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Effect of Solvent Type on Tannin Extractability from Three *Tetrapleura Tetraptera* (Schum. & Thonn.) Taubert Positions for Wood Composite Adhesive Formulation

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Abstract
Raw materials for adhesive production are conventionally from expensive petrochemicals, which affect synthetic resins relative to total costs of glued products. Phenol replacement with tannins (i.e., plant polyphenols) in Phenol-Formaldehyde resins is imperative since tannin adhesives are equally resistant to moisture and microbial degradation. Tannin was extracted from *Tetrapleura tetraptera* (i.e., bark, leaf and fruit) using distilled water and 1% NaOH through Soxhlet extraction. Tannin presence, Extract yield and polyphenol/tannin content (i.e., Stiasny numbers) were respectively determined from qualitative and quantitative analyses. The solvent type and plant part influenced the yield and tannin content. All the three parts, especially the bark, contained tannin. Extract yield was greater in 1% NaOH (39.54% [from leaf] to 77.05% [from fruit]) than in distilled water (12.96% [from fruit] to 18.16% [from leaf]**).** Conversely, Stiansy numbers for tannin, at all plant parts, were greater for the water-soluble extracts (i.e., 67.50, 68.96 and 87.50% from the leaf, fruit and bark respectively) than in 1% NaOH (i.e., 33.72, 21.94 and 37.42% correspondingly). The large extract yields (i.e., 39.54 - 77.05% for 1% NaOH) and high Stiasny numbers particularly for the water-soluble extracts (e.g. 87.50% for the bark) demonstrate the potential of *T. tetraptera* extracts as agents for tanning and adhesive formulation for leather, wood and related industries.

Keywords: extract yield, polyphenol, quantitative test, sodium hydroxide, soxhlet extractor**,** tannin adhesive

INTRODUCTION

Adhesives, in liquid or semi-liquid state, bond materials together through surface attachment (Lau *et al*., 2002; BASF, 2006). The wood industry currently emphasizes on the manufacture and export of lumber, veneer, plywood, other panel boards and furniture, which use adhesives as their backbone. Thus, the full development of the wood-processing industries and the increasing wood composite as well as paper products are directly linked with availability, affordability and new formulations of suitable adhesives (Jetuah *et al.*, 2001). Two adhesive types exist: natural and synthetic. The natural comprises animal (e.g. hide, fish and casein or milk protein) and vegetable sources. The animal type is made from collagen (skin/bone) with sugar and glycerol added for flexibility. With hot water, it slowly becomes soluble to form either gelatin or glue. Fish glues dissolve to form liquids (at 20-25^{o} C), are resistant to water and bond wood, leather and porous materials well. Casein can be converted to strong adhesives by mixing with lime [$Ca(OH)_2$] suspension; the calcium cross-links the protein to form a strong, water-resistant film. Casein glues were often used to fasten wood together but are now used to improve adhering characteristics of paints and coatings. Synthetic resins (man-made polymers) resemble natural resins in physical characteristics meet specific wood-working requirements; these are based on elastomers, thermoplastics, emulsions, and thermo-sets (Anon., 1977; Todd *et al*., 1994). Synthetic adhesives could not only be stronger, more rigid and durable than wood, but also have much greater resistance to water than adhesives from natural polymers. Two distinct categories, thermosetting and thermoplastic, exist.

Thermosetting adhesives have a condensation type of polymerization reaction and include Urea-Formaldehyde (UF), Melamine Formaldehyde (MF), Phenol-Formaldehyde (PF) and Resorcinol-Formaldehyde (RF) along with Phenol-Resorcinol Formaldehyde (PRF). They remain in a reversible state and can readily be softened by heating. Polyvinyl acetate emulsions (white glue) and hot melt glues are thermoplastic adhesives (Pizzi, 1983). Although UF and PF abound in the international market, UF is mostly for interior grade plywood (because they withstand short-term high humidity), particleboard and extensively for producing hardwood plywood for furniture or assembly and interior panelling. However, PF is for exterior grade plywood because they withstand long-term water-

soaking and drying (e.g. for external house walls and roofs) and widely for softwood plywood for severe service conditions (Anon., 1977; Pizzi, 1983; Jetuah *et al*., 2001). The synthetics, especially PF, are expensive due to the progressively increasing demand for crude oil from which phenol is synthesized (Mohandos, 1992). Release of free formaldehyde, rising price of oil-based derivatives, strict environmental demands, and increasing ecological awareness have necessitated numerous attempts to produce adhesives, which could be based on natural and renewable sources (Ugovsek *et al.*, 2010). Thus, several attempts have been made to replace part of the petroleum-derived phenols in wood-bonding adhesives with phenolic compounds from renewable sources. These include adhesive development from relatively cheap plant tannins (Pizzi, 1983), which replace part of the phenol or resorcinol in synthetic phenol-formaldehyde and resorcinol-formaldehyde adhesives (Grigsby and Warnes, 2004; Vázquez *et al*., 2002 cited in Ugovsek *et al.*, 2010). Thus, contemporary tannin applications involve adhesive formulations, which include tannin-based types for the manufacture of wood composite products. Tannins are polymeric phenolic astringent molecules in plants, which characteristically bind, precipitate and combine readily with proteins (Cobzac *et al.*, 2005) but, unlike lignin, are not structural.

