Synthesis, characteristics and evaluation of antioxidant activity of [1-(tannin-ether)-ethyl]stearate

Kang Zhang¹ · Xiaohua Zhang¹ · Yan Li¹ · Xinxin Wang¹ · Qing Cao¹ · Li'e Jin¹

Revised: 25 April 2017 / Accepted: 10 August 2017 / Published online: 13 September 2017
© Association of Food Scientists & Technologists (India) 2017

Abstract The [1-(tannin-ether)-ethyl]stearate (TEES) was synthesized by two-stage process successfully. 1-Chloroethyl tannin ether (CTE), as an intermediate, was initially prepared with tannic acid (TA) and paraldehyde. Then, the TEES was synthesized by sodium stearate and CTE in the presence of FeCl₃-PEG-400 as phase-transfer catalyst. Synthetic conditions were optimized. The structural characteristics of TEES were analyzed by FTIR, ¹H NMR and UV–vis techniques. And the thermal stability of TEES was investigated. Moreover, the antioxidant activity of TEES for linseed oil was evaluated and compared with other substance such as TA and butylated hydroxyanisole (BHA). The results showed that the yield reached 88.19 wt% (theoretical value: 88.80 wt%, relative deviation: 0.80 ± 0.34%) under the optimized condition, in which the ratio of TA: FeCl₃: PEG-400 was 1 g: 0.09 g: 0.693 mL, the reaction temperature and time was 75 °C and 240 min, respectively. The antioxidant activity of TEES was higher than TA and comparable to BHA in linseed oil. The *POV* of oil samples with TEES, TA and BHA were 63.4, 201.3 and 84.2 meq/kg after 20 days, respectively. The reason of this was relate to the better oil solubility of TEES and its unique structure. More importantly, the interaction between the TEES and SC was weaker than that of TA and SC by the fluorescence experiment.

Keywords [1-(tannin-ether)-ethyl]stearate · Tannic acid · Sodium stearate · Antioxidant activity · Phase-transfer catalysis

Introduction

Tannic acid (TA) exists in many plants extensively, which is derived from the plant secondary metabolite. It contains a great deal of phenolic hydroxyl groups (Sehrawat et al. 2006). It has various bioactivities and pharmacological activities, such as anti-arteriosclerotic, anti-carcinogenic, anti-mutagenic, anti-microbial properties and exhibits strong antioxidant capacity that is potential in food additives (Wang et al. 2015; Wu et al. 2004; Zhao et al. 2005). As a kind of excellent antioxidant, it is extensively applied in foods to combat oxidative stress either from environment or in the human body and to protect against lipid oxidation and off-flavor development (Fu et al. 2014). However, TA as natural antioxidant is severely limited due to the defects of high water solubility and low oil solubility. That is to say, it can not be used in the edible oils or cosmetics directly as an antioxidant. The structure of TA must be modified so as to convert hydrophilic groups into hydrophobic groups, which would enhance its lipophilicity without affecting biological activities. Its application in lipophilic media will be expanded (Chen et al. 2015).

Zhong and Shahidi (2001) reported the results about synthesis of stearyl tannic acid ester and its surface activity; Aouf et al. (2013) and Soto et al. (2005) described the synthesis of gallic acid alkyl ester using gallic acid and higher aliphatic alkanol as raw materials, p-toluene sulfonic acid as catalyst, and dioxane as solvent. However, they all used highly toxic thionyl chloride, which may be existed in the products. That is to say, some potential

✉ Li'e Jin
lejin2003@163.com

¹ Department of Engineering and Technology, Taiyuan University of Technology, Taiyuan 030024, People's Republic of China

hazards must be considered due to the influence of the direct application in food. Moreover, the yield would be severely affected by the catalyst since the esterification is reversible. Therefore, it is important to find a catalyst that is green and high performance.

