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FULL PAPER

Structural characterisation, citral retention and thermal properties of the inclusion complex of rice starch–lemongrass extract

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Abstract

The citral compound that contributes to the strong-lemony odour of lemongrass has high volatility and low physicochemical stability. To overcome the problems, the inclusion complex of the encapsulation technique was applied with rice starch as a coating material to improve the stability and protect against any unfavourable reaction. Therefore, this study was conducted to determine the structural characterization, citral retention and thermal properties of native rice starch, gelatinised rice starch, inclusion complex of rice starch–citral compound, and inclusion complex of rice starch–lemongrass extract. Lemongrass extract and standard citral compound were homogenised into rice starch dispersion at 80°C for 15 mins and freeze-dried at −50.0±2.0°C. The formation of the inclusion complex powder was determined using different analyses including morphological structure using the scanning electron microscope, crystallinity structure was determined with X-ray diffractometer, identification and quantification of citral compound using HS-SPME-GC-FID and the thermal properties of inclusion complex analyzed using differential scanning calorimetry. The microstructure of both inclusion complex of rice starch-lemongrass extract and rice starch-citral compound exhibited a laminated multiangular shape with crumble formation together with the characteristics of V-type pattern of crystalline complexes. The low degree of crystallinity of the inclusion complex of rice starch–lemongrass extract obtained high in citral entrapment (29.34±3.13%) with the highest concentration of citral retention (7.33±0.78 ppm). Both inclusion complex of rice starch-citral compound and rice starch-lemongrass extract displayed an endothermic peak at 138°C, which is attributed to an inclusion complex occurrence with significant difference (p<0.05) of enthalpy of 0.44±0.05 J/g and 1.61±0.70 J/g, respectively. These findings showed that rice starch was effective in complexing with aroma compounds in improving the stability and protecting the citral compound of lemongrass extract from any unwanted changes. This inclusion complex should be regarded as an important strategy in designing a novel model of citral compound of lemongrass for food flavouring application.

1. Introduction

Lemongrass (*Cymbopogon citratus*) is a well-known aromatic herb that is widely cultivated in tropical and subtropical climates in Indochina, Indonesia, Malaysia, Sri Lanka as well as Northern and Southern of India (Francisco *et al*., 2011). It is commercially used in pharmaceutical (Shah *et al*., 2011), cosmetic (Mohamed Hanaa *et al*., 2012), and food flavouring (Katsukawa *et al*., 2010) industries due to its strong lemony odour contributed by the geometric citral isomers of neral and geranial (Weisheimer *et al*., 2010) that makeup to 65–80% of the total volatile composition (Carlson *et al*., 2001; Schaneberg and Khan, 2002; Nakahara *et al*., 2003). Nevertheless, the instability and volatility of citral compound are inconveniences causing a short flavour lifespan (Vaughn *et al*., 2009; Xiao *et al*., 2015) that is linked to oxidation and volatilisation (Ruktanonchai *et al*., 2011).

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The adverse effect on the citral compound of lemongrass can be overcome using encapsulation process through the inclusion complex technique (Cohen *et al*., 2008; Putseys *et al*., 2010) by entrapping the aroma compound within starch polymer chains in heterogeneous or homogenous matrices (Wang, Yang and Yue, 2015). This application is to secure the susceptibility of the citral compound by protecting it from any unfavourable changes (Nazarro *et al*., 2012; Yahya *et al*., 2016). Starch is a suitable material in the preparation of inclusion complex and act as encapsulating guest molecules that fulfil the selection criteria including bland taste, inertness, and economic viability (Gharsallaoui *et al*., 2007; Nazarro *et al*., 2012) such as β-cyclodextrin (Wang *et al*., 2011), tapioca starch (Itthisoponkul *et al*., 2007), corn starch (Cohen *et al*., 2008; Zhang *et al*., 2013), and rice starch (Keatkrai *et al*., 2017).

Starch consists of amylose and amylopectin chains that bind with aroma compounds or guest molecules. Amylose chains interact with the hydrophobic part of guest molecules on their helical cavity in structuring the inclusion complex (Conde-Petit *et al*., 2006; Itthisoponkul *et al*., 2007; Zhang *et al*., 2013), whereas amylopectin chains form a network structure between guest molecules (Conde-Petit *et al*., 2006) under an aqueous solution (Wulff *et al*., 2005). Amylose was reported to form helicoidally inclusion with small molecules like iodine, emulsifiers, lipid, and flavour compound (Arvisenet and Cayot, 2001) while amylopectin has a weak ability to form inclusion complexes with hydrocarbon compounds (Arvisenet *et al*., 2002). The presence of water is to augment the polar interaction of the hydrogen bonds between the hydroxyl groups of starch and volatile compounds (Van Ruth and King, 2003) during the inclusion complex formation. Weak chemical forces like van der Waals forces, dipole-dipole interactions, and hydrogen bonding are involved in the entrapment of volatile compounds with the helical structure of starch (Gupta *et al*., 2016). Therefore, the study aimed to characterize the morphology, crystallinity structure and thermal properties of native rice starch, gelatinised rice starch, inclusion complex of rice starch-citral compound, and inclusion complex of rice starch-lemongrass extract as well as to determine the retention concentration and entrapment efficiency of citral compound from different types of inclusion complex powders.