Tannins are extractable from wood and bark by soaking or percolating in water. Calvi *et al.* (1995) described tannins as any of a group of pale-yellow to light-brown amorphous substances in the form of powder, flakes or a spongy mass widely distributed in all plant parts (especially in the growth areas of trees, such as the secondary phloem and xylem and the layer between the cortex and epidermis) and contribute to regulate the growth of these tissues.

They are used chiefly in tanning leather, dyeing fabric, making ink, and for various medical applications. Tannin content depends on the type of plant, as hardwoods generally have higher tannins than softwoods. Tannins from eastern hemlock, chestnut oak and tan oak barks are used to tan leather, modify its physical characteristics and impart resistance to decay by chemical interaction, while those from western hemlock, Douglas-fir and redwood barks are used in phenolic-resin adhesives (Wenger, 1984). Two main tannin types (i.e., hydrolysed and condensed) exist. Hydrolysed tannins are mostly limited to dicotyledons (Anon., 2002). On heating with HCl or H_2SO_4 yields garlic or ellagic acid. Examples include gallotannins, ellagitannins, and caffetannins (Hagerman, 1998). Condensed tannins cannot be hydrolyzed either by acids or enzymes nor split easily, and are therefore difficult to analyze. On heating with HCl, they yield phlobaphenes like phloroglucinol, an organic compound used in the synthesis of pharmaceuticals and explosives. Most condensed tannins are water-soluble but very large ones are insoluble (Anon., 2002). However, condensed tannins, constituting more than 90% of the total world production of commercial tannins (200,000 tons per year), are chemically and economically important for the preparation of adhesives and resins (Pizzi, 2003). Tannins are extracted using different solvents (e.g. methanol, ethanol, water, ether, 1% NaOH, petroleum ether, and alkali). Many techniques (e.g. water extraction with addition of chemicals, solvent extraction and fractionation of extracts with ultra-filtration) have also been developed in attempting to increase yield of the pine bark tannins and improve their quality for wood adhesives (Li and Maplesden, 1998).

Although tannins occur in almost any part of nearly every plant ranging from roots to leaves, bark to unripe fruit all over the world in all climates, most trees contain more amount than others. They are concentrated in the bark layer where it forms a barrier against micro-organisms. Thus, many plants could, at one time and country or another, be important sources of tannin (http://www.braintan.com/barktan/2tannins.htm). Li and Maplesden (1998) reported that the potential exists for production of radiata pine bark tannins for wood adhesives but commercial production has not succeeded due to high production costs associated with the appropriate quality of high yield extracts. Unsurprisingly, tannin concentration in several countries, including those of tropical Africa, is barely determined. Nonetheless, pod extracts of *T. tetraptera* contain phyto-chemicals including tannins, saponins, glycosides, proteins and essential oils (Olajide Awofisayo *et al*., 2010). The dry fruit has a pleasant aroma (Aladesanmi, 2007) and is used as a popular seasoning spice and a dietary supplement rich in vitamins (Okwu, 2003; Essien *et al*., 1994 in Aderibigbe *et al.*, 2010). The leaves, bark, roots and kernels are medicinal (Orwa *et al.*, 2009). The plant is widely distributed and is common in high forest zone of tropical Africa, especially on the fringe of the West African rainforest belt in the secondary and throughout riverian forests, southern savannah-woodland and forest outliers in the East and mostly West African plains. However, information on tannin extraction from its positions is non-existent, which this work sought to assess and as well as to establish the influence of solvent type in the extraction. As an abundant, renewable and organic resource, materials from its various parts can be put to several industrial applications including formulation of tannin adhesives for the wood and other related industries, which utilize resins.

MATERIALS AND METHODS

(a) Sample Preparation for Extraction

Bark, leaves and fruits were collected from three 20-year old *T. tetraptera* (20-25 m high; 95-100 cm diameter) from the Faculty of Renewable Natural Resources Demonstration Farm, Kwame Nkrumah University of Science and Technology (KNUST), Kumasi in the Semi-deciduous Forest Zone of Ghana (1200-1800 mm p.a., **lat**. 6°43′N; long. 1°36′W, Altitude 287 m and mean **temperature** 25.6 °C). The samples were air-dried to 14% moisture content (mc), milled to a fine particle size (40-60 mesh) with a Wiley mill and sieved through 0.5 µm mesh. 1% NaOH was prepared by dissolving NaOH (10 g) in distilled water (100 ml) in a 1000 ml volumetric flask, while distilled water was added up to the 1000 ml mark. The content was thoroughly stirred and clarified by centrifugation at 1000 x g for 20 min., and the cooled solution stored in sterile conical flasks. Each milled sample (5 g) kept in a thimble was deposited in a Soxhlet extractor with 1% NaOH (250 ml). There were eight runs for each extraction process, which lasted for about 6 h. The extract was collected in the round-bottomed flask of the apparatus. The mixture was heated under reflux for 30 min. The suspension was filtered through a sintered glass filter, the precipitate washed with hot water and then dried at 105° C until constant weight. Similarly, milled samples (5 g) from each stem-position of the hardwood were extracted with distilled water, filtered and dried.

c

d

Plate 1: (a) *T. tetraptera* plant with (b) scaly bark, (c) leaves, (d) fruits.

a

b

(b) Qualitative Test to Determine the Presence of Tannin in Distilled Water and 1% NaOH Extracts

To determine the presence of tannin in each plant part, Iron (III) chloride (5 drops) was added to each extract solution (20 ml) obtained from either distilled water or 1% NaOH in Petri-dishes. The contents were shaken thoroughly, allowed to settle and the colours developed, which indicated the presence of phenols (i.e., tannin), noted. Each test was duplicated.

(c) Quantitative Test to Determine the Total Extract Yield and Stiasny Number (i.e., Tannin Content)

The second series of experiments were carried out to determine the quantity of tannin present in the distilled water or 1% NaOH extracts and the solvent that recovered the greater amount of tannin from the various plant parts established. A mixture (1:2 v/v) of HCl (150 ml) and Formaldehyde (300 ml) was prepared in a volumetric flask, stirred similarly centrifuged (at 1000 x g for 20 min.) and stored in conical flasks. Each extract (250 ml) was oven-dried at 105 ± 2 °C for 4 h, cooled in a desiccator for 1 h and weighed. The extracts were allowed to react individually with 20 ml of the mixture of HCl and formaldehyde (1:2 v/v) for 3 h to enable the solute (i.e., the precipitate) dissolve effectively. The suspension was filtered through a sintered glass filter,

while the precipitate was washed with hot water and dried at 105 ± 2° C until constant weight. The processes were repeated and the yield in each extract calculated:

$$\%\ Extract\ \ yield\ \ (w/w) \ = \ \frac{W_2}{W_1} \ x \ 100. \quad (1)$$

Where: W_1 = Oven-dried weight of sample (g); W_2= Weight of total dry extract (g).

The Stiasny number (a quantitative estimation of the total polyphenols in tannin) of each extracts, was also determined according to the procedure proposed by Yazaki and Hillis (1980) and cited in Vázquez *et al*. (2010). The amount of Stiasny precipitate produced was then calculated as:

$$Stiasny \ \ number \ \ (\%) \ = \ \frac{W_3}{W_4} \ x \ 100 \ . \quad (2)$$

Where: W_3= weight of precipitate (g); W_4= Weight of dry extract used (g).

RESULTS

Determination of tannins in different parts of *T. tetraptera*

(a) Qualitative assessment for the presence of tannins

The change of colour of each extract was compared with a **Standard Chart (i.e.,** the Axis Gear standard Colour Chart), which was used as reference point (www.axisgear.ca). The colour of water-soluble extracts from *T. tetraptera* leaves before reaction with Iron (111) chloride was described as toffee, unlike the cocoa colour of the bark and fruit extracts (Table 1). The two colours changed to Army green (a deep shade of green) and lime (a lighter shade of green) respectively, which all indicated the presence of tannins. For extracts in 1% NaOH, which reacted with Iron (III) chloride, the respective colours of those removed from the leaves, fruits and bark were citrus, lime and tangerine. The first two colours changed to lime and citrus respectively, while the tangerine colour remained the same after the reaction.

Table 1: Reaction of distilled water and 1% NaOH extracts from various parts of *T. tetraptera* with Iron (III) chloride

Source of extract	Solvent for extraction	Extract colour before reaction with $FeCl_3$*	Extract colour after reaction with $FeCl_3$*	Inference
Leaf	Distilled water	Toffee	Army green	Tannin is present.
Bark		Cocoa	Lime	Tannin is present.
Fruit		Cocoa	Lime	Tannin is present.
Leaf	1% NaOH	Citrus	Lime	Tannin is present.
Bark		Tangerine	Tangerine	Tannin is present.
Fruit		Lime	Citrus	Tannin is present.

*Darkwah and Jetuah (1996).

(b) Extract Yield and Stiasny Number for *T. tetraptera* Water and 1% NaOH Extracts

i. Extract Yield

Table 2 shows the total extract yield given in weight and in percentages. The yield for 1% NaOH (39.5 - 77.05%) was greater than for the extraction using distilled water from all the plant parts (12.96 – 18 .16%). Mean extract yields for the distilled water for the various plant parts rank as: Leaf > Bark > Fruit, and those for 1% NaOH as: Fruit > Bark > Leaf. For each ranking, differences in extract yield from *T. tetraptera* plant parts are significant ($p < 0.05$). