldehyde, cinnamaldehyde, furfural, salicylaldehyde, β-hydoxy-α-naphthaldehyde, p-anisaldehyde, p-hydroxybenzaldehyde and vanillin), are studied by the thiocyanate method. Even though all the complexes exhibited significant antioxidant properties, their activities are found to be less than the corresponding free curcuminoid analogues.

Keywords: Antioxidant Studies, Thiocyanate Method, Curcuminoid Analogues, Pr(III), Nd(III), Sm(III), Dy(III), Er(III) and Yb(III) Complexes.

INTRODUCTION

Metal complexes of many plant products are receiving much importance in recent years due to their applications in various fields[1-3]. The metal complexes of curcumin, a naturally occurring conjugated diketone, have been studied in detail in view of its structure and medicinal applications[4]. Synthetic curcuminoid analogues and their metal chelates have also been investigated by various research groups due to their applications in various biological fields[5-11]. Majority of these works are based on the complexes with various main group and transition metal ions. The biological applications of the lanthanide chelates of synthetic curcuminoids are not studied in detail as revealed in the literature survey. In continuation of the studies on the metal complexes of curcuminoids[6-11], in this paper we report the antioxidant activities of Pr(III), Nd(III), Sm(III), Dy(III), Er(III) and Yb(III) complexes of curcuminoid analogues.

MATERIALS AND METHODS

All the chemicals and solvents used for the synthesis of curcuminoid analogues and their Pr(III), Nd(III), Sm(III), Dy(III), Er(III) and Yb(III) complexes were of reagent grade (Merck, Fluka and Sigma-Aldrich). For the preparation of metal complexes, Pr(III), Nd(III), Sm(III), Dy(III), Er(III) and Yb(III) nitrates were used. The antioxidant activities were studied by measuring the absorbance using a Bausch & Lomb Spectronic 1001 UV-Visible Spectrophotometer.

Synthesis of curcuminoid analogues and their complexes with Pr(III), Nd(III), Sm(III), Dy(III), Er(III) and Yb(III) ions

The curcuminoid analogues (HL^1–HL^8) were synthesized by condensing aromatic aldehydes with acetylacetone by the methods reported in our previously published papers[6-11]. The aromatic aldehydes used for the condensation were benzaldehyde, cinnamaldehyde, furfural, salicylaldehyde, β-hydroxy-α-naphthaldehyde, p-methoxybenzaldehyde, p-hydroxybenzaldehyde and vanillin.

Pr(III), Nd(III), Sm(III), Dy(III), Er(III) and Yb(III) complexes of these curcuminoid analogues were also prepared by our earlier reported methods[12-13].

Determination of antioxidant activities

The thiocyanate method[14,16] was employed for determining the antioxidant activity.

RESULTS AND DISCUSSION

The structure of the lanthanide chelates of curcuminoid analogues (Fig. 1) was reported earlier[12,13,15] based on various analytical and spectral techniques.

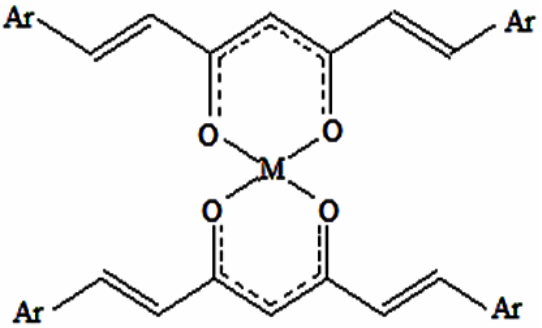

Fig. 1. Structure of the Pr(III), Nd(III), Sm(III), Dy(III), Er(III) and Yb(III) complexes of curcuminoid analogues; L stands for the deprotonated ligand; Ar = phenyl (L^1); styryl (L^2); 2-furyl (L^3); 2-hydroxyphenyl (L^4); 2-hydroxy-1-naphthyl (L^5); 4-methoxyphenyl (L^6); 4-hydroxyphenyl (L^7); and 4-hydroxy-3-methoxyphenyl (L^8); M = Pr(III), Nd(III), Sm(III), Dy(III), Er(III) and Yb(III); The proposed structure also contains one bidentate nitrate ion and two coordinated water molecules with the formula $[M(L)_2(NO_3)(H_2O)_2]$

The antioxidant assays of lanthanide chelates of curcuminoid analogues are shown graphically (absorbance at 500 nm Vs number of days) in Figure 2 to Figure 9.