2. Materials and methods

Fresh lemongrass stalks were purchased from a local market at Kuala Nerus, Terengganu, Malaysia. The fresh lemongrass stalks with the moisture content of 80.0±5.0% (w.b) were cut into 16 cm length and chopped into small pieces for preparation of freeze-dried lemongrass powder. Rice starch and standard of citral compound (assigned as 99.8% purity) was purchased from Sigma-Aldrich Co. The analytical grade chemical solvents of dichloromethane and n-hexane were supplied by Merck KGaH (Darmstadt, Germany) and HmbG Chemical (Hamburg, Germany) respectively.

2.1 Preparation of gelatinised rice starch powder

The gelatinised rice starch was prepared using the modified method following Jouquand *et al*. (2006) and Xi *et al*. (2015). About 6.00±0.05 g of rice starch was homogenised with 200 mL of distilled water, heated up to 80.0±3.0°C and remained for 20 mins along with cooling down to 30°C. Then, it was frozen at −80.0±2.0°C prior to freeze-drying at −50.0±2.0°C for 48 hrs. The heating plate of the freeze dryer was automated to 20.0±2.0°C on vacuum degree at 0.203 KPa. It was then ground into a powder form using a 0.25 mm microfine grinder (IKA® Werke Staufen - MF 10.21, Germany). The dispersed powder was fixed into a size of 250 μm using a sieve shaker (Retsch Model AS 200 digit, Germany) by stacking and vibrating at the amplitude of 60 for 20 mins. Then, the powdered samples were collected and kept at 4.0±2.0°C in a zip-lock polyethylene bag for further analysis.

2.2 Preparation of the inclusion complex of rice starch-citral compound powder

The preparation method of the inclusion complex of rice starch-citral compound was conducted similar to the preparation of gelatinised rice starch powder in Section 2.1 by following the method of Jouquand *et al*. (2006) and Xi *et al*. (2015) with some modifications. After gelatinised rice starch remained constant for 5 mins at a temperature of 80.0±3.0°C, 25.00±0.05 mL of 25 ppm standard citral compound was added slowly while being homogenised and maintained at 80.0±3.0°C for another 15 mins at 200 rpm. Then, the cooled dispersion was collected with the aqueous layer and frozen at −80.0±2.0°C prior to the freeze-drying process at −50.0±2.0°C for 48 h. Then, the powdered samples were collected and kept at 4.0±2.0°C in a zip-lock polyethylene bag for further analysis.

2.3 Preparation of lemongrass extract

About 300.0±0.5 g of chopped lemongrass stalk was frozen in the freezer (MDF-U55V-PE, Panasonic, Japan) for 24 hrs at −80±2.0°C prior to freeze-drying at −50.0±2.0°C, following Ding *et al*. (2012). The heating plate of the freeze dryer was automated to 20.0±3.0°C on vacuum degree at 0.203 kPa. After the drying process

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ended, the dried lemongrass was ground into a powder form for 30 s with a microfine grinder (IKA® Werke Staufen - MF 10.21, Germany) prior to the hydrodistillation extraction of the lemongrass extract. In this study, the freeze-dried of lemongrass powder was chosen as our previous research found that it obtained higher citral concentration when compared to fresh lemongrass stalk and other lemongrass dried powders (Hashim *et al*., 2019).

The hydrodistillation method was modified from the study done by Tajidin *et al*. (2012) in which about 10.00±0.50 g of freeze-dried lemongrass powder was mixed with 250 mL of distilled water upon extraction for 2 hrs at 100.0±3.0°C to obtain a lemongrass extract from the Clevenger-type apparatus. The lemongrass extract was separated from the distilled water by liquid-liquid separation with the addition of 100.0±0.05 mL of dichloromethane. The organic solvent was then removed with a rotary evaporator at 40°C for 10 min to make a yellowish lemongrass extract appeared at the bottom of the round-bottom flask. The extract was transferred into a 2 mL vial for storage at 4°C before being encapsulated with rice starch. The yield of lemongrass extract was calculated using the following equation:

$$\text{Yield of lemongrass extract (\%)} = \frac{\text{Lemongrass extract (g)}}{\text{Freeze-dried lemongrass powder (g)}} \times 100$$

2.4 Preparation of inclusion complex of rice starch-lemongrass extract

The preparation method of the inclusion complex of rice starch–lemongrass extract is similar to the preparation of gelatinised rice starch in Section 2.1 according to the method of Jouquand *et al*. (2006) and Xi *et al*. (2015) with some modifications. After remaining the gelatinised rice starch for 5 min at a temperature of 80.0±3.0°C, a 1.00±0.05 mL of lemongrass extract was added slowly while being homogenised and maintained at 80.0±3.0°C for another 15 min at 200 rpm. Then, the cooled dispersion was collected with the aqueous layer frozen at −80.0±2.0°C prior to the freeze-drying process at −50.0±2.0°C for 48 h. Then, the powdered samples were collected and kept at 4.0±2.0°C in a zip-lock polyethylene bag for further analysis.

2.5 Determination of morphological structure

The morphological structures of the rice starch, gelatinised rice starch, inclusion complex of rice starch–citral compound, and inclusion complex of rice starch–lemongrass powder were observed using Scanning Electron Microscopy (SEM) (JEOL, JSM – 6360 LA, Japan) following Tonon *et al.* (2008). The sample powder was attached to a double-sided adhesive tape mounted on the SEM stubs. It was coated with 3.5 mA gold under a vacuum condition using an auto fine coater (JEOL, JFC – 1600, Japan). Then, it was examined and operated at an accelerating voltage of 5Kv under magnification of 300×.

2.6 Determination of crystallinity structure

X-ray diffraction (XRD) using Siemens D – 500 Diffractometer was used to determine the XRD pattern and crystallinity degree of the rice starch, gelatinised rice starch, inclusion complex of rice starch–citral compound, and inclusion complex of rice starch–lemongrass extract according to Wang *et al*. (2002) method. Each of the samples was placed and slightly pressed on an aluminium holder using a glass slide. It was operated at a wavelength of 0.154 nm and the output energy was set at 15 mA and 30kV. Diffractogram was taken at 5° – 50° (2θ) at a steep 0.1° angle and a scan rate of 2 s per steep. The XRD patterns were plotted to compare all the samples and the degree of crystallinity was determined using the following equation:

$$\text{Crystalllinity Degree (\%)} = \frac{\text{Area of the crystallised region}}{\text{Area of the crystallised region + Area of the amorphous region}} \times 100$$

2.7 Determination of citral concentration

2.7.1 Extraction of citral compound

The concentration of the citral compound on the inclusion complex of rice starch–citral compound and inclusion complex of rice starch–lemongrass extract was determined by Headspace-Solid Phase Microextraction (HS-SPME) following Hashim *et al*. (2019) with minor modifications. A 20 mL of 1000 ppm stock solution of standard citral compound (assigned as 99.8% purity) was subjected to be prepared by diluting with distilled water for HS-SPME procedure with a series of concentrations of 25, 50, 75, 100 and 125 ppm.

A weight of 1.00±0.05 g of the inclusion–complex powder was added to the 45 mL of headspace vial. A heating block was used to equilibrate the temperature surrounding the vial. The citral compound extraction was conducted at 60°C for 30 mins along with SPME fibre coating composed of carboxen/polydimethylsiloxane (CAR/PDMS). The SPME CAR/PDMS coating was selected due to the less polar with high extraction efficiency and sensitivity in extracting hydrocarbon and monoterpenes compound (Caldeira *et al*., 2007). The CAR/PDMS fibre was immediately inserted into the injection port of the gas chromatography (GC 2010 - Shimadzu, Japan) for 5 mins at 250°C. The SPME fibre was then conditioned for the first usage for an hour at 350°C and reconditioned between analyses to prevent carryover. A blank test was conducted by desorbing the fibre for a second time to check the possibility of a carryover.

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The citral compound in lemongrass extract was identified and quantified by following Yahya *et al*. (2010) with minor modifications. A 1.00±0.05 mL of lemongrass extract was added with 10.00±0.05 mL of *n*-hexane into a 45 mL headspace vial before injected into the GC for analysis with splitless mode.

2.7.2 Identification and quantification of citral compound

Gas Chromatography-Flame Ionization Detector (GC-FID) was used to identify and quantify the citral compound of samples with GC 2010 (Shimadzu, Japan). The programme temperature setting was started at 60°C then increased by 4°C/min to 150°C, followed increased to 250°C at 20°C/min and maintained at equilibrium for 5 min. A RTX-5 capillary column (30 m × 0.25 mm internal diameter, 0.25 µm film thickness) was used in this analysis. The chromatographic conditions were as follows: helium was used as a carrier gas. The flow of helium, hydrogen and air were set at 30.0 mL/min, 40.0 mL/min and 400 mL/min, respectively; the temperature of the injector and detector was set at 250°C with the pressure of 100 kPa.

The two isomers of citral compound; neral and geranial were identified by comparing their retention times to the authentic standards. The concentration of citral compound was expressed as the sum of concentration of neral and geranial obtained from separated standard curve (peak area vs concentration).

2.7.3 Entrapment efficiency of the citral compound

The efficiency of citral entrapment was calculated using the equation from Zhang, Zhou, Cao *et al*. (2015):

$$\text{Entrapment Efficiency of Citral Compound (\%)} = \frac{\text{Citral concentration from rice starch inclusion complex (ppm)}}{\text{Initial concentration of citral compound (ppm)}} \times 100$$

The initial citral concentration of standard citral compound and lemongrass extract was 25.00 ± 0.53 ppm.

2.8 Determination of thermal properties

The thermal properties of the rice starch gelatinised rice starch, inclusion complex of rice starch-citral compound, and inclusion complex of rice starch-lemongrass extract were determined using differential scanning calorimetry (DSC Q2000, TA Instruments, USA) with some modifications on the method of Simi and Abraham (2008). The DSC was calibrated for heat flow and temperature using standard indium. About 3.00±0.50 mg of the sample powder was added with distilled water with the ratio of 1:4 (w/w) and sealed in an aluminium pan with a similar empty pan used as a reference. The sealed sample was stood for an hour while being agitated at 100 rpm. Scanning was carried out at 10°C/min from 30 to 150°C. Heating and cooling were carried out in a nitrogen gas atmosphere. Scanning of the samples was measured the temperature value of onset (T_o), peak (T_p), conclusion (T_c), phase transition temperature range (T_r), and enthalpy of gelatinisation (ΔH_{gel}) from the thermographs of the samples.

2.9 Statistical analysis

Data of the samples were analysed using MINITAB 14 software (MINITAB Inc., PA, USA). The one-way analysis of variance (One-way ANOVA) was used to determine the significant differences between the mean values of the samples followed by Fisher's Least Significant Difference (LSD) test at $p<0.05$ for crystallinity degree and thermal properties among the samples. The independent *t*-test analysis was performed to compare the mean values between the citral retention from the inclusion complex of rice starch–citral compound and inclusion complex of rice starch–lemongrass extract.

3. Results and discussion

3.1 Morphological structure

Figure 1 shows the morphological structure of the rice starch, gelatinised rice starch, inclusion complex of rice starch-citral compound, and inclusion complex of rice starch-lemongrass extract under SEM with a magnification of 300×. The micrograph of rice starch granules exhibited a smooth polyhedral structure with a laminated appearance (Figure 1a) which is similar to the observation of Singh *et al*. (2006), Wani *et al*. (2012), and Chrungoo and Devi (2015). Figure 1b shows the prominent irregular structure with hole-like structure of the gelatinised rice starch. A small intercept on the large hole-like microstructure was observed which connected the edges as previously reported by Jung *et al*. (2017) on the structure of gelatinised rice grain. It indicates that the central region of the native starch was disrupted and became very loose with more water-uptake at a high heating temperature (Liu and Zhao, 1990).

The inclusion complex of rice starch–citral compound (Figure 1c) exhibited a similar observation to the inclusion complex of rice starch–lemongrass extract (Figure 1d) with irregular agglomerate-like structure with the presence of crumble on the laminated surface. This is due to the self-agglomeration of the rice starch with the volatile compound of the lemongrass extract during the inclusion complex formation as previously stated by Seo *et al*. (2010). The significant attributes shown by the microstructure of the rice starch–lemongrass extract inclusion complex indicate the successful formation of the inclusion complex as

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reported by Zhang, Zhou, Cao *et al*. (2015) and Zhang *et al*. (2016).

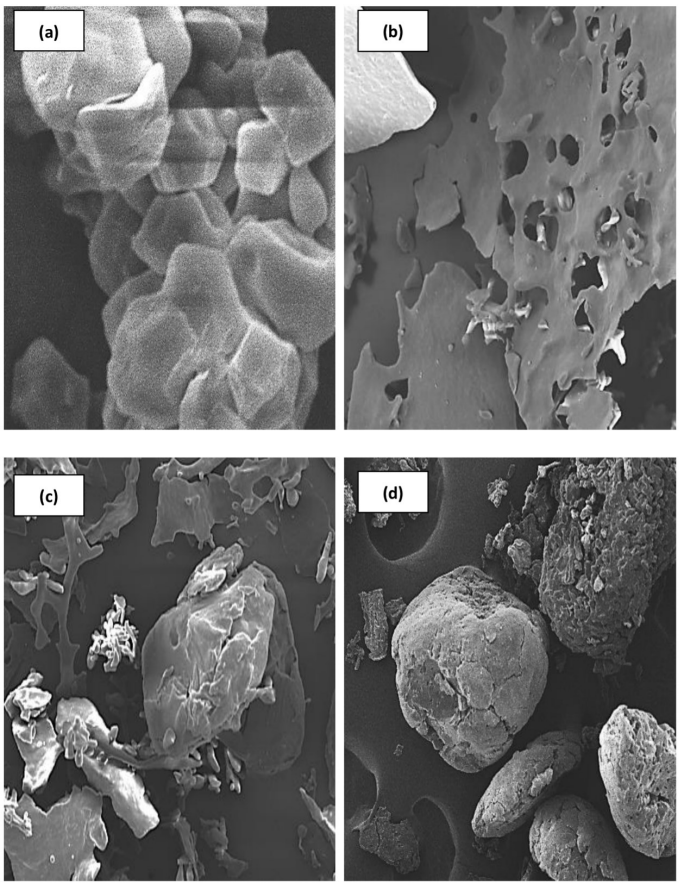

Figure 1. SEM micrograph of a) rice starch, b) gelatinised rice starch, c) inclusion complex of rice starch-citral compound and d) inclusion complex of rice starch-lemongrass extract at 300x magnification.

