

Synthesis, Characterization, and Thermal Behaviors of Tannin Stearates Prepared from Quebracho and Pine Bark Extracts

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ABSTRACT: Reported is the preparation of various condensed tannin steirates and the associated chemical characterization and thermal properties of these products. Stearate esters of condensed tannins from both quebracho and pine bark extracts were prepared in generally high, isolated yields from reaction with stearic acid chloride. Tannin esterification was confirmed by both Fourier transform infrared and nuclear magnetic resonance (NMR), and the average degree of steirate substitution was calculated from ¹H-NMR analysis. Product degree of substitution (DS) was observed to proportionately increase with higher stearic acid chloride ratio with maximum DS values of 4.0 and 5.1 achieved for quebracho and pine tannins, respectively. Thermal analysis revealed that tannin steirate products have increased thermal stability with a degradation

onset at significantly higher temperature for those samples possessing relatively greater DS. Analysis using differential scanning calorimetry revealed isolated products to consist of multiple components which exhibit interesting melt behaviors, a likely result from their work up on isolation. However, multiple melt features of the individual components in products were lost on heating to give single, broad melt endotherms due to coalescence of sample components. Furthermore, tannin steirate samples with high DS show relatively greater endothermic melting at higher temperature than those samples with lower DS. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 352–360, 2010

Key words: antioxidants; biopolymers; oligomers; polyphenolics; thermal analysis

INTRODUCTION

Tannins are naturally occurring polyphenolic compounds distributed ubiquitously throughout the plant kingdom. These compounds are secondary metabolites and possess a range of diverse properties having multiple biological activities, such as, antioxidant, anti-carcinogenic, antiviral, and anti-inflammatory properties.^{1–4} Such activities can find application in food, cosmetic, and pharmaceutical formulations.^{5,6} However, due to their polyhydroxylated nature, tannins have low stability to oxidation and are usually relatively insoluble in lipophilic media, which potentially limits their applications. To improve both their lipophilic solubility and relative stability, different modification methods have been explored including esterification. The synthesis of

various polyphenolic esters including longer chain fatty acids have been reported using both chemical and enzymatic acylation methods.^{7–23} In the case of enzymatic approaches, these methods offer selective acylation products over direct chemical methods as the use of enzymes is regioselective, with typically 3-O-acetylated flavonoids synthesized through either enzymatic acylation or enzyme catalyzed alcoholysis of peracylated flavonoids.^{8,19,22} If regioselective acylation is unnecessary, then chemical esterification methods are generally used. In chemical procedures, various acylating agents have been used with the activated acyl donor being either acid halide, acid anhydride, acid ester, or acid amide. Typically, it has been acid chlorides preferentially used as acylating agents.^{13–15,17,20,21,23} Tannin esterification reactions have been catalyzed by conventional esterification catalysts, including both organic or inorganic acids and bases with suitable solvents used to allow partial solubilization of the starting polyphenol compounds. Although preparations of polyphenolic ester preparations are well-documented,^{7–13,15–17,22} there is relatively little reported information on the chemical and the physical properties of these esterified materials.

Reported in the current study is the synthesis of various condensed tannin steirates designed for a

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range of industrial applications. A conventional chemical approach using acid chloride coupling was used to prepare these tannin esters. The various stearate esters were prepared from both quebracho (*Schinopsis*) and radiata pine bark tannin extracts to have differing degrees of esterification with stearate groups. The resulting degree of substitution (DS) of tannin stearates has been investigated by spectroscopy and related to the chemical and thermal properties characterized by polymer thermal analysis techniques. The intent of the work is to provide material property data for relevant industrial and cosmetic applications of the tannin stearates.

MATERIALS AND METHODS

Materials

The quebracho tannin used was a commercially available Colatan GT100 product sourced from Unitan (Argentina). Pine bark tannin was obtained by hot water extraction of *Pinus radiata* bark followed by spray drying of the extract liquor. Both tannin materials were vacuum dried at 80°C for 24 h before their use. Stearic acid ($\geq 95\%$) was obtained from Sigma-Aldrich and used as received. 1-Methylimidazole ($\geq 99\%$, Sigma-Aldrich) and thionyl chloride ($\geq 99\%$, Merck) were distilled before use. Acetone (AR) solvent was also dried with K_2CO_3 and distilled before use. Acetic anhydride ($\geq 97\%$) purchased from Ajax Finechem was used as the acetylation agent.

Preparation of stearic acid chloride

Stearic acid (60 g, 0.21 mol) was added in four aliquots to a 250 mL three-neck flask containing thionyl chloride (20 mL, 0.33 mol). The flask was fitted with a condenser, nitrogen inlet, and stirrer. After the addition of stearic acid, the reaction mixture was heated with stirring at 55°C under nitrogen for 2 h. The excess thionyl chloride was removed by rotary evaporation to yield stearic acid chloride, which was refrigerated under nitrogen until use. The yield of stearic acid chloride was 100% with purity confirmed by 1H -NMR analysis.

