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# Synthesis and application of rare earth organic fertilizers on cucumbers

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ABSTRACT

Organic fertilizers of La, Nd, and Pr with tartaric acid ligands have been successfully synthesized. The efficiency of the complexing reaction was over 80%. The molecular formula of the complex was $Ln_2(C_4H_4O_6)_3.nH_2O$ (Ln: La, Nd, Pr). The synthesized complexes were tested for the ability to stimulate growth and improve productivity for Thai cucumber. The study results showed that the complexes reduced the growth time of the plants and increased the yield by > 20%. Yields of cucumbers sprayed with rare earth tartrate complexes reached ~62 tons/ha and increased by 20% compared with control samples.

## Introduction

Since the last few years of the twentieth century, rare earth trace elements have been studied and applied to agricultural production in the Soviet Union, Australia, and China to bring high efficiency to the agriculture of these countries. La, Nd, and Pr are elements with large concentrations in rare earth elements, which have been studied and synthesized with organic ligands to produce rare earth complexes with practical applications on agricultural plants [ 1-3]. In Vietnam, rare earth fertilizers have also been studied and applied to agricultural crops, and a good yield has recently been reported [2,8,9].

Tartaric acid is an organic acid [4] that can be found in fruits such as grapes, bananas, tamarinds, and citrus. It belongs to the carboxylic acid family and has two -COOH functional groups in the molecule. Therefore, it is easy to involve reactions with metal ions. In agriculture, tartaric acid is used as a ring ligand to bind metal ions in the soil and micro-organic fertilizers. Organic ligands are more preferred than inorganic ligands - or inorganic acid radicals because of easily acidification of the soil leading to soil discoloration, acidity, and dullness over time.

Some research groups have successfully synthesized rare earth complexes [5-7] using different methods such as crystallization and hydrothermal. These methods can produce a complex in the form of $Ln_2(C_4H_4O_6)_3.nH_2O$ (Ln: La, Ce, Nd, Pr). Previous studies showed that during thermal analysis, the rare earth tartrate complexes decomposed to form $Ln_2(C_2O_4)_3$ and $Ln_2(CO_3)_3$ intermediates before forming the rare earth oxide (i.e., $Ln_2O_3$) [7].

In this study, rare earth tartrate complexes (RETCs) were synthesized using a relatively simple method before applying for the growth of cucumbers as fertilizers.

## Experiments

### *Chemical and research method*

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All chemicals, including $La_2O_3$ (99.9%); $Nd_2O_3$ (99.9%); $Pr_6O_{11}$ (99.9%); tartaric acid, $HNO_3$, $CH_3COONa$, were purchased from the Sigma Aldrich and used without any further purification; and deionization water.

The synthesized RETCs were characterized by using differential thermal analysis on the Labsys Evo thermal analyzer (France). The measuring conditions were from room temperature to 900°C in the air environment, heating rate 10 °C/min at the Division of Inorganic Materials, Institute of Materials Science.

The bonds in the complexes were examined by FT-IR spectrometry in the range from 400 $cm^{-1}$ to 4000 $cm^{-1}$ on a Cary 630 Infrared spectrometer (Agilent Technology) at the Institute of Geography.

To investigate the efficiency of RETCs on the ability to stimulate growth and increase crop yield, a 360 $m^2$ field of cucumber at Luc Nam agricultural production cooperative was chosen. The exact address was Gan village, Dong Phu commune, Luc Nam district, Bac Giang province.

### *Complex synthesis*

Tartrate rare earth complex was synthesized by a simple chemical reaction [9].

Firstly, the rare earth nitrate solutions were prepared as follows: Dissolve 82.1 g of $La_2O_3$ in 125ml of $HNO_3$ 12M, heat gently until completely dissolved to create a transparent solution. Then, the solution was evaporated to almost dry in purpose of removing excess $HNO_3$ (repeated three times). Distilled water was adjusted the solution to pH 3. The obtained solution was diluted to 500 ml by distilled water and titrated to re-determine the exact concentration by the complexometric titration method with DTPA solution and arsenic (III) indicator and a buffer solution (pH ranges 3.8-4.0). Final obtained solution of $La(NO_3)_3$ was 0.5M. Similar procedures were applied to prepare $Pr(NO_3)_3$ 0.5M and $Nd(NO_3)_3$ 0.5M.