3.2 Crystallinity structure

Figure 2 shows the X-ray diffraction (XRD) patterns of the rice starch, gelatinised rice starch, inclusion complex of rice starch–citral compound, and inclusion complex of rice starch–lemongrass extract. The XRD pattern of the native rice starch (Figure 2a) shows a typical A-type pattern with strong diffraction peaks at 15°, 17°, 18°, and 23° which are usually shown by cereal starch as reported in previous studies (Aguirre *et al*., 2011; You *et al*., 2015). Afterwards, the gelatinisation process was significantly attributed to the disappearance of the original peak and XRD pattern of the native starch (Aguirre *et al*., 2011). However, the V-type pattern was attributed to the appearance of a weak peak existing at 20° (Ribotta *et al*., 2004) on the XRD pattern of gelatinised rice starch (Figure 2b) as reported by Khanh (2015). Both of the XRD patterns on the inclusion complex of rice starch–citral compound (Figure 2c) and inclusion complex of rice starch–lemongrass extract (Figure 2d) show V-type patterns similar to the gelatinised rice starch. The rice starch granules experienced mechanical damage during gelatinisation caused by the loss of its double helix structure and crystalline order (Eliasson and Wahlgren, 2004). The changes are associated with the chemical interaction of rice starch molecules with the citral compound to form an inclusion complex. The distinct change of diffraction patterns indicates a new solid crystallite was formed (Zhang, Li, Yu *et al*., 2015) due to the adjustment in the molecular structures (Abarca *et al*., 2016). The inclusion complex can be validated based on the merging of diffraction patterns, formation of new peaks, and disappearance of original peaks (Sinha *et al*., 2005).

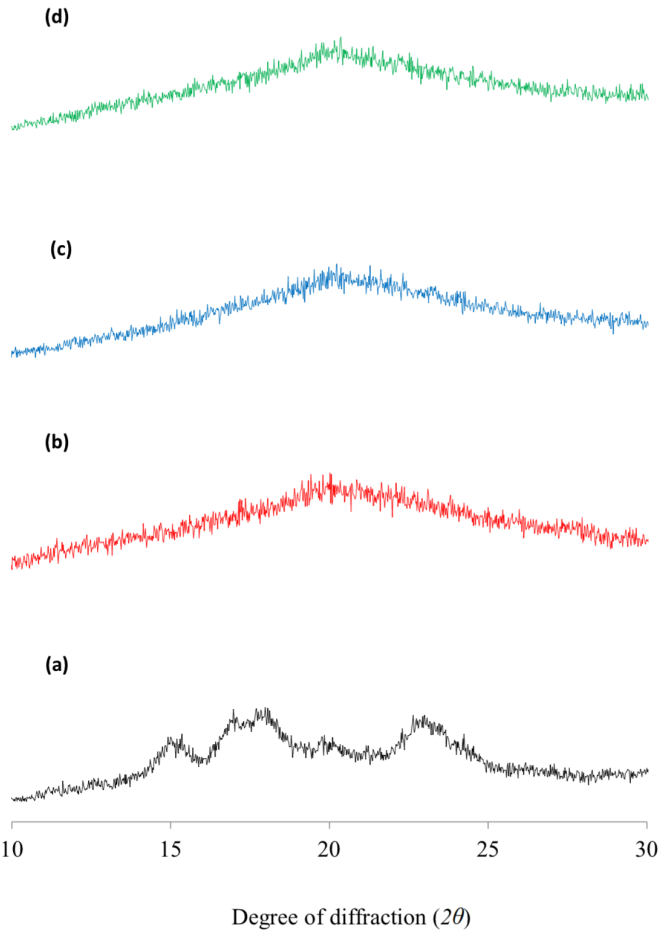

Figure 2. The X-ray diffraction (XRD) patterns of a) rice starch, b) gelatinised rice starch, c) inclusion complex of rice starch-citral compound and d) inclusion complex of rice starch-lemongrass extract.

Table 1 shows the crystallinity degree was significantly different (p<0.05) for all of the rice starch, gelatinised rice starch, inclusion complex of rice starch–citral compound, and inclusion complex of rice starch–lemongrass extract with a range of 2.75–11.81%. As can be seen, the inclusion complex of the rice starch–citral compound showed the highest crystallinity degree (11.81±0.78%) while the gelatinised rice starch showed the lowest crystallinity degree (2.75±0.33%). The unexpected low crystallinity degree of the rice starch as reported by Yu *et al*. (2012) was due to the differences in rice cultivars, starch structure and distribution of amylose, and short and long side-chain amylopectin in

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the starch granules (Singh *et al*., 2007; Yu *et al*., 2012). Rice starch granules are mainly composed of amorphous fractions rather than crystalline fractions as the rice starch components are presented as a semi-crystalline structure (Wani *et al*., 2012) with a proportion of 30% crystalline and 70% amorphous region (Donald, 2004). Meanwhile, the low crystallinity degree of the gelatinised rice starch is associated with a predominantly amorphous composition (Donald, 2004). Previous studies reported that gelatinised starch has no crystallites (Amagliani *et al*., 2016). It can be explained that the rice starch granules swelled and the crystalline organisation broke down into an amorphous region (Aguirre *et al*., 2011) while the double helix of the starch structural chains (Hu *et al*., 2014) and molecular orders of amylose and amylopectin (Biliaderis and Zawistowiski, 1990) were disrupted in the starch crystallites.

Table 1. Crystallinity degree (n=3) of rice starch, gelatinised rice starch, inclusion complex of rice starch-citral compound and inclusion complex of rice starch-lemongrass extract powder

Powder	Crystallinity degree (%)
Rice starch	11.67±1.63[a]
Gelatinized rice starch	2.75±0.33[c]
Inclusion complex of rice starch-citral compound	11.81±0.78[a]
Inclusion complex of rice starch-lemongrass extract	8.23±0.47[b]

Mean with the different superscript letter in the same column is significantly different at $p<0.05$

The presence of standard citral compound caused a minor effect on the starch recrystallisation. The amylose chains of rice starch were recrystallised with amylopectin chains and in turn, chemically formed an inclusion complex of rice starch–citral compound soon after gelatinisation while being cooled down at the room temperature as reported by Yu *et al*. (2018) with a high rate at the first hours of cooling (Ribotta *et al*., 2004; Wang *et al*., 2015). In addition, the amorphous amylose fraction was organised into a crystalline fraction (Vandeputte *et al*., 2003; Wani *et al*., 2012) while the amylopectin fraction was directly recrystallised (Ribotta *et al*., 2003). On the contrary, the presence of lemongrass extract inhibited the rice starch recrystallisation by disturbing the reassociation between amylose and amylopectin chains during the cooling stage that the hydroxyl groups of guest molecules of lemongrass extract were chemically forming hydrogen bonds with the starch molecules as previously reported by Fu *et al*. (2014). The guest molecules of lemongrass extract acted as a physical barrier to prevent recrystallisation between amylose and amylopectin (Li *et al*., 2017). Nevertheless, the retardant effect of the starch recrystallisation was caused by both amylose and amylopectin interacting with the composition of lemongrass extract especially with the citral compound to form the inclusion complex of rice starch–lemongrass extract. For this reason, the retardant effect has the advantage of forming new starch –guest molecule helical complexes during the complex process (Gunaratne and Corke, 2007).

3.3 Citral retention

3.3.1 Retention concentration of citral compound

Table 2 shows the retention concentration of citral compound on the inclusion complex of rice starch–citral compound and inclusion complex of rice starch–lemongrass extract. The retention concentration of citral compound showed a significant difference ($p<0.05$) between both type of inclusion complexes as determined by HS-SPME at 60°C for 30 mins with the retention concentration of inclusion complex of rice starch-citral compound was 4.71±0.16 ppm and inclusion complex of rice starch-lemongrass extract was 7.33±0.78 ppm. It explains that the citral compound (MW=152.23 g mol^{-1}) is easily diffuse out from the rice starch inclusion complex where previous studies reported that low molecular weight (Shahhoseini *et al*., 2013) compounds are easy to release from a solid sample. At the same time, this finding shows that rice starch is substantially able to act as a physical barrier in order to retain and lower the diffusion of citral compound out into the headspace. Aroma retention is strengthening with the chemical bonding between aroma molecules and starch structural chains (Kant *et al*., 2004) which justified the decreased in the mass transfer of aroma compounds (Lafarge *et al*., 2008). The non-polar aroma compounds are favoured by owing a greater degree of sorption in created structural bonding on the amylose structural chains as similarly reported by Samavati *et al*. (2012) on ethyl acetate retention in xanthan gum matrices. Citral compound is also formed weak inclusion complex with the side branches of amylopectin chains (Langourieux and Crouzet, 1995; Arvisenet *et al*., 2002) then forming an unstable interaction (Hansson *et al*., 2003) that contributed to the easy release of the citral compound during HS-SPME procedure.

It is interesting to note that thermal transformation might occur to other volatile composition of lemongrass extract into citral isomers of neral and geranial during inclusion complex formation. Previous studies reported that the verbenol have the potential to transform into citral isomers by opening their 4- and 6- membered rings under thermal condition (Maksimchuk *et al*., 2004). Baritaux *et al*. (1992) stated that linalyl acetate hydrolysed and transformed into linalool. Linalool is easily isomerized into geraniol and nerol and oxidizes to form neral and geranial (Misharina *et al*., 2003). This

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reaction increased the geranial and neral composition and at the same time, decreased the compounds with a similar chemical structure as citral isomers. Aoge *et al.* (1996) summarized the chemical reaction as geranyl acetate → geraniol → geranial → neral. This finding was in contrast with inclusion complex of rice starch-citral compound that thermal degradation and hydro-degradation of the citral compound occurred during the inclusion complex formation. The preparation temperature of inclusion complex gave significant impact to the formation of new compounds on the oil composition under oxidation reaction (Rasheed *et al*., 2016). A previous study reported that isomers of citral compound are degraded through oxidation into isomeric *m*- and *p*-cymene (Misharina *et al*., 2003).

From that steric hindrance effect is formed from the inclusion complex formation by the host molecules of rice starch to give protection against the evaporation of aroma compounds (Wang *et al*., 2011) resulting in a lower concentration aroma concentration in the headspace (Hansson *et al*., 2003). It is a consequence of the adsorption, complexation by specific binding interactions between polysaccharide chains and aroma compounds (Secouard *et al*., 2003).

Table 2. Retention concentration and entrapment efficiency of citral compound from the inclusion complex of rice starch-citral compound and inclusion complex of rice starch-lemongrass extract.

Inclusion complex	Retention concentration (ppm)	Entrapment efficiency (%)
Rice starch-citral compound	4.71±0.16^{b}	18.85±0.66^{b}
Rice starch-lemongrass extract	7.33±0.78^{a}	29.34±3.13^{a}

Mean with the different superscript letter in the same column is significantly different at p<0.05

3.3.2 Entrapment efficiency of citral compound

Table 2 shows the entrapment efficiency of the citral compound was significantly different (p<0.05) between the inclusion complex of rice starch–citral compound and the inclusion complex of rice starch–lemongrass extract. The entrapment efficiencies of the citral compound were 18.85 – 29.34 ppm where the inclusion complex of rice starch–lemongrass extract exhibited a greater entrapment efficiency of the citral compound. It is in a good agreement with Hill *et al*. (2013) and Tao *et al*. (2014) due to the effect of the aroma composition of lemongrass extract competing with other compounds as compared to the pure compound of citral. Rakmai *et al*. (2017) reported that carvacrol has to compete with other essential components of yarrow essential oil-hydroxypropyl-β-cyclodextrin encapsulation. Despite that, it shows that rice starch was able to entrap the citral compound of lemongrass extract in the rice starch inclusion complex even though the aroma compound experienced high competition from other compositions of the lemongrass extract. This phenomenon is beneficial as stated by Arvisenet *et al*. (2002) regarding the cooperative effect where the first molecules are favoured in the formation of a second molecule complex.

3.4 Thermal properties

Table 3 shows the thermal transition temperatures (onset, T_o; peak, T_p; conclusion, T_c) were significantly different (p < 0.05) between the native rice starch, gelatinised rice starch, inclusion complex of rice starch–citral compound, and inclusion complex of rice starch–lemongrass extract. Thermal transition temperatures appeared in the range of T_o (64.52–138.83°C), T_p (70.56–138.95°C), and T_c (79.34–142.93°C). It can be seen that the rice starch granules started to gelatinise at 64.52°C to 79.34°C which agrees to the endotherm range of 60.0–85.0°C as previously stated by Singh *et al*. (2006) and Simi and Abraham (2008). The starch granule structurally swelled from absorbing water, causing a breakdown on the birefringence of granules as explained by Liu *et al*. (2002), Singh *et al*. (2003) and Li *et al*. (2004). When the rice starch gelatinised at 80°C, the

Table 3. Thermal properties of rice starch, gelatinised rice starch, inclusion complex of rice starch-citral compound and inclusion complex of rice starch-lemongrass extract.

Sample	Temperature (°C)				ΔH_{gel} (J/g)
	T_o	T_p	T_c	T_c - T_o/T_r	
A	64.52±0.23^{b}	70.58±1.11^{b}	79.34±0.80^{b}	14.82±1.03^{a}	0.80±0.31^{ab}
B	136.84±2.00^{a}	137.19±1.57^{a}	141.32±0.30^{a}	2.23±0.86^{b}	1.85±0.32^{a}
C	138.66±0.45^{a}	138.88±0.40^{a}	141.98±0.40^{a}	3.33±0.83^{b}	0.44±0.05^{b}
D	138.83±0.28^{a}	138.95±0.27^{a}	142.93±1.51^{a}	4.10±1.23^{b}	1.61±0.70^{a}

Mean with the different superscript letter in the same column is significantly different at p<0.05. Key: A) rice starch, B) gelatinised rice starch, C) inclusion complex of rice starch-citral compound and D) inclusion complex of rice starch-lemongrass extract. T_o: onset temperature, T_p: peak temperature, T_c: conclusion temperature, T_r: phase transition temperature, ΔH_{gel}: enthalpy of gelatinisation.

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original thermal transition temperatures disappeared, and a small endothermic peak appeared at a higher temperature of 137.19±1.57°C. The small amount of lipid content in the rice starch granule was at 0.3–0.56% as mentioned by Mohan *et al*. (2005) and Gani *et al*. (2017) where it caused higher thermal transition temperatures as reported by Dupuis *et al*. (2014). Previous studies identified that the high temperature of the endothermic peak is related to the melting of amylose –lipid complexes (Singh *et al*., 2007). The lipid content consequently interacted with the starch components in establishing the amylose–lipid complex formation during the gelatinisation process at 80°C and Tester (1997) identified that the lipid molecules extent complexed with amylose chains, directly affecting the gelatinisation properties. Meanwhile, the inclusion complex of rice starch–citral compound and inclusion complex of rice starch–lemongrass extract showed an insignificant thermal transition temperature at 138°C as shown in Table 3. It is similar to the inclusion complexes of eugenol-β-cyclodextrin (Seo *et al*., 2010) and garlic oil-β -cyclodextrin (Wang *et al*., 2011). The presence of the standard citral compound and lemongrass extract in the form of essential oil affected the gelatinisation process by increasing the transition temperatures of inclusion complex powder which has a similar effect as reported by Baker and Rayas (1998). To some extent, the standard citral compound and composition of lemongrass extract replaced the water molecules and substituted on the rice starch structure, creating a stable structure interaction that improved the thermal stability of both rice starch inclusion complexes, as stated by Yoshimura *et al*. (1996).