Esterification of condensed tannins with stearic acid chloride

The general procedure for stearic acid chloride coupling with both tannin types is outlined below. A 250 mL flask equipped with a condenser and a nitrogen inlet was charged with tannin, 1-methylimidazole, and acetone (100 mL). The corresponding amount of stearic acid chloride was then added dropwise into the flask with stirring of the reaction

mixture. The mole ratio of 1-methylimidazole to stearic acid chloride was 2 : 1 for all reactions. To ensure complete reaction, the reaction mixture was heated under reflux for at least 3 h maintaining a nitrogen atmosphere. On work up, the reaction mixture was cooled and poured into ethanol. The resulting precipitate was recovered by filtration to yield an orange-brown solid. Each product was further purified twice by extraction and precipitation with chloroform–methanol before vacuum drying at 45°C for 24 h.

Procedure for treatment of tannin stearates with acetic anhydride

For selected tannin stearate samples acetylation was undertaken before NMR analysis. The general acetylation procedure was for tannin stearate (1 g) to be treated with excess acetic anhydride (10 mL) and 1-methylimidazole (5 drops). The reaction mixture was stirred at 65°C under nitrogen atmosphere for 4 h. The reaction mixture was then poured into ice-cold water (200 mL). The resulting precipitate formed was isolated on filtering and washed with water until neutralized. The product was vacuum dried at 45°C.

Spectroscopic analyses

Fourier transform infrared (FTIR) spectra were obtained with a Nicolet 8700 research FTIR spectrometer (Thermo Electron Corp.) in a continuous sequence. Samples were incorporated into KBr disks.

1H nuclear magnetic resonance (NMR) spectra were obtained on a Bruker Avance DRX-400 instrument using $CDCl_3$ solution and TMS as internal standard unless otherwise stated. Standard pulse sequences were used. Integrated peak areas of the flavonoid aryl protons were compared with key CH_2 and CH_3 signals of the stearate ester chains.

Solid state ^{13}C -NMR analysis was performed on a Bruker Avance 200 spectrometer with a 7 mm HX probe with samples packed in a zirconia rotor fitted with a Kel-F endcap. Samples were spun at 5 KHz and 2048 scans were acquired per spectrum, which were collected in the region between -50 ppm and 250 ppm.

Thermal analysis

Differential scanning calorimetry (DSC) experiments were carried out using a TA Instruments Q1000 Differential Scanning Calorimeter. Samples (5–10 mg) were placed into aluminum pans and run under a nitrogen purge. Samples were run using a heat/cool/heat cycle and were heated at 10°C/min with a

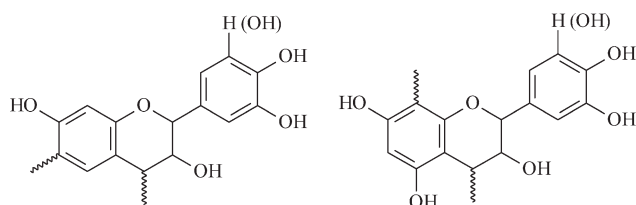


Figure 1 Chemical structures of resorcinolic type condensed tannins with 4–6 interflavanil linkages in quebracho extracts (left) and phloroglucinolic type condensed tannins in pine species with 4–8 interflavanil linkages (right).

cooling rate of 5°C/min. Duplicate runs were made for each sample.

Thermogravimetric analysis (TGA) measurements were performed using a TA Instruments Q500 Thermogravimetric Analyzer. Samples (8–14 mg) were weighed onto platinum pans and then heated at 10°C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Synthesis of tannin stearates

Quebracho and pine bark tannin stearates having varying degrees of esterification were produced by the coupling of the respective tannin extract with stearic acid chloride. Tannins extracted from quebracho and radiata pine bark were used as both have inherently differing flavonoid units due to their respective hydroxylation patterns and interflavanil linkages (Fig. 1). The molar ratio of tannin (based on flavonoid unit) to stearic acid chloride was varied from 2 : 1 to 1 : 8 with the latter ratio designed to promote full esterification of the tannin unit (Table I). Acetone was selected as solvent and the reactions were carried out at reflux temperatures for at least 3 h to promote full reaction. In attempting to move toward more benign chemistry approaches, acetone

TABLE I
The Relationship of Esterification Ratio, DS, and Isolated Yield of Quebracho and Pine Bark Tannin Stearates

Reaction Entry	Ratio M_T/M_{A-Cl}	Condensed tannin extract			
		Quebracho		Radiata pine	
		DS	yield (%)	DS	Yield (%)
Q1	1 : 0.5	1.5	30	0.59	78
Q2	1 : 1	2.2	35	1.1	75
Q3	1 : 2	3.4	56	2.3	76
Q4	1 : 4	3.5	60	3.8	69
Q5	1 : 6	4.0	74	5.1	81
Q6	1 : 8	4.0	74	5.1	81

M_T/M_{A-Cl} is the molar ratio of quebracho or pine tannin (T) to stearic acid chloride (A-Cl); DS is degree of stearate esterification calculated by $^1\text{H-NMR}$; Yield is the isolated yield based on tannin.