Secondly, the tartrate complexes were synthesized as follows: 0.75g of tartaric acid was diluted into 10 ml of distilled water in a 100-ml beaker. Next, the tartaric solution was transferred to a beaker with 10 ml of the $La(NO_3)_3$ solution, stirred thoroughly until a clear solution obtained. Then, the pH was adjusted to precipitate the complex by using $CH_3COONa$ 0.1N and 0.1N $HNO_3$. The solution was filtered to separate the precipitation and the liquid. The precipitation was washed with distilled water and absolute ethanol to obtain a clean tartrate-La complex. The complex was stored in a desiccator for further analysis. The liquid fraction was diluted with 100ml by distilled water and analyzed for the content of rare earth elements remaining in the solution by using the ICP method.

The reaction efficiency of the synthesis complex was calculated as follows:

$$H(\%) = \frac{C_i - C_f}{C_i} \times 100\%$$

Where: H: efficiency , $C_i$: initial rare earth concentration.

$C_f$: Solution rare earth concentration after made complex Pr and Nd tartrate complexes were the same as La

## Results and discussion

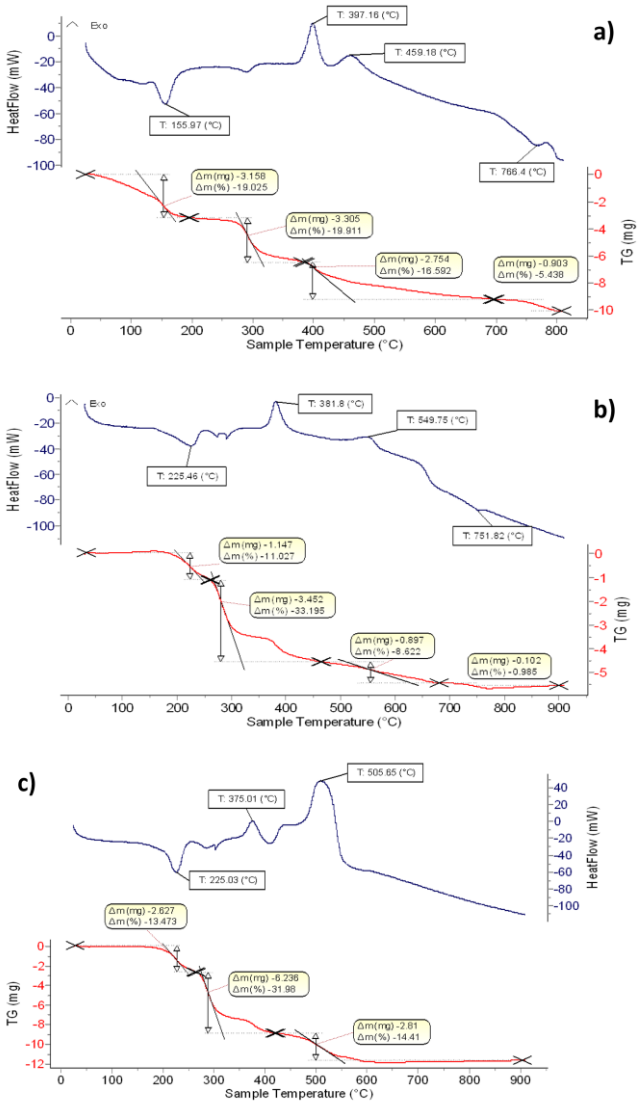


Figure 1: Thermal analysis of complexes including a) $La_2(C_4H_4O_6)_3.nH_2O$; b) $Nd_2(C_4H_4O_6)_3.nH_2O$; c) $Pr_2(C_4H_4O_6)_3.nH_2O$

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The molecular formula of the rare earth tartrate complexes.

The rare earth complexes $Ln_2(C_4H_4O_6)_3.nH_2O$ (Ln: La, Nd, Pr) were synthesized and determined compositions by thermal analysis. The results were shown in Figure 1.

From the differential analysis diagram in Figure 1, both three complexes (i.e., $La_2(C_4H_4O_6)_3.nH_2O$, $Nd_2(C_4H_4O_6)_3.nH_2O$, and $Pr_2(C_4H_4O_6)_3.nH_2O$) showed a similar endothermic peak around 200 °C which was attributed to the evaporation of adsorbed water on the surface of the complex. The water content was different in each complex that can be indicated by the mass loss at the endothermic peak (i.e., 19.02%, 11.02%, and 13.47%, for $La_2(C_4H_4O_6)_3.nH_2O$, $Nd_2(C_4H_4O_6)_3.nH_2O$, and $Pr_2(C_4H_4O_6)_3.nH_2O$, respectively).