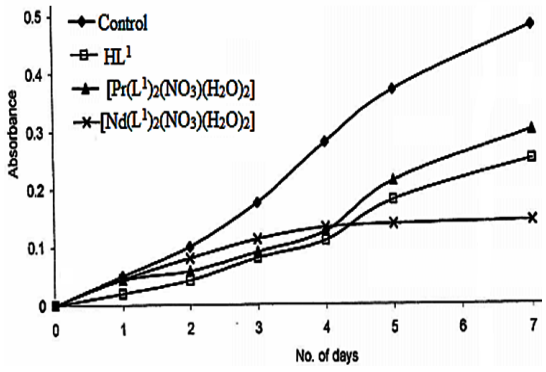

Fig. 2. Antioxidant assay of HL^1 and its lanthanide chelates

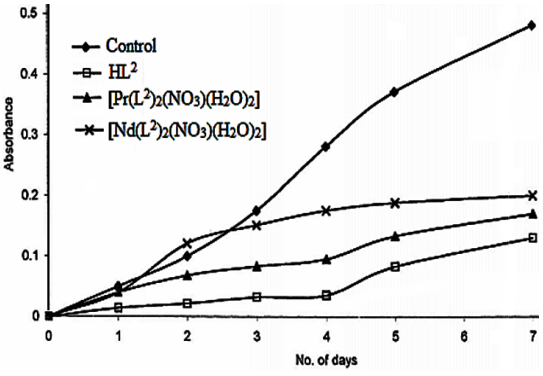

Fig. 3. Antioxidant assay of HL^2 and its lanthanide chelates

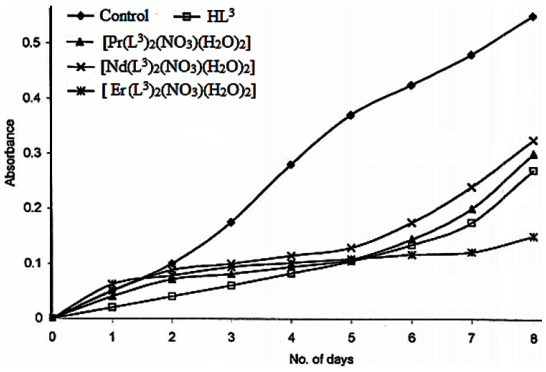

Fig. 4. Antioxidant assay of HL^3 and its lanthanide chelates

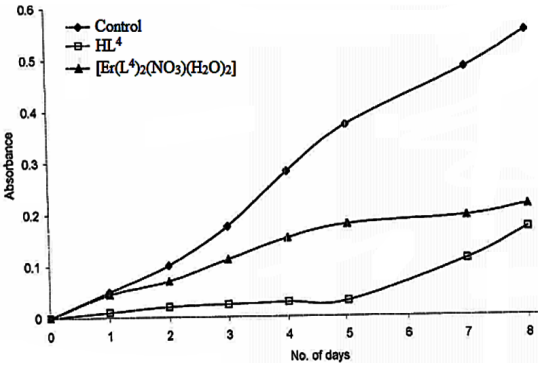

Fig. 5. Antioxidant assay of HL^4 and its Er(III) complex

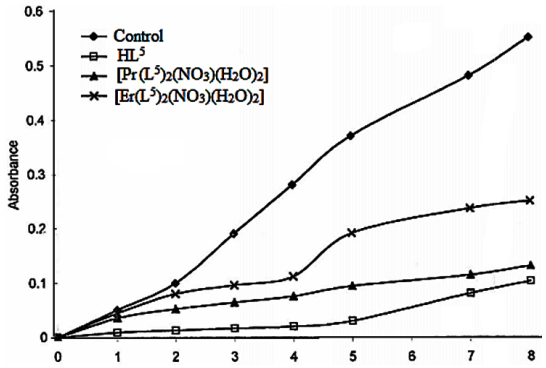

Fig. 6. Antioxidant assay of HL^5 and its lanthanide chelates

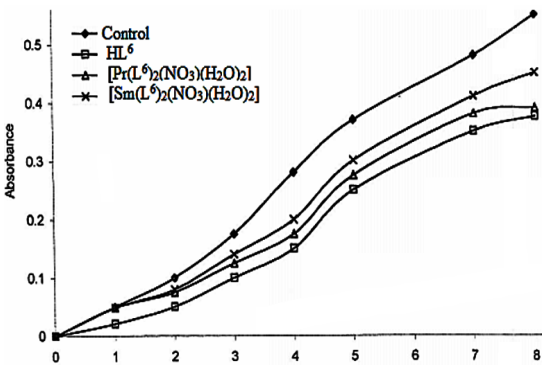

Fig. 7. Antioxidant assay of HL^6 and its lanthanide chelates

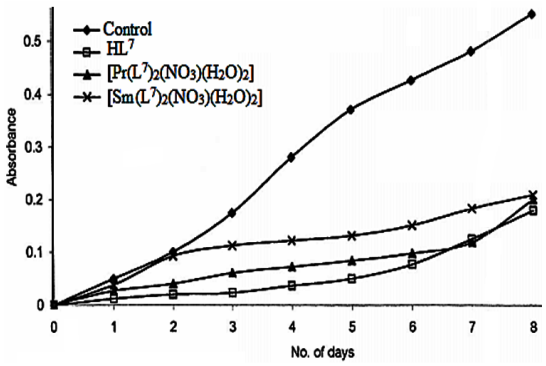

Fig. 8. Antioxidant assay of HL^7 and its lanthanide chelates

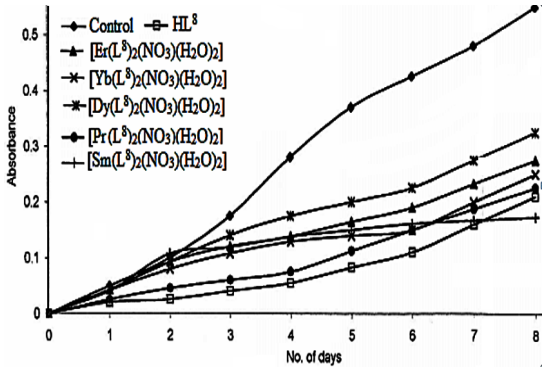

Fig. 9. Antioxidant assay of HL^8 and its lanthanide chelates

The findings showed that all lanthanide chelates possess significant antioxidant activity. A comparison with the corresponding reported curcuminoid analogues[16] indicates that the antioxidant activities of these lanthanide chelates are less than the corresponding free curcuminoids.

It was reported that curcuminoids having a hydroxyl group in the aryl ring show maximum antioxidant activity[6-8,10,16,17]. But the results revealed that Pr(III), Nd(III), Sm(III), Dy(III), Er(III) and Yb(III) complexes of curcuminoids which contain a hydroxyl group in the aryl ring also showed lower activity than the corresponding curcuminoid analogues. Thus it can be inferred that the –OH group alone is not a sufficient condition to promote antioxidant activity. This indicates the importance of free and enolised dicarbonyl moiety in imparting the antioxidant property of