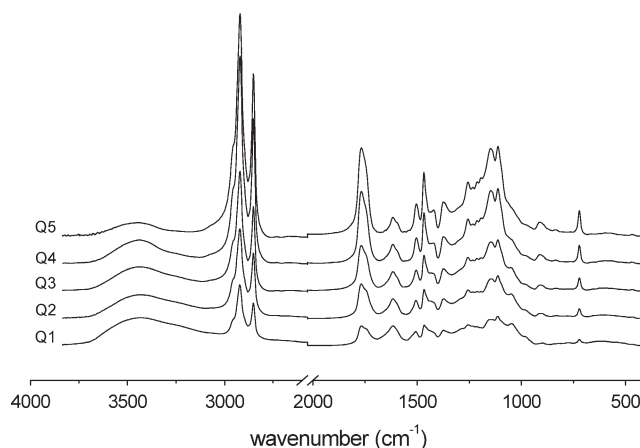


Figure 2 Normalized (1612 cm⁻¹, aromatic ring νC=C) FTIR spectra of quebracho tannin stearate with differing tannin: stearic acid chloride molar ratio 2 : 1, 1 : 1, 1 : 2, 1 : 4, and 1 : 6.

solvent was used as reaction media and ethanol in work up, where product isolation was simplified by its precipitation into ethanol. This procedure ensured removal of stearic acid and unwanted by-products, which were increasingly present at higher stearic acid chloride ratios. Table I shows the isolated yields of the various tannin stearates from the series of esterifications. These yields ranged from 30 to 80% for the various tannin stearate products. Evident for the quebracho tannin products was an increase in yield with greater stearic acid chloride ratio. In the case of the pine bark tannin stearates, the yields were relatively similar with products obtained in 70–80% isolated yield. These products were qualitatively assessed by FTIR and $^{13}\text{C-NMR}$ with $^1\text{H-NMR}$ used to confirm the degree of esterification in each product.

FTIR initially provided evidence of successful ester formation and an indication of the extent of product esterification (Figs. 2 and 3). FTIR spectra of

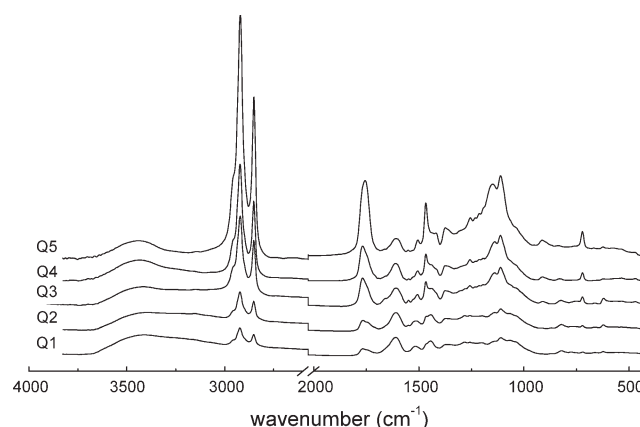


Figure 3 Normalized (1612 cm⁻¹, aromatic ring νC=C) FTIR spectra of pine tannin stearate with differing tannin: stearic acid chloride molar ratio 2 : 1, 1 : 1, 1 : 2, 1 : 4, and 1 : 6.

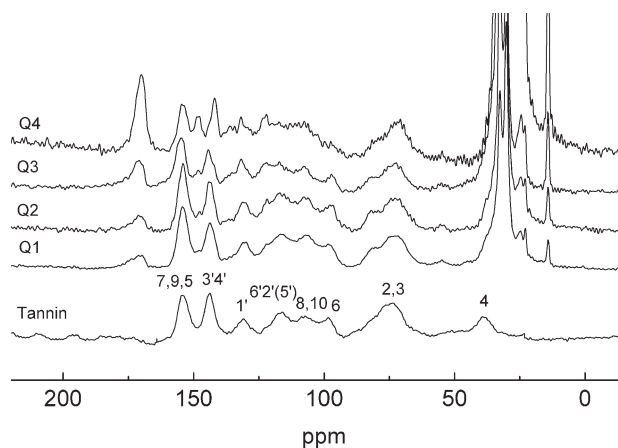


Figure 4 ^{13}C -NMR spectra of quebracho tannin and quebracho tannin stearates with differing tannin: stearic acid chloride molar ratio 2 : 1, 1 : 1, 1 : 2, and 1 : 4.

both quebracho and pine tannin stearates have three strong absorptions at 2925, 2850 (νCH_2), and 1770 ($\nu\text{C}=\text{O}$) cm^{-1} with a weak shoulder at 1742 cm^{-1} also attributable to the stearate ester carbonyl. The broad absorption between 2500 cm^{-1} and 3700 cm^{-1} attributable to hydroxyl stretching vibrations was also observed to decrease. The relative DS of both quebracho tannin and pine tannin stearate products can be estimated by comparing FTIR spectra normalized with the tannin aromatic ring stretching vibration (1612 cm^{-1}). Evident as the ratio of tannin to stearic acid chloride increases from 2 : 1 to 1 : 8 was a greater relative intensity of the key stearate peaks 2925, 2850, and 1770 cm^{-1} . This indicated a trend for greater esterification with higher reaction ratio across both quebracho and pine tannin products. However, the degree of esterification appears to be maximized at the higher reaction ratios of 1 : 6 and 1 : 8 as similar ester carbonyl intensities were observed for these reactions with both condensed tannin types.