When the temperature increases from 300°C to 600°C, there were exothermic peak occurred which corresponding to the decomposition of organic part of the complex (i.e., tartrate) and the inorganic part of the complexes (i.e., $NO_3$). The decomposition might from $Ln_2(C_4H_4O_6)_3.nH_2O$ to $Ln_2(C_2O_4)_3$, $Ln_2(CO_3)_3$ and the final product were the corresponding rare earth oxides $Ln_2O_3$. This result was similar to the study [8,9]. The mass loss was agreeable with the proposed formular of the complexes.

After 600 °C, there still a small decreasing in mass which is attributed to the burning of carbon residual. There were no thermal effects and weight loss after 800 °C on the thermal analysis diagram of three tartrate rare earth complexes. This was proved that the final product of the thermal analysis was the rare earth oxides $Ln_2O_3$.

For further understanding about the linkage in the complex, FT-IR spectroscopy was used to determine the bonds between metal cations and complexes and characteristic groups of tartrate ligands. The results were summarized in Table 1:

Table 1: Adsorption frequencies of $Ln_2(C_4H_4O_6)_3.nH_2O$ complexes

| Vibration group | Wavelength ($cm^{-1}$) | | |
|---|---|---|---|
| | La - tartrate | Nd - tartrate | Pr - tartrate |
| ν(O – H) of $H_2O$ | 3263 | 3264 | 3216 |
| ν(C – H) | 2684 | 2664 | 2642 |
| ν(O – C = O) | | 1711 | 1710 |
| ν(O – C = O) | 1573 | 1577 | 1576 |
| ν(C – O) | 1413 | 1400 | 1399 |
| ν(C – H) +π(C – H) | 1142 | 1135 | 1126 |
| ν(C – OH), δ(O – H), π(C – H) | 1067 | 1063 | 1064 |
| ν(C – C) | 934 | 930 | 934 |

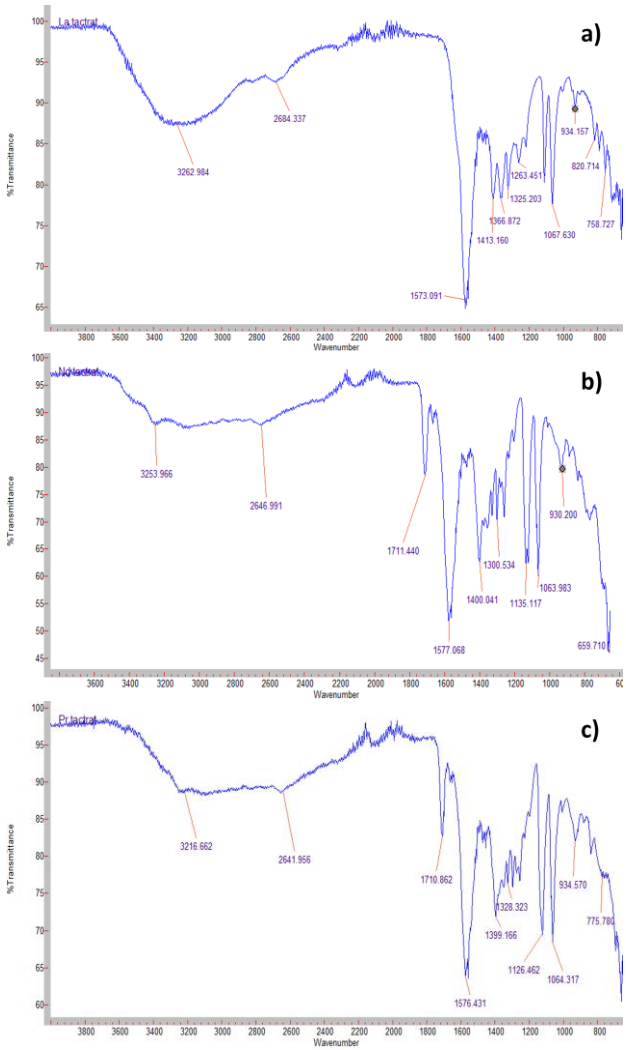


Figure 2: Infrared spectrum of tartrate rare earth complex: a) $La_2(C_4H_4O_6)_3.nH_2O$; b) $Nd_2(C_4H_4O_6)_3.nH_2O$; c) $Pr_2(C_4H_4O_6)_3.nH_2O$

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In Figure 2, the peaks around 3300 $cm^{-1}$ were attributed to the OH stretching and adsorbed water on the surface. Whereas the band around 2660 $cm^{-1}$ were attributed to the stretching vibration of $CH_2$ in the tartrate ions. In addition, the band around 1600 $cm^{-1}$ were due to the stretching of carbonyl groups in the carboxylate compound which appears at 1744 $cm^{-1}$ in pure tartaric acid. The absorption bands of asymmetric vibration ($\nu_{as}$(CO)) and symmetric vibration ($\nu_s$(CO)) were characteristic of C=O bonds also decreased accordingly. This showed that $Ln^{3+}$-$COO^-$ bonds in the complexes were characteristic by the red-shifted change of the C=O stretching. The result also implies that the rare earth ions were connected to the carbonyl groups by chelate coordination [10]. Especially on the absorption spectrum of complexes, the appearance of the peak was characterized by the bond between $Ln^{3+}$ and $COO^-$ in the 1573 $cm^{-1}$ region corresponded by a complex $Ln_2(C_4H_4O_6)_3.nH_2O$ further confirming that the connection mode is chelate coordination. The formation of a bond between the metal cation and the oxygen atom of the COO-group was weakened the CO bond in the ligand. The absorption band of the OH and CH groups in the complex shifted clearly to the lower wavelength region. Especially, this could indicate that the complexation occurred between $Ln^{3+}$ and the OH group of the ligand [11]. In addition, vibration clusters with wide-leg absorption bands in the region from 3100 $cm^{-1}$ to 3500 $cm^{-1}$ confirmed that the complex contained water and was suitable for the results of thermal analysis.

Thus, it could be concluded that the rare earth tartrate complex was successfully synthesized by the chemical method by linking between the metal cations $Ln^{3+}$ and ligands through two groups of carboxylic $COO^-$.

The complex solution fraction was analyzed La, Nd, and Pr content by ICP-MS method. The efficiency of the rare earth tartrate complex was calculated as follows:

Table 2: The reaction efficiency of tartrate rare earth complex

| Complex | $C_i$ (M) | $C_f$ (M) | H (%) |
|---|---|---|---|
| La-tartrate | 0.50 | 0.094 | 81.2 |
| Nd-tartrate | 0.50 | 0.091 | 81.8 |
| Pr-tartrate | 0.50 | 0.097 | 80.6 |

The efficiency of the tartrate rare earth complex was over 80%.

*Test of the growth stimulant ability of the rare earth tartrate complex on cucumbers*

The studied area (360 $m^2$) was divided into five segments. In which four segments of testing of lactate rare earth complex fertilizers [9] and one control bed of foliar fertilization in the market under the label of Thien Nong and followed the manufacturer's instructions.

The spraying time and fertilizer dosage of rare earth tartrate (LnA) were as follows:

+ First time: cucumbers planted one week with the ratio of LnA/water = 1/1000; the final content of rare earth complexes was 50 mg/L.

+ Second time: the dosage of LnA fertilizers was used as follows: use 15 - 20 ml of LnA fertilizer mixed in 16-20 L of water, spray for an area of 360 $m^2$.

Tartrate rare earth complexes were tested for the ability to stimulate growth and increase the yield of cucumbers. The cucumber used was a Thai cucumber kind with a growth time of about 75-80 days and a yield of ~62 tons/ha.

Experimental results (Table 3 and Figure 3) showed that tartrate rare earth complexes significantly stimulated growth when the harvest time was reduced from 38 days to 30 days, with both sizes and weights increasing simultaneously. The yield of trees increased from 50 tons/ha to 62 tons/ha, higher than 20%.



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Figure 3: The growth and development of cucumber plants were sprayed with lactate rare earth complexes. a) Down seed; b) After one week; c) After two weeks; d) After three weeks; e) After four weeks.

Table 3: The results of analysis of growth and yield on cucumber plants for rare earth tartrate micronutrients

| Target | Unit | Control sample | Test | Comparison |
|---|---|---|---|---|
| Time to down seed | | 05/09/2020 | 05/09/2020 | |
| Time to make bed | | 12/09/2020 | 12/09/2020 | |
| Time to harvest | days | 38 | 30 | -8 |
| Number of fruit/trees | Fruit | 12-13 | 16-17 | +4 |
| Fruit length | cm | 16-18 | 18-20 | +2 |
| Mean weight | gam | 110-115 | 119-121 | +7.5 |
| Productivity | Tons/ha | 50 | 62 | 12 |

## Conclusion

Tartrate rare earth complexes were successfully synthesized with the following components: $La_2(C_4H_4O_6)_3.10H_2O$; $Nd_2(C_4H_4O_6)_3.5H_2O$; $Pr_2(C_4H_4O_6)_3.5H_2O$ and experimentally studied by Thai cucumber. The experimental results showed that the tartrate rare earth complexes had a markedly stimulating ability, reduced harvest time from 38 days to 30 days, and increased yield >20% compared to the control sample. The size and weight of the experimental cucumbers increased while increasing yield was higher than 20% compared to the control sample, and yield increased 62 tons/ha.

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