curcuminoids. During complexation, the enolic proton is removed with the formation of a six membered pseudo-aromatic C_3O_2M chelate ring with the metal ion, thereby losing the enolic nature of curcuminoids. Earlier reports of certain transition metal complexes of curcuminoids also showed lesser activity than the corresponding curcuminoids[18]. It has been reported that the antitumour activity of curcuminoids increases on complexation with Cu(II) and Al(III) ions[6-10]. The results of the present investigation clearly indicate that the antioxidant activity of curcuminoids decreases on complexation with Pr(III), Nd(III), Sm(III), Dy(III), Er(III) and Yb(III) ions.

CONCLUSION

The effects of complexation of Pr(III), Nd(III), Sm(III), Dy(III), Er(III) and Yb(III) ions on the antioxidant properties of curcuminoid analogues were studied. Even though all the lanthanide chelates exhibited significant antioxidant activity, the metal complexation lowered the activities of all the curcuminoids. The results revealed that the enolised and intramolecularly hydrogen bonded dicarbonyl moiety is mainly responsible for the antioxidant property of all curcuminoids. The decrease in the antioxidant property during complex formation arises due to the replacement of this intramolecularly hydrogen bonded enolic proton by metal cation.

ACKNOWLEDGEMENT

The authors express sincere thanks to University Grants Commission, New Delhi, India for providing financial assistance; and Department of Life Sciences, University of Calicut, India for providing facilities for the antioxidant studies.

Conflicts of Interest

No conflict of interest regarding this article.

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