Figures 4 and 5 show the solid state ^{13}C -NMR spectra of the stearate ester products and the quebracho and pine bark tannin extracts, respectively. As observed with FTIR, there was the emergence of characteristic peaks on ester formation. Aliphatic carbon signals for the stearate were evident at $-\text{CH}_3$ (14 ppm), $-\text{CH}_2-$ (22, 24, 30, and 32 ppm) and $\text{C}=\text{O}$ (170 ppm). These peaks increase in intensity and dominate the NMR spectra at higher stearate contents. The peak pattern and chemical shifts for the hydroxylated carbons (130–160 ppm) also change on increasing degree of esterification. The two peaks at 156 ppm and 146 ppm for the hydroxylated carbons split and broaden, particularly with the pine tannin, as a higher degree of esterification was achieved.

Solution state ^1H -NMR was used to quantify the degree of esterification of each tannin stearate prod-

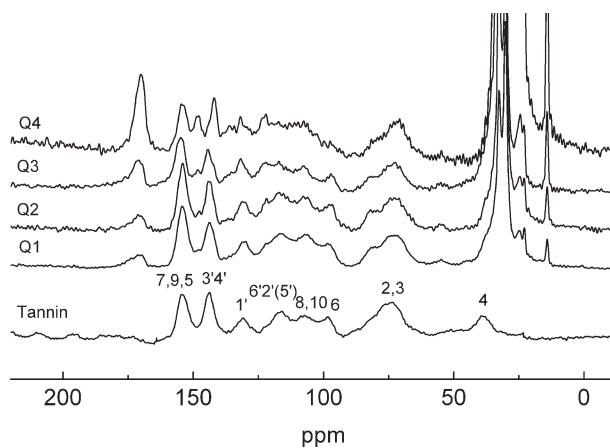


Figure 5 ^{13}C -NMR spectra of pine tannin and pine tannin stearate with differing tannin: stearic acid chloride molar ratio 2 : 1, 1 : 1, 1 : 2, and 1 : 4.

uct. Although unreacted tannin and higher tannin stearate esters could be solubilized in either water or organic solvents, those tannin stearate products obtained from reactions using lower stearic acid chloride ratios were found to be only partially soluble. To overcome these inherent insolubility issues, acetylation of residual hydroxyls and, therefore, full esterification was used as a means to readily solubilize all the tannin stearate products through preparation of the respective mixed ester tannin stearate acetates. That is, capping any residual hydroxyl groups with acetate groups enabled all tannin stearate products to be completely solubilized and analyzable by ^1H -NMR. Figures 6 and 7 represent ^1H -NMR spectra of tannin and the acetylated tannin stearates. Evident in the tannin stearate spectra are the presence of the $-\text{CH}_3$ (0.88 ppm) and $-\text{CH}_2-$ peaks (1.26, 1.69, and 2.48 ppm) attributable to the stearate esters. With higher stearic acid chloride content, these peaks increase relative to the tannin aromatic protons (7.1 ppm). Also notable in the spectra

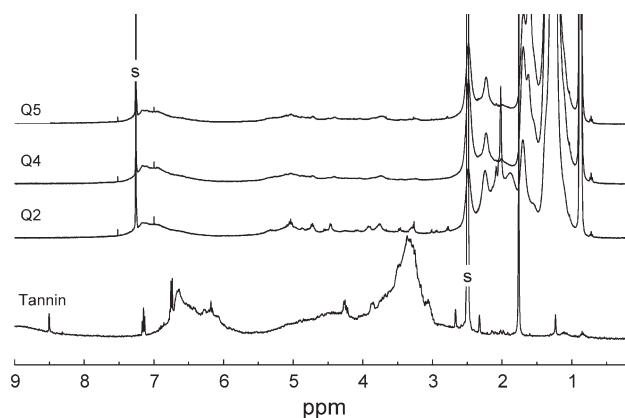


Figure 6 ^1H -NMR spectra of quebracho tannin and quebracho tannin stearate/acetate with reactant molar ratio (tannin: stearic acid chloride) of 1 : 1, 1 : 4, and 1 : 6.

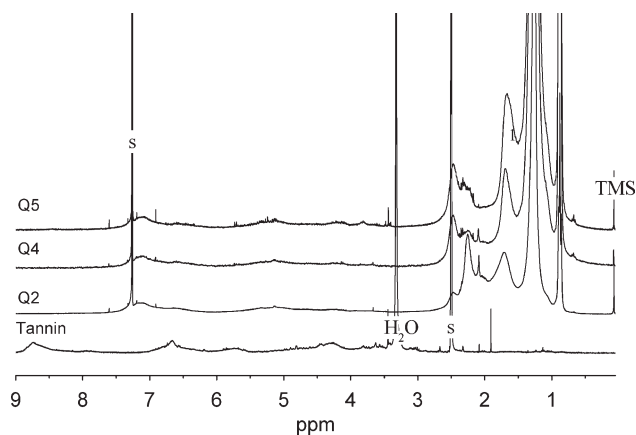


Figure 7 ^1H -NMR spectra of pine tannin and pine tannin stearate/acetate with reactant molar ratio (tannin: stearic acid chloride) of 1 : 1, 1 : 4, and 1 : 6.

is an absence of carbohydrate signals (3.0–4.5 ppm), which were present in the tannin extract spectrum. Although this polysaccharide material was co-extracted with the tannin, it appears to be removed on esterification work up yielding relatively pure tannin stearate products.

