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STABILITY OF CURCUMIN IN TURMERIC OLEORESIN- β-CYCLODEXTRIN INCLUSION COMPLEX DURING STORAGE

(KESTABILAN KURKUMIN DI DALAM KOMPLEKS RANGKUMAN OLEORESIN- β-SIKLODEKSTRIN SEMASA PENYIMPANAN)

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Abstract

To improve the stability of curcumin in turmeric rhizome (*Curcuma domestica*) oleoresin during storage, complexation with β-cyclodextrin was studied. Pressurised liquid extraction (PLE) is a fast method to extract high quality turmeric rhizome oleoresin. Extraction conditions was optimised based on maximum major volatile compounds (1,8-cineol, tumerone + ar-tumerone, α-zingeberene, β-zingeberene and α-phellandrene). Turmeric oleoresin exhibit sensitivity to light, heat, oxygen and have short storage lives. Therefore, oleoresin obtained was encapsulated with β-cyclodextrin (BCD) using kneading method. The stability of curcumin in inclusion complex was monitored for 64 days with exposure to heat and light. The shelf-life of the product was estimated based on half life $t_{1/2}$ (day) and activation energy, E (kJ/mol). Shelf life of turmeric oleoresin inclusion complex, stored at 5^{o}C in dark containers can be extended to 154 days.

Keywords: curcumin, light, storage, kinetic study, half life and activation energy.

Abstrak

Untuk memperbaiki kestabilan kurkumin di dalam oleoresin kunyit (*Curcuma domestica*) semasa penyimpanan, kompleks rangkuman dengan β-siklodekstrin dikaji. Pengekstrakkan cecair bertekanan tinggi (PLE) dapat menghasilkan oleoresin kunyit yang bermutu tinggi. Parameter pengekstrakkan dioptimumkan berdasarkan maksimum bahan meruap utama (1,8-sineol, tumerona + ar-tumerona, α-zingeberena, β-zingeberena and α-felandrena). Oleoresin kunyit sensitif dengan perubahan cahaya, suhu, oksigen dan menpunyai jangka hayat yang pendek. Oleh kerana itu, oleoresin kunyit yang di ekstrak menggunakan PLE, dirangkumkan dengan β-siklodekstrin dengan mengunakkan teknik pengulian. Jangka hayat produk diramal dengan menghitungkan tenaga pengaktifan, E (kJ/mol) dan separuh hayat, $t_{1/2}$ (hari). Jangka hayat kompleks rangkuman oleoresin kunyit dapat diperpanjangkan ke 154 hari, jika di simpan pada suhu 5^{o}C didalam keadaan bertutup dan gelap.

Kata kunci: kurkumin, simpanan, kajian kinetik, jangka separa hayat dan tenaga pengaktifan

Introduction

Curcumin [1,7-bis (4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione] is a natural yellow-orange natural dye in turmeric rhizome [1]. It is a fat soluble pigment but insoluble in aqueous medium. Curcumin is sensitive to light but is moderately stable to heat [2]. Microencapsulation protects oleoresin against destructive changes, converts it into a free-flowing powder, delivering more flavour impact in finished products, separate reactive materials from one another, alter surface properties of the materials, control the release of materials, reduce volatility or flammability of liquids, and to mask the bitter taste of certain compounds [3]. Attempts to prepare water-soluble curcumin by complex formation or interaction with various macromolecules (e.g. gelatine, polysaccharides) have been reported [4]. Cyclodextrin can bind to various kinds of low molecule compounds into its cave structure, thereby stabilising the low molecule organic compounds by the inclusion effect. Curcumin and turmeric oleoresin had been encapsulated with β-cyclodextrin using suspension and co-crystalisation technique by Szente [5]. He reported that β-cyclodextrin complexation provided shelf life improvement for curcumin and turmeric oleoresin (Soxhlet-extraction using *n*-hexane). However, limited information is available concerning curcumin stability in microencapsulated turmeric oleoresin. There exists a need to investigate the storage stability of this curcumin in

inclusion complex that contributes to unique yellow colour of turmeric oleoresin. The results will be useful in the application of this inclusion complex in food system.