Phase-transfer catalyst (PTC) is widely used to induce reactions between reactants in immiscible phases, generally achieving high conversion and product selectivity at mild conditions (Makosza 2000; Yang et al. 2014). It is applied to organic reactions as catalyst and exhibits several advantages such as easy separation from product, high-effective, high yields, mild condition and short reaction time (Ge et al. 2011; Yang and Wu 2003). In view of this fact, FeCl_3 -PEG-400 was selected as PTC for the synthesis of [1-(tannin-ether)-ethyl]stearate (TEES). In this study, 1-Chloroethyl tannin ether (CTE), as an intermediate, was prepared first with tannic acid and paraldehyde through aldol condensation; then the TEES was prepared through nucleophilic substitution reaction under PTC. A lipid-soluble antioxidant based on TA was prepared successfully. The main factors and the optimal synthetic conditions were optimized through uniform design experiments. The chemical structure of TEES was analyzed by FTIR, ^1H NMR and UV-vis spectra. The antioxidant activity of TEES was evaluated through lipid oxidation. Due to the usage of green PTC, the products as antioxidant can be used directly in the field of edible oil. In addition, the oil solubility was improved by introducing the long-chain aliphatic hydrocarbon hydrophobic group to TA, the application range of TA was expanded to a large extent.

Materials and methods

Materials

All chemicals were of analytical grade unless stated otherwise. Tannic acid (TA), paraldehyde, sodium stearate, sodium hydroxide, FeCl_3 , butylated hydroxyanisole (BHA), PEG-400, fresh linseed oil and milk were purchased from marketplace. All chemicals were obtained from Sinopharm Chemical Reagent (Taiyuan, China).

Methods

Synthesis of TEES

Two steps were carried out for the synthesis of TEES: Firstly, approximately 1 g TA and 20 mL paraldehyde were placed in a 250 mL three-necked flask that was put in the ice-water bath. Then dry hydrogen chloride gas was introduced to the mixture when the temperature declined

to 0 °C. The reaction was maintained for 4–6 h with a stirring speed of 120 rpm. Subsequently, the hydrogen chloride gas was closed. After standing for 15 min, the supernatant was separated with a separating funnel and dried with calcium chloride for 2 h. Next, 1-Chloroethyl tannin ether (CTE) was obtained by filtration to remove the calcium chloride.

Secondly, appropriate amounts of sodium stearate, dioxane, and the FeCl_3 -PEG-400 (phase transfer catalyst, PTC) were mixed in a reactor flask equipped with a reflux condenser. Then, when the reactant was heated to 75–100 °C, the prepared CTE was slowly dropped into flask with a stirring speed of 300 rpm, and the reaction was carried out for 4–6 h under nitrogen atmosphere. At the end of the reaction, the reaction liquid was cooled to room temperature. The residue was obtained through filtering and washed with ethyl ether until the color of residue was white. Next, the ethyl ether was removed by rotary evaporator. The resulting viscous liquid was dissolved with water, purified and crystallized under low temperature, and dried in a vacuum drying oven at 40 °C. The product [1-(tannin-ether)-ethyl]stearate (TEES) was obtained, which was a brown yellow solid with special aroma. The synthesis process of TEES is depicted in Fig. 1a. It can be seen from Fig. 1a that the structure of TEES contains both ether functional group and ester group. Moreover, the solubility of TEES in linseed oil was 0.35 g/100 g linseed oil at room temperature, which was higher than that of TA (0.03 g/100 g linseed oil).

Since FeCl_3 -PEG-400 had double complex effect, it was selected to act as the PTC in the synthesis process of the TEES. The Na^+ from $\text{C}_{17}\text{H}_{35}\text{COONa}$ was combined with PEG-400, and the Cl^- from CTE was combined with FeCl_3 simultaneously in the reaction. The transfer of $\text{C}_{17}\text{H}_{35}\text{COO}^-$ from solid phase into liquid phase and the nucleophilic substitution of $\text{C}_{17}\text{H}_{35}\text{COO}^-$ and CTE were promoted by complexation. Besides, The Lewis acidity of FeCl_3 was weakened after the dissolution of PEG-400, which promoted the concerted catalysis of FeCl_3 -PEG-400. The synthesis mechanism for TEES in the presence of PTC is shown in Fig. 1b.