In achieving solubilization and ^1H -NMR characterization of all tannin stearates as their tannin stearate acetates, the DS could be determined for these products. The spectrum of each tannin stearate product was integrated using the relative intensities of the terminal methyl group of the stearate with the aromatic protons of the tannin unit and the DS calculated using eq. (1). Due to inherent differences in chemical structure and number of aromatic protons between quebracho and pine tannins (Fig. 1), the value of n will differ, where n , a reference for the proportion of pyrogallolyl and catechol B ring protons (Fig. 1), is 5.0 for quebracho and 3.9 for pine tannin, respectively.²⁴ The results of DS calculated from NMR spectra are given in Table I and were found to confirm observations made with FTIR and ^{13}C -NMR that the relative DS of products increase with greater stearic acid chloride ratio. Although some of these values have been calculated for the mixed tannin stearate acetate esters, analysis of the tannin stearates from 1 : 6 to 1 : 8 reactions before and after acetylation show no loss of stearate due to transesterification with acetate. Furthermore, in determining the relative degree of acetylation in the tannin stearate acetates, this provided further corroborating evidence for the calculated DS values for each tannin stearate.

$$\text{DS} = \frac{I_1/3}{I_2n} \quad (1)$$

where I_1 is the stearate methyl protons integral, I_2 is tannin unit aromatic protons integral, and n is the

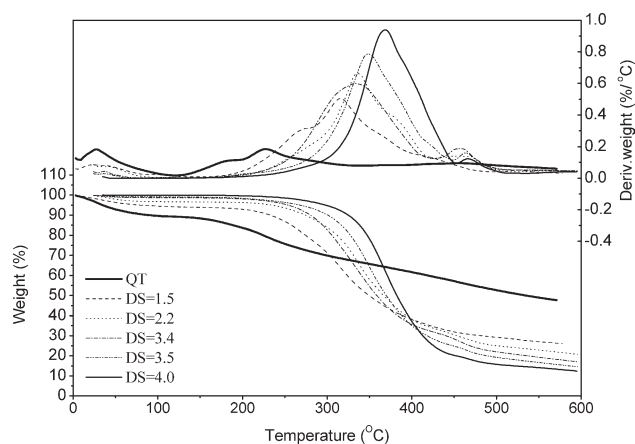


Figure 8 TGA thermograms of quebracho tannin stearates with differing degrees of stearate substitution.

number of aromatic protons based on the hydroxylation pattern of the base tannin unit.

The relative thermal stabilities of the tannin stearates was investigated by using TGA and heating samples to 600°C under an inert atmosphere (Figs. 8 and 9). Generally, with both tannin types, on heating up to 100°C, there was an initial weight loss which was attributable to loss of water. This was particularly evident for the tannin extracts, which are relatively hygroscopic. On further heating above 100°C, the onset for initial decomposition was apparent from 150°C and, for tannin stearates, associated with relatively high weight loss to 400°C. Both quebracho and pine tannins initially begin to degrade from 150°C and exhibit pyrolytic degradation.²⁵ About 400°C, there was relatively lower rates of weight loss for both tannin types with residue weights up to 40% depending on the sample.

For the tannin stearates analyzed by TGA, it was apparent that a higher degree of esterification was

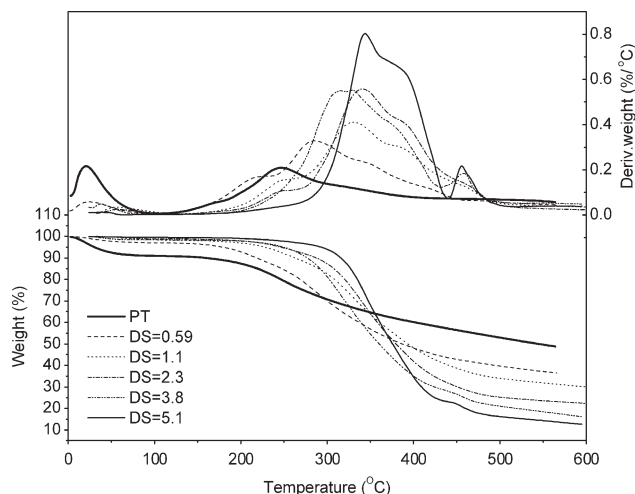


Figure 9 TGA thermograms of pine tannin stearates with differing degree of stearate substitution.

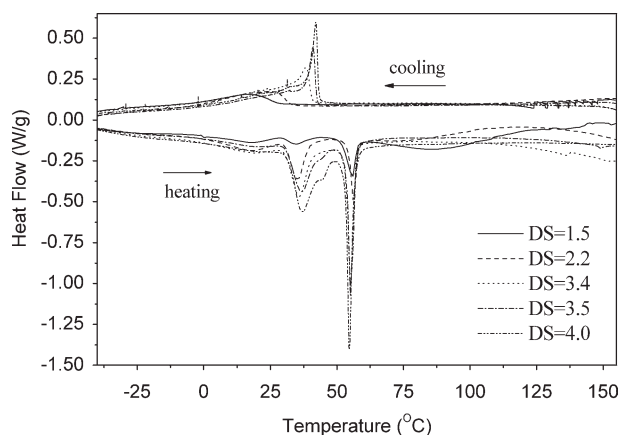


Figure 10 DSC thermogram of the first heating cycle for quebracho tannin stearates with differing degree of stearate substitution.

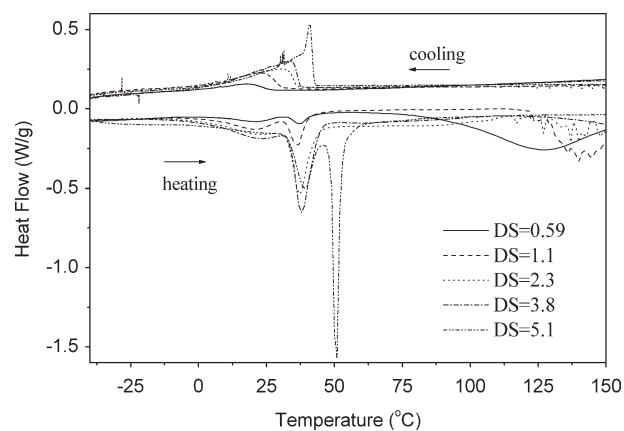


Figure 12 DSC thermogram of the second heating cycle for quebracho tannin stearates with differing degree of stearate substitution.

associated with samples having lower quantities of absorbed water, consistent with a reduced number of available hydroxyl groups and increasing sample hydrophobicity (Figs. 8 and 9). Greater esterification also led to a relatively higher degradation onset temperature and increases in relative thermal stability. For those tannin stearate samples with DS values of 0.6–1.0, the observed degradation onset temperatures were about 50°C higher than the respective tannin extracts. For products with relatively high DS values (>3.5) the degradation onsets were further elevated toward about 300°C. Additionally, those tannin stearate samples possessing higher DS were also observed to have greater sample weight loss between 200°C and 400°C, which presumably was associated with stearate group loss.

DSC was undertaken to investigate any thermal transitions and melt behaviors of the various tannin stearates. The DSC thermograms for both quebracho and pine tannin stearates are shown in Figures 10–13. Associated information on the temperature and

enthalpies for melt behaviors are given in Table II. Generally, on initial heating of tannin stearate samples for both tannin types as many as three endothermic features were observed between 18°C and 60°C. The presence and intensity of these endothermic features in each sample was dependent on both the tannin type and relative DS and appear as distinct melt features. On cooling from 180°C, a common exothermic feature was evident at about 35°C (Figs. 10 and 12). For the second heating cycle, the melt features of samples appear as a single, broad transition which had an onset below 0°C and maximum about 50°C (Figs. 11 and 13). A similar trend for both tannin types was evident on the second heating cycle, where an increasing DS was associated with the melt feature shifting toward 50°C with greater endothermic intensity.

The observed DSC melt behaviors exhibited in Figures 10–13 were subjected to further investigation to determine the nature of these behaviors. It was uncertain if the distinctions in melt behaviors during the first heating cycle were due to differences in

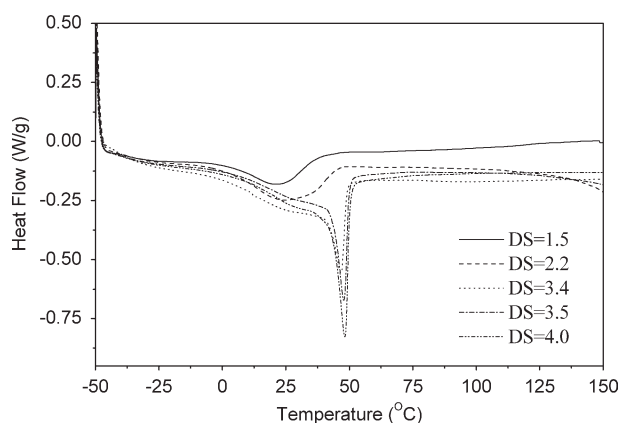


Figure 11 DSC thermogram of the first heating cycle for pine tannin stearates with differing degree of stearate substitution.

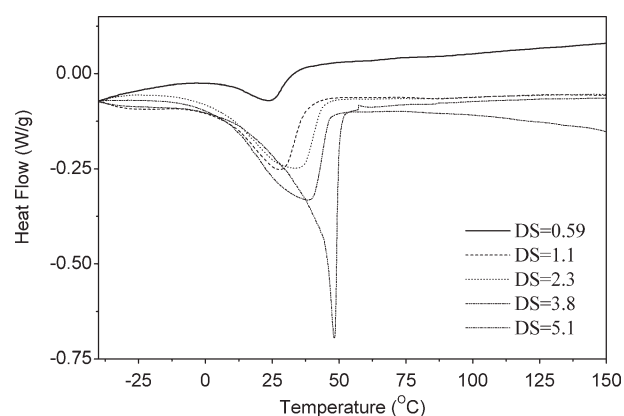


Figure 13 DSC thermogram of the second heating cycle for pine tannin stearates with differing degree of stearate substitution.

TABLE II
DSC Thermal Transitions and Relative Enthalpies for Various Tannin Stearate Samples

Calculated DS		Melt feature temperature (°C) and enthalpy (mW/g)									
		Quebracho tannin stearate					Pine tannin stearate				
		1.5	2.2	3.4	3.5	4.0	0.59	1.1	2.3	3.8	5.1
First heating	T_{m1} (°C)	17.4	17.5	16.8	17.9	17.9	20.8	20.4	20.9	21.1	18.1
	T_{m2} (°C)	34.8	35.4	36.0	36.9	37.0	37.7	36.7	37.4	37.9	39.1
	T_{m3} (°C)	55.8	56.2	55.0	55.3	54.6					50.5
Second heating	T_m (°C)	22.1	25.0	46.8	47.9	48.2	24.2	27.9	34.1	38.2	48.2
First heating	ΔH_{m1} (J/g)	3.52	5.03	3.38	1.58	0.86	2.41	4.79	2.05	3.00	0.28
	ΔH_{m2} (J/g)	1.59	7.58	10.8	13.0	17.5	1.66	5.11	14.9	19.5	11.2
	ΔH_{m3} (J/g)	5.04	6.02	13.6	13.9	16.9					23.3
Second heating	ΔH_m (J/g)	17.0	26.0	38.5	38.6	41.5	7.61	22.1	28.8	36.7	49.9

T_{mn} is the temperature of the three ($n = 1, 2,$ or 3) common endothermic absorptions on initial heating or the temperature maximum on the second heating cycle. Similarly, ΔH_{mn} is the calculated enthalpy of melting for each endothermic feature.

relative thermal history, adsorbed water content or chemistry differences within samples. To understand this further, both quebracho tannin stearate (DS = 4.0) and pine tannin stearate (DS = 5.1) samples were further analyzed using incremental heating cycles, which had increasing maximum temperature. The resulting thermograms are shown in Figures 14 and 15 and exhibit similar results for the respective samples. In the case of the pine tannin stearate (Fig. 15), on initial heating to 50°C, the subsequent heating cycle shows the sample's thermal behavior below 50°C was lost, but above 50°C, it was retained when compared with Figure 12. Similarly, a second heating cycle heating to 60°C loses any residual melt behavior below this temperature. However, with successive heating cycles above 60°C, the separate thermal transitions characterized in Figure 12 were lost with only a single, broad melt feature evident

for those heating cycles having greater maximum temperature and exhibit a thermogram-like that of Figure 13. With the initial melt behaviors lost below 60°C, this indicates it was unlikely adsorbed water was a contributor, but instead, the likelihood coalescence of individual sample components on melting was the probable cause of the observed thermal behaviors.

As shown in Figures 11 and 13, the second heating cycle thermograms revealed that these samples with greater stearate substitution have shifted the melt endotherm to higher temperature. It became evident in comparing the first and the second heating cycle behaviors and those results above (Figs. 10 and 12) that, there was likely a relationship with product DS and an implication, the samples were a mixture of distinct components. For tannin stearates with relatively low DS, the predominant endothermic

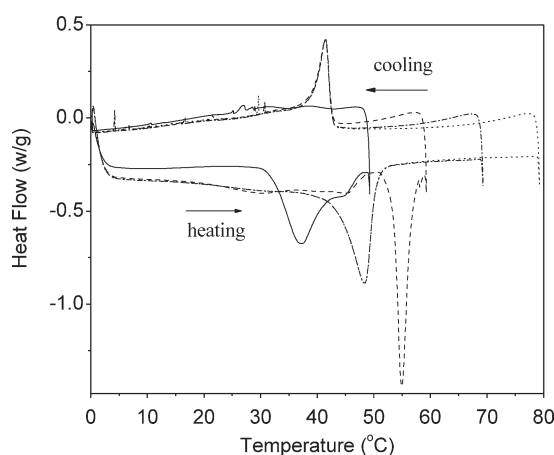


Figure 14 DSC thermograms of quebracho tannin stearate (DS = 4.0) showing successive heating cycles with increasing maximum temperature.