Materials and Methods

Sample Preparation

Fresh turmeric rhizome was obtained from local supplier in Banting, Selangor. The sample were washed under running tap water, sliced (3mm thickness) and air-dried until the moisture content reached 13.63 ± 0.67%. Samples were stored in sealed plastic bags at room temperature until needed for analysis. Prior to extraction, samples were further chopped to 3 mm diameter.

Pressurised Liquid Extraction (PLE)

Extractions were done using ASE 200 accelerated solvent extractor (Dionex Ltd. Camberly, Surrey, UK). Oleoresin was extracted using *n*-hexane with predetermined optimised conditions (Design Expert 6.0.4, Stat Ease Software): temperature of 130^{o}C, pressure of 11308 kPa and static time of 16 minutes. The extract was evaporated to dryness using rotary evaporator.

Preparation of Inclusion Complex

Inclusion complex was prepared following the method used by Zhang [6].

Storage Study

Inclusion complex (0.2 g) in clear screw capped vials were placed at three different places; chiller at 5^{o}C (Frost DOR, USA), closed incubator at 33^{o}C (Thermo Scientific Thermolyne Oven Incubator 142300, USA) and oven at 45^{o}C (Memmert, Germany). Half of the samples were covered with aluminium foil as control, whereas the other half was exposed to bright light, 2800-3000 lux, Philips energy saving cool daylight bulbs (5 W). The intensity of the light was measured using EKO Multimeter, Japan.

Curcumin

Curcumin was determined following ASTA method [7].

Results and discussion

Arrhenius' law was empirically derived to describe the temperature dependence of simple chemical reactions. The key parameter of this equation to estimate shelf-life at different temperature is the activation energy. Usually the reaction rate is determined at three or more temperatures and the logarithms of these values are regressed versus 1/temperature to obtain the activation energy from the resulting slope. For irreversible first order reaction kinetics, the rate constant at constant temperature can be determined through fraction conversion, f:

$$f = (C_o - C) / (C_o - C_\infty) \quad [1]$$

where C_∞, the measured non-zero equilibrium curcumin value at infinite time, C_o, the measured curcumin value at zero time and C, curcumin value at time *t*. First order reaction in terms of the fraction conversion may be presented as

$$ln (1-f) = -k.t \text{ or } ln [(C - C_\infty) / (C_o - C_\infty)] = - k.t \quad [2]$$

Dependence of the degradation rate constant on temperature is represented by the Arrhenius equation:

$$k = k_o \exp (-E/RT) \quad [3]$$

where k_o, frequency factor (min^{-1}); E, activation energy (kJ/ml); R= universal gas constant (8.314 J/mol K) and T= absolute temperature (K).

A plot of ln (1-*f*) against t, give k value from the slope (Figure 1). The rate of curcumin degradation in inclusion complex was determined by linear regression; and the coefficients are reported in Table 1. The r^2 values showed

strong correlation except for 33°C/dark and 5°C/dark; and standard errors were less than 0.0181 for the entire range. A plot of ln k against 1/T able to give (-E/R) from the slope (Figure 2). Since R value is known, E value can be calculated. The activation energy can be seen as the energy barrier that molecules need to cross in order to be able to react [8]. Activation energy in the presence of light was 23.88 kJ/mol and in the dark was 13.65 kJ/mol. Usually when high activation energy is found, the conclusion is sometimes drawn that the reaction will proceed slowly or will be difficult. This is not necessarily true, because the reaction may proceed quite fast at very high temperature. The point is that higher activation energy in the presence of light indicates strong temperature dependence; that is to say, it will run very slowly at low temperature, but relatively fast at high temperature. Relatively low activation energy obtained in this study for both with or without light indicates that degradation will continue at a measurable rate at low temperatures, for instance, during storage, leading to a limited shelf life.

Table 1: Kinetic parameters for the degradation of curcumin in turmeric oleoresin:β-cyclodextrin inclusion complex during storage

	Light			*Dark*		
	45°C	33°C	5°C	45°C	33°C	5°C
k (min^{-1})	0.0483	0.0386	0.0134	0.0096	0.0052	0.0045
r^2	0.9908	0.9873	0.9499	0.9866	0.8632	0.7625
S.E.	0.0146	0.0138	0.0095	0.0181	0.0054	0.0138
$t_{½}$ (days)	14.35	17.95	51.72	72.19	133.27	154.00
Activation energy, E (kJ/mol)		23.88			13.65	

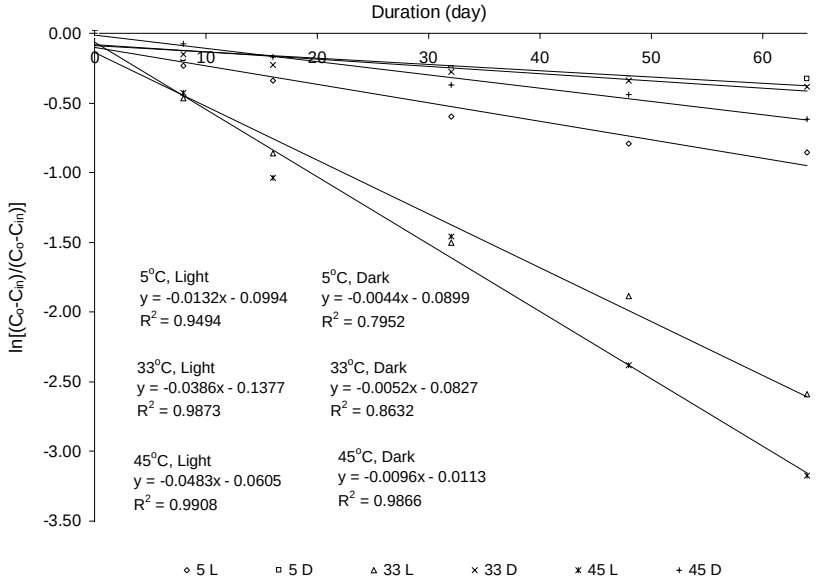

Figure 1: First order degradation kinetics of curcumin (mg/100g) in turmeric oleoresin: BCD inclusion complex formed using kneading method at selected temperatures with or without the presence of light (L=light, D=dark, in=infinity).

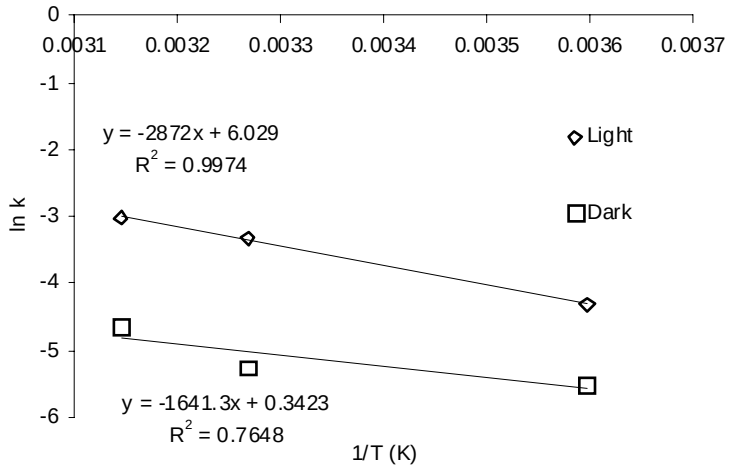

Figure 2: Variation of curcumin degradation rate constants with temperature, with and without the presence of light.

The half-life, $t_{1/2}$, that is the time required for the reduction of a value to 50% of its original value was calculated from the slope k as $t_{1/2} = 0.693/k$. Exposure to light and heat significantly reduced the shelf life of this inclusion complex. Therefore, in order to extend the shelf life, this product has to be stored in dark containers at 5°C. Based on half life $t_{1/2}$ data (Table 1), the shelf life of this product can be extended to 154 days.

Conclusion

The results of this study indicate that the shelf life of turmeric oleoresin inclusion complex can be extended to 154 days if it is stored at 5°C in dark containers.

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