Uniform design is the one of the efficient optimal experimental methods (Fang et al. 2000). The main purpose of uniform design is to scatter its design points to be uniform on the experimental domain under a particular uniformity measure. Uniform design allows the largest possible level for each factor, and the number of levels can be equal to the number of experiment runs. This design has been successfully used for developing, improving, and optimizing processes (Luo 2012). In general, uniform design is preferred because it significantly reduces the number of experiments to evaluate multiple parameters and their interactions. Therefore, it is less laborious and time

Fig. 1 **a** Scheme of the synthetic routes of TEES. **b** Mechanism of the TEES synthesis through the phase transfer catalyst method

consuming than other approaches required for optimizing a process (Li et al. 2014). In order to optimize the synthesis conditions for TEES, its yield is considered as target value in the uniform design. The investigated variables are as follows: X_1 (reaction temperature, °C), X_2 (m_{FeCl_3} - g + $V_{\text{PEG-400}}$ mL), and X_3 (reaction time, min). They are designed to nine variation levels on the synthesis process. $U_9^*(9^4)$ design was shown in Table 1.

Preparation of TEES-SC compound

The preparation process of TEES-sodium caseinate (SC) compound was as follows: 1.0 g casein extracted from milk, 0.5 g sodium hydroxide and 25 mL distilled water were placed in a 100 mL beaker. The casein hydrolyzed for 3 h at 95 °C and cooled to room temperature. So the SC solution was obtained. Next, appropriate amounts of TEES

Table 1 Variables and levels of the $U_9^*(9^4)$

Level	X_1 (°C)	X_2	X_3 (min)
1	75.0	0.01 g + 0.077 mL	240
2	78.0	0.02 g + 0.154 mL	255
3	81.0	0.03 g + 0.231 mL	270
4	84.0	0.04 g + 0.305 mL	285
5	87.0	0.05 g + 0.385 mL	300
6	90.0	0.06 g + 0.462 mL	315
7	93.0	0.07 g + 0.538 mL	330
8	96.0	0.08 g + 0.610 mL	345
9	100.0	0.09 g + 0.693 mL	360

were added to the SC solution and the mixture was degassed at 50 °C for 1 h. Finally, the TEES-SC was obtained after the mixture was dried at 70 °C for 24 h.

FTIR, ¹H NMR, UV–vis and fluorescence spectroscopy analysis

Potassium bromide (KBr) discs were used to analyze the TA and TEES by FTIR spectrophotometer (BRUKER TENSOR 27). The spectra were obtained with the following parameters: resolution, 4 cm⁻¹; scan frequency, 32 Hz; and scan range, 400–4000 cm⁻¹.

The chemical structure of TA and TEES was also characterized by ¹H NMR analysis recorded on a 600 MHz spectrometer (ADVANCE III, Bruker, Germany) with tetramethylsilane as the internal standard. Additionally, CDCl₃ was used as a solvent.

The UV–vis spectroscopy measurements were carried out in a spectrophotometer (Shimadzu Corp., Kyoto, Japan) with a matched pair of silica cuvettes of 1 cm optical path length. The spectra were recorded in the range of 200–500 nm. Anhydrous ethanol was applied as a solvent and the concentrations of TA and TEES were 1 × 10⁻³ mol/L.

Intrinsic fluorescence of the TEES-SC was measured using a fluorescence photometer (F-280, Tianjin) at room temperature. The emission spectra were recorded in the range of 300–750 nm upon excitation at 280 nm. And the slit widths for the excitation and emission were set at 5.0 nm.

Thermal stability analysis

Thermal behavior analyses of TA and TEES were performed using a thermogravimetric analyzer (Netzsch STA 409C). Up to 10 mg of sample was placed in a crucible and heated in accordance with the designated temperature for N₂ atmosphere at a heating rate of 10 °C/min.

Antioxidant activity assay

Lipid oxidation contains a series of free radical-mediated chain reaction processes that can be prevented by the free radical initiators and antioxidants (Min and Boff 2002). Antioxidant activity can be assessed by the peroxide value (POV) of oil (Maqsood et al. 2015). And the POV of linseed oil was determined according to GB/T5538–2005/ISO 3960:2001 (National Standard, China) in this study. Firstly, 0.1 g TEES, TA, and BHA were added to 50 g of fresh linseed oil, respectively. A blank linseed oil with no addition of any antioxidants was used as a blank sample. The mixture was then thoroughly homogenized and placed in the oven at 70 °C. During this process, 10 mL chloroform and 15 mL acetic acid were added to the 5 mL linseed oil sample in a 250 mL conical flask with glass stopper and it was intensively shaken. Subsequently, saturated KI solution of 1 mL was added and the flask was

sealed with the glass stopper and left in a dark place for 5 min before adding 75 mL distilled water containing starch as indicator. Then, the mixture was titrated by Na₂S₂O₃ solution until the blue color disappeared. The samples were determined for POV after 4, 7, 10, 15 and 15 d. The POV was expressed as follows:

$$POV(\text{meq/kg}) = [c(V_1 - V_0)/m] \times 1000$$

where V_1 is the volume of Na₂S₂O₃ standard solution consumed by the tested oil samples (mL), V_0 is the volume of Na₂S₂O₃ standard solution consumed by the blank oil sample (mL), c is the concentration of the Na₂S₂O₃ standard solution, and m is the weight of the oil samples (g).

Results and discussion

Optimization design of synthesis process

According to Fig. 1a designed by employing U₉*(9⁴), a series of experiments were performed, the results are shown in Table 2a.

The measured values were analysed for multiple regression. The empirical relationship between the yield and the variables can be described as Eq. (1).

$$Y = 75.405 - 0.1X_1 + 368.233X_2 - 0.051X_3 \quad (1)$$

where Y was the yield, X_1 , X_2 , and X_3 were the coded levels of the three variables, respectively.

Table 2 (a) U₉*(9⁴) experimental and the yield corresponding. (b) The analysis of variance

Run	X_1 (°C)	X_2			X_3 (min)	Yield (%)
(a)						
1	1 (75.0)	7 (0.07 g + 0.538 mL)			9 (360)	76.08
2	2 (78.0)	4 (0.04 g + 0.305 mL)			8 (345)	63.49
3	3 (81.0)	1 (0.01 g + 0.077 mL)			7 (330)	55.41
4	4 (84.0)	8 (0.08 g + 0.610 mL)			6 (315)	79.09
5	5 (87.0)	5 (0.05 g + 0.385 mL)			5 (300)	70.71
6	6 (90.0)	2 (0.02 g + 0.154 mL)			4 (285)	58.18
7	7 (93.0)	9 (0.09 g + 0.693 mL)			3 (270)	85.43
8	8 (96.0)	6 (0.06 g + 0.462 mL)			2 (255)	76.32
9	9 (100)	3 (0.03 g + 0.231 mL)			1 (240)	63.44
Source of variance	Df ^a	SS ^b	MS ^c	F	F _{0.01} (3,5)	Significance
(b)						
Regression	3	825.63	275.21	136.13	12.10	**
Residual	5	10.10	2.02			
Aggregate	8	835.73				

^aDegree freedom; ^bStdev square; ^cMean square

The correlation coefficient (R^2) was 0.98, implying that the accuracy of the polynomial model was adequate. In order to further test reliability of the model, the analysis of variance for the model was employed, that results are shown in Table 2b.

Based on the multivariate analysis of variance, the model F-value (136.13) was higher than the value of $F_{0.01}(3,5) = 12.10$, as well as $F \gg F_{0.01}(3,5)$, implying that the model was pretty significant. Therefore, the Eq. (1) was reliable.

Equation (1) showed the coefficient of X_2 was positive, which indicated that the experimental index would be increased with the increment of the factor X_2 . The coefficients of X_1 and X_3 were both negative, which indicated that the experimental index would be decreased with the decrement of the factors X_1 and X_3 . Thus, the X_2 value should be inclined to the upper limit and the X_1 and X_3 values should be inclined to the lower limit. So, the optimum conditions for the synthesis of TEES were selected as follows: the reaction temperature was 75 °C; the PTC amount was 0.09 g $\text{FeCl}_3 + 0.693$ mL PEG-400 and the reaction time was 240 min. The theoretical value of Y from the fitted equations was 88.80 wt% under the above conditions. Obviously, reaction condition was mild. According to the optimized conditions, a mean value of the TEES yield obtained from three independent actual experiments reached 88.19 wt%. And the relative deviation was $0.80 \pm 0.34\%$, which confirmed that the simulative method was logical and the result was reliable.

FTIR analysis

The FTIR spectra of TA, CTE and TEES are shown in Fig. 2a. The broad absorption bands at around 3419, 3420 and 3421 cm^{-1} belonging to O–H stretching vibration were observed. Moreover, the band intensity at 3419 cm^{-1} of TEES decreased significantly compared with that of TA, indicating that TEES had less phenolic hydroxyl than TA. The band at 1386 cm^{-1} was assigned to $-\text{CHCl}-$ stretching vibrations and the band correspond to C–O–C stretching vibrations was observed at 1157 cm^{-1} , thereby illustrating the existence of chlorinated ether structure of CTE. The strong bands at 2910 and 2831 cm^{-1} of TEES were ascribed to the C–H and $-\text{CH}_2-$ stretching vibrations of aliphatic hydrocarbon (Lee and Lan 2006). These bands at 1705 and 1275 cm^{-1} were assigned to $-\text{C}=\text{O}$ and C–O–C stretching vibrations, respectively, which were more obvious than that of TA. This is due to the formation of many ester bonds and ether bonds. The band at 721 cm^{-1} was associated with the $-(\text{CH}_2)_n-$ ($n > 4$) swing vibration. From these facts, the reaction could be inferred to occur, and long aliphatic hydrocarbon was successfully generated in TEES.

^1H NMR analysis

The ^1H NMR spectra in Fig. 2b provide more detailed information about the chemical structures of TA, CTE and TEES, and their possible assignments are shown in Table 3a. The observed peaks from 0.88 to 1.80 ppm in the spectra were attributed to aliphatic protons. The peaks of $-\text{OH}$ protons were estimated at 3–5 ppm. Moreover, the content of aliphatic protons and $-\text{OH}$ protons in CTE increased and decreased sharply, respectively, compared with that of TA. These findings were in accordance with the FTIR spectroscopy results. The peaks at 2–3 ppm originated from the protons of $-\text{COCH}_2-$. The peaks between 6 and 8 ppm corresponded to aromatic protons from benzene units, with percentages accounting for 6.67 and 57.35% of TEES and TA, respectively. And the content of aliphatic protons of 85.54% in TEES was the most than that of TA and CTE. So it can be inferred that long-chain aliphatic hydrocarbon appeared in TEES.

UV–vis analysis

Figure 2c shows the UV–vis absorption spectra of the TA, CTE and TEES in the range of 200–500 nm, which are the curves of the absorbance versus wavelength. It was well known that the strong absorption band at around 200 nm was caused by $\pi \rightarrow \pi^*$ electron transition of aromatic ring, and it was shifted to longer wavelengths (the red shift) once chromophore or auxochrome was introduced to aromatic ring. So the absorption band at 217 nm of TA reflected the effect of auxochrome group ($-\text{OH}$) to TA structure and indicated the presence of a large number of $-\text{OH}$. And for the spectra of CTE, the absorption band about $\pi \rightarrow \pi^*$ electron transition was shifted to 230 nm due to the influence of the chlorinated ether. However, there was an absorption maximum in 200 nm and no absorption band upon 200 nm for TEES, it illustrated that there was no $-\text{OH}$ group in its structure. Notably, the difference in the UV–vis spectra of TA and TEES which the band at 277 nm disappeared in the spectra of TEES was probably related to the destruction of conjugate chain in TA due to the introduction of ether ester bond.

Thermal stability analysis

The thermal behavior of TA and TEES is depicted in Fig. 2d. A significant difference between the TG profiles of TA and TEES could be observed. The initial decomposition temperatures for TA and TEES were 213.7 and 260.6 °C, respectively, corresponding to 94.8 and 99.7%, and the final temperatures after weight loss by 53.3 and 46.8% were 311.8 and 317.4 °C, respectively.

Fig. 2 FTIR (a), ^1H NMR (b) and UV-vis (c) spectra of the TA, CTE and TEES. **d** Curves of TG and DTG for TA and TEES. **e** Fluorescence quenching spectra of the TEES-SC

As indicated by the DTG curves of TA and TEES, the temperatures of TA and TEES at the maximum weight loss rate were 278.4 and 301.9 °C, respectively. Notably, the

remaining weights of TA and TEES were 34.3 and 34.8%, respectively, even after the temperature increased to 600 °C. These findings indicated that the TEES had

Table 3 (a) Possible assignments for ^1H NMR spectra of TA, CTE and TEES. (b) Fluorescence quenching constant of the TEES-SC

Chemical shift/ppm		6–8	3–5	2–3	1.2–1.8	0.88
(a)						
Percentage/ %	TA	57.35	34.93	7.53	0.02	0
	CTE	19.22	2.50	6.94	71.34	0
	TEES	6.67	7.29	5.50	79.22	6.32
Structure assignment					–CH ₂ –	–CH ₃
TEES series	[Q] (mol L ^{–1})	F	F ₀ /F	K _q (L mol ^{–1} s ^{–1})		
(b)						
TEES-0	0	364.53				
TEES-0.05	1.18 × 10 ^{–3}	272.05	1.34	2.88 × 10 ¹⁰		
TEES-0.10	2.35 × 10 ^{–3}	254.12	1.43	1.83 × 10 ¹⁰		
TEES-0.15	3.53 × 10 ^{–3}	242.23	1.50	1.42 × 10 ¹⁰		
TEES-0.20	4.70 × 10 ^{–3}	232.38	1.57	1.21 × 10 ¹⁰		
TEES-0.25	5.88 × 10 ^{–3}	225.11	1.62	1.05 × 10 ¹⁰		

excellent thermal stability against the frying temperature compared with the BHA, which would be sublimated under 100 °C.

Fluorescence analysis

The SC will launch a certain intensity of fluorescence after inspired by a particular light due to the existence of tryptophan and tyrosine in SC (Zhang et al. 2008). So the fluorescence spectra of the TEES-SC were investigated to clarify the influence of TEES on the structure of SC. And the effects of contents of TEES in compound on the fluorescence intensity are shown in Fig. 2e.

As shown in Fig. 2e, the fluorescence peak of the SC was observed at 445 nm, whereas the peak positions of all the TEES-SC were shifted to 429 nm. Moreover, the fluorescence intensity was gradually decreased with increasing the amounts of TEES in compound, indicating that the occurrence of interaction between TEES and SC.

The fluorescence quenching type could be analyzed by the Stern–Volmer Eq. (2) (Gong et al. 2007):

$$F_0/F = 1 + K_q t_0 [Q] = 1 + K_{sv} [Q], \quad (2)$$

where F_0 and F are the fluorescence intensities of SC in the absence and presence of TEES respectively, K_q is the quenching rate constant, t_0 is the average lifetime of the protein without the quencher (10^{-8} s), $[Q]$ is the concentration of quencher and K_{sv} is the Stern–Volmer quenching constant.

For all the TEES-SC, the calculated Stern–Volmer parameter values are listed in Table 3b. As shown in Table 3, the values of K_q were less than the maximum dynamic quenching constant (2.00×10^{10} L mol $^{-1}$ s $^{-1}$)

except for the K_q value of TEES-0.05, indicating that the occurrence of static quenching and dynamic quenching at the same time. So the interaction between TEES and SC was weaker than that of TA and SC by comparing the fluorescence quenching type (Li et al. 2015). Therefore, the TEES, as an antioxidant, would engender very little influence for nutritional composition of food.

Antioxidant activity

The relations of the *POV* of linseed oil with the storage time are described in Fig. 3. The *POV* of all samples increased with the increment of storage time, indicated that the linseed oil had been oxidized. Notably, the difference of *POV* was not obvious when the storage time was short (less than 10 days). However, all samples showed an abrupt increase in *POV* up to 10 days of storage, and the *POV* of blank oil sample showed the highest at the same storage time than others due to the absence of antioxidant, the *POV* could reach 235.6 meq/kg. The *POV* of oil sample added with TA was only slightly lower than the blank sample, this might be caused by the poor solubility of TA in linseed oil. The *POV* of linseed oil treated with TEES showed a tendency similar to that with BHA within 15 days. However, the *POV* of oil samples with TEES and BHA were 63.4 and 84.2 meq/kg after 20 days, respectively. Moreover, the safety of BHA had been questioned because of its toxicity (Sun and Fukuhara 1997). So the treatment of linseed oil with TEES was more effective in lowering the *POV* than TA and BHA, which was caused by the better oil solubility of TEES and its unique structure. Due to the long aliphatic hydrocarbon was connected to TA by ester bond and ether bond, the oil solubility was greatly increased. The oxygen of phenol hydroxyl in TA was sp^2 hybridization, and $\text{p}-\pi$ conjugated system was formed between benzene ring and phenol hydroxyl of TA. When the ester bond and ether bond (Takahashi and Koshijima 1988) was introduced to TA, the $\text{p}-\pi$ conjugated system

Fig. 3 Effect of TA, TEES and BHA on the *POV* of linseed oil

was expanded and the TEES was oxidized prior to others. So, TEES could act as a natural tannin-based antioxidant. It could effectively delay the oxidation and peroxidation of unsaturated aliphatic compounds and prevented the formation of off-flavors and toxic compounds in linseed oil.

Conclusion

The TEES was synthesized via two-step method in the presence of the PTC. The synthetic conditions optimized by uniform design were mild and the reaction time was short (240 min). The yield achieved was 88.1 wt%. And the raw material used in the experiments had no toxicity. FTIR, ^1H NMR and UV–vis spectra suggested that almost all the phenolic hydroxyl of TA were protected in the reaction, and the chain of hydrophobic aliphatic hydrocarbon was connected to TA by ether bond. Moreover, the TEES had excellent thermal stability against the frying temperature. The results from the *POV* of linseed oil revealed that TEES was capable of preventing the occurrence of oxidation process of oils. And its antioxidant activity was higher than TA and similar to BHA. The *POV* of oil samples with TEES, TA and BHA were 63.4, 201.3 and 84.2 meq/kg after 20 days, respectively. Therefore, TEES, as a kind of synthesized antioxidant, exhibited superiority and utility for the storage of oils. What's more, the interaction between the TEES and SC was very weak by the fluorescence experiment. The idea will be valuable for development of other similar polyphenol compounds.

Acknowledgments The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 51174144).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Aouf C, Nouailhas H, Fache M, Caillol S, Boutevin B, Fulcrand H (2013) Multi-functionalization of gallic acid. Synthesis of a novel bio-based epoxy resin. *Eur Polym J* 49:1185–1195
- Chen W, Qi ZF, Zhou YD (2015) Constructing uniform designs under mixture discrepancy. *Stat Probab Lett* 97:76–82
- Fang KT, Lin DKJ, Winker P, Zhang Y (2000) Uniform design: theory and application. *Technometrics* 3:237–248
- Fu YQ, Zhang Y, Hu HY, Chen Y, Wang R, Li D, Liu SB (2014) Design and straightforward synthesis of novel galloyl phytochemicals with excellent antioxidant activity. *Food Chem* 163:171–177
- Ge N, Zhang Y, Shi D, Gu Q, Zhu X, Ding ZY (2011) Novelty of solid–liquid phase transfer catalyzed synthesis of benzyl diethyl phosphate from the sodium salt of diethyl phosphate. *Eur J Chem* 2:269–271
- Gong AQ, Zhu XS, Hu YY, Yu SH (2007) A fluorescence spectroscopic study of the interaction between epiristeride and bovine serum albumin and its analytical application. *Talanta* 73:668–673
- Lee WJ, Lan WC (2006) Properties of resorcinol-tannin-formaldehyde copolymer resins prepared from the bark extracts of Taiwan acacia and China fir. *Bioresour Technol* 97:257–264
- Li DJ, Song JF, Xu AQ, Liu CQ (2014) Optimization of the ultrasound-assisted synthesis of lutein disuccinate using uniform design. *Ultrason Sonochem* 21:98–103
- Li Y, Gong SL, Gao HY, Cao Q, Jin LE (2015) Analysis of the interactions between tannic acid and sodium caseinate. *Mod Food Sci Technol (China)* 31:111–115
- Luo DH (2012) Optimization of total polysaccharide extraction from *Dioscorea nipponica* Makino using response surface methodology and uniform design. *Carbohydr Polym* 90:284–288
- Makosza M (2000) Phase-transfer catalysis. A general green methodology in organic synthesis. *Pure Appl Chem* 72:1399–1403
- Maqsood S, Abushelaibi A, Manheem K, Rashedi AA, Kadim IT (2015) Lipid oxidation, protein degradation, microbial and sensorial quality of camel meat as influenced by phenolic compounds. *LWT Food Sci Technol* 63:953–959
- Min DB, Boff JM (2002) Chemistry and reaction of singlet oxygen in foods. *Compr Rev Food Sci Food Saf* 13:58–72
- Sehrawat A, Sharma S, Sultana S (2006) Preventive effect of tannic acid on 2-acetylaminofluorene induced antioxidant level, tumor promotion and hepatotoxicity: a chemopreventive study. *Redox Rep* 11:85–95
- Soto R, Freer J, Baeza J (2005) Evidence of chemical reactions between di- and poly-glycidyl ether resins and tannins isolated from *Pinus radiata* D. Don bark. *Bioresour Technol* 96:95–101
- Sun BX, Fukuhara M (1997) Effects of co-administration of butylated hydroxytoluene, butylated hydroxyanisole and flavonoids on the activation of mutagens and drug-metabolizing enzymes in mice. *Toxicology* 122:61–72
- Takahashi N, Koshijima T (1988) Ester linkages between lignin and glucuronoxylan in a lignin-carbohydrate complex from beech (*Fagus crenata*) wood. *Wood Sci Technol* 22:231–241
- Wang Q, Li Y, Sun FS, Li XY, Wang PD, Sun JT, Zeng J, Wang C, Hu W, Chang JL, Chen MJ, Wang YS, Li KX, Yang GX, He GY (2015) Tannins improve dough mixing properties through affecting physicochemical and structural properties of wheat gluten proteins. *Food Res Int* 69:64–71
- Wu LT, Chu CC, Chung JG, Chen CH, Hsu LS, Liu JK, Chen SC (2004) Effects of tannic acid and its related compounds on food mutagens or hydrogen peroxide-induced DNA strands breaks in human lymphocytes. *Mutat Res Fund Mol Mech Mutat* 556:75–82
- Yang HM, Wu HS (2003) Interfacial mechanism and kinetics of phase-transfer catalysis. *Catal Rev* 45:463–540
- Yang HM, Hung YH, Tu CY (2014) Synthesis of butyl salicylate by phase-transfer catalysis with dual-site phase-transfer catalyst and ionic liquid in tri-liquid system. *J Taiwan Inst Chem Eng* 45:1421–1427
- Zhang GW, Que QM, Pan JH, Guo JB (2008) Study of the interaction between icariin and human serum albumin by fluorescence spectroscopy. *J Mol Struct* 881:132–138
- Zhao XY, Sun HD, Hou A, Zhao QS, Wei TT, Xin WJ (2005) Antioxidant properties of two gallotannins isolated from the leaves of *Pistacia weinmannifolia*. *BBA Gen Subj* 1725:103–110
- Zhong Y, Shahidi F (2001) Lipophilized epigallocatechin gallate (EGCG) derivatives as novel antioxidants. *J Agric Food Chem* 59:6526–6533