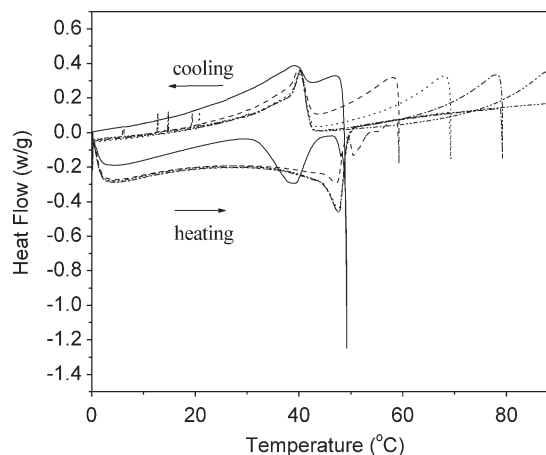


Figure 15 DSC thermogram of pine tannin stearate (DS = 5.1) showing successive heating cycles with increasing maximum temperature.

features were at lower temperatures (ca. 17–20°C and 35–39°C) and associated with a proportionately lower enthalpy absorption (Table II). Those samples with higher DS values were dominated by endothermic features at relatively higher temperatures (34–39°C and 50–56°C). In the case of the pine tannin stearate with a DS of 5.1, only a single melt feature at 50°C was evident on initial heating. As discussed earlier, melting likely allows the sample components to mix and coalesce on cooling, and with further heating (second heating cycle), give a single endothermic feature which was a composite of those behaviors observed in the first heating cycle.

The results of DSC analysis in Figures 10–13 showing differing melt behaviors can be readily explained in terms of the relative DS of tannin stearates within isolated samples. The origins of this behavior were likely due to the individual tannin components having varying degrees of stearate esterification within the isolated sample. A comparison of the NMR calculated average DS values of isolated samples shows a relationship with DSC melt features in the initial heating cycle. Samples with components likely to have relatively low DS values tended to be associated with endothermic melt behaviors at 15–20°C, whereas samples with components possessing medium or relatively higher average DS values have endothermic melt behaviors at 34–39°C and 50–56°C, respectively. Because of poor selectivity and the randomness of the stearic acid chloride reaction, isolated products likely have a mixture of DS values, but will analyze (NMR) as a single, average DS value (Table I). The relative sharpness and defined melting point of the melt feature at ca. 50°C suggests the tannin stearate with the highest DS had the most uniform distribution of stearate chains. In contrast, the broadness of other endothermic features at lower temperatures indicates the likelihood samples with lower DS values have a more random distribution of attached stearate chains. This observation is consistent with those for the chemical approach used for stearate substitution.^{7,9,10}

Both FTIR and NMR confirm the average DS of tannin stearate reaction products was greater with a corresponding increase in the molar ratio of stearic acid chloride to tannin. The stepwise increase in stearic acid chloride led to proportionately greater average sample DS value until a maximum DS was achieved. In the case of quebracho tannin, the highest DS achieved was 4.0 and attained with a tannin to acid chloride ratio of 1 : 6. For pine tannin the maximum average DS achieved was 5.1 and also used a ratio of 1 : 6. For both tannin types these maximum DS values were relatively close to those theoretically possible (Fig. 1) indicating little significant steric hindrance in acid chloride coupling to

hydroxyl groups about the respective tannin units. NMR also indicated the tannin stearates obtained were relatively pure and free of carbohydrate material. Furthermore, the isolated yields of the tannin stearates were considered very good, given crude tannin extracts were used and contain a significant proportion of carbohydrate.²⁴ Only in the case of the low DS quebracho tannin stearates (Q:S > 1:2) were the yields of this material considered low. An increasing degree of stearate substitution was also associated with relatively greater thermal stability, where higher DS gave significantly higher degradation onset temperatures between 200°C and 280°C. The absence of carbohydrate material can also be considered as a contributor to the improved thermal stability of esterified samples above 150°C.²⁵

The esterification of both pine and quebracho tannins with stearic acid chloride did not produce a single, uniform esterified product, but likely an isolated mixture of products varying in DS, which collectively gave an average DS value consistent with the reaction stoichiometry. DSC thermograms show that on initial heating of tannin stearate samples, there were up to three distinct thermal melt transitions, consistent with the samples being of a multicomponent nature. Obtaining products consisting of components with varying DS was not unexpected as this acid chloride esterification reaction can be considered relatively heterogeneous as the tannin extracts and the reaction products exhibit only partial solubility in the acetone solvent used. Anecdotal evidence of the partial solubilities of reaction products with lower DS values also support the heterogeneity of the reaction products. As described earlier, the varying DS within each product manifested in differing melt behaviors. These separate thermal transitions indicate a separation of distinct components within the isolated products, which was likely a function of how the product was isolated by precipitation from solution. However, moderate heating allowed the product components to flow and coalesce giving a broad, indistinct melt feature which was common to the various tannin stearate ester samples produced in this study.

CONCLUSIONS

Tannin stearate esters with varying degrees of substitution have been successfully prepared by reaction of both quebracho and pine bark tannins with stearic acid chloride. The degree of esterification for isolated samples was higher with increasing molar ratio of stearic acid chloride. The tannin stearates were found to have progressively greater organic solubility and reduced water binding capacity with increased tannin esterification. A higher degree of tannin stearate esterification also led to relatively

increased thermal stability and associated higher degradation onset temperatures. Although a greater DS value was associated with higher melt temperatures, the tannin stearates show interesting DSC melt behaviors attributable to varying stearate substitution of components within isolated samples. Up to three separate melt features were observed in isolated tannin stearate samples on initial DSC heating. However, after melting these individual components coalesce and upon cooling, produce a single, broad melt feature on further heating.

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