The phase transition temperature range (T_r) of starch gelatinisation directly reflected the quality and heterogeneity of the granular crystalline structure (Tester and Debon, 2000; Simi and Abraham, 2008). The thermal properties of T_r were significantly different (p<0.05) between the native rice starch, gelatinised rice starch, inclusion complex of rice starch-citral compound, and inclusion complex of rice starch-lemongrass extract. The T_r was in the range of 2.33–14.82°C with native rice starch obtained the highest T_r at 14.82±1.03°C and gelatinised rice starch shows the lowest T_r at 2.23±0.86°C. The broad T_r of the rice starch indicated that wider heating temperature needed during gelatinisation to dissociate the crystalline region of the rice starch granule, as according to Singh et al. (2003), the starch gelatinisation process is firstly favoured in the amorphous regions due to the weak hydrogen bonding followed by crystalline regions.

The T_r of gelatinised rice starch was significantly lower at 2.23±0.86°C but it was determined at the temperatures of 136.84–141.32°C, which represent the T_r for amylose–lipid complexes. It explains that the order of crystallite fractions of the rice starch granules was disrupted and disintegrated during gelatinisation which is in line with Amagliani *et al*. (2016), as the gelatinisation turned the crystalline regions of starch into amorphous regions. The low T_r of gelatinised rice starch indicates that new amylose chain interactions were formed with endogenous lipid molecules of the rice starch during gelatinisation (Le Bail *et al*., 1999). Low T_r for both rice starch inclusion complexes indicate the inclusion complex formation is structured less ordered and weak crystalline inclusion complex as identified by Sasaki *et al*. (2000) and Singh *et al*. (2003).

The enthalpy of gelatinisation (ΔH_{gel}) reflects the energy required in the cause of losing the double-helical molecular order and crystallinity (Singh *et al*., 2006). It was significantly different (p<0.05) between the rice starch, gelatinised rice starch, inclusion complex of rice starch-citral compound, and inclusion complex of rice starch-lemongrass extract as shown in Table 3. The ΔH_{gel} was in the range of 0.44–1.85 J/g where surprisingly, the inclusion complex of rice starch–citral compound resulted in the lowest ΔH_{gel} of 0.44±0.05 J/g and unexpectedly, the gelatinised rice starch obtained the highest ΔH_{gel} of 1.85±0.32 J/g. In this study, lower thermal energy required to disintegrate rice starch granules under excess water might denote by the presence of high amylose content in the starch granules as reported by Biliaderis *et al*. (1986) on the presence of amylose fraction which promoted the decreasing in ΔH of waxy and normal rice starches. The gelatinised rice starch shows high in ΔH_{gel} at 1.85±0.32 J/g where Anugrahati *et al*. (2017) previously reported that a high enthalpy could be due to the presence of non-starch components such as lipid and protein because lipid fractions absorb more heat energy (Singh *et al*., 2000).

The inclusion complex of rice starch–citral compound obtained a low ΔH_{gel} at 0.44±0.05 J/g due to the lower thermal energy required to dissociate the new structured and unstable interaction between the citral compound and rice starch granule. This is due to the interaction between the hydrophilic character of the hydroxyl (-OH) group of the guest molecules of citral and the side chains of starch molecules, binding to the amorphous region of starch granules to various degrees in lowering the heat transfer rates and decreasing the mobility of water in the system (Xiao *et al*., 2011). The enthalpy of the inclusion complex of rice starch–lemongrass extract was significantly higher than that of the inclusion complex of rice starch–citral compound. The compositions of lemongrass extract compound were co-operating to interact with the starch that strengthened

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the chemical bonding instead of the citral compound forming a chemical interaction with the starch polychains. The guest molecules of citral replaced the water molecules from the host cavity of starch and formed an inclusion composite, strengthening the interaction in the thermal stability (Zhang *et al*., 2018).

4. Conclusion

This study demonstrated that the morphological structure of the inclusion complex of rice starch–lemongrass extract exhibited the presence of large penetrated holes forming on the smooth laminated multi-angular inclusion-complex powders. The V-type diffraction pattern of the inclusion complex of rice starch –lemongrass extract showed a diffraction peak at 20^{o} with the crystallinity degree of 8.23±0.47%. The formation of the rice starch inclusion complex is highly retained and efficiently entrapped the citral compound of lemongrass extract. The citral compound of lemongrass extract was protected inside the rice starch cavity from degradation as shown by the DSC thermogram with increased endothermic temperatures of the inclusion complex of rice starch–lemongrass extract from 138.83 to 142.93^{o}C with the enthalpy of gelatinisation of 1.61±0.70 J/g. The stability of the citral compound from lemongrass extract is improved and protected by complexing with the rice starch inclusion complex from any unwanted modifications. This inclusion complex technique is regarded as an important strategy in designing a novel model of citral compound of lemongrass for food flavouring application.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this research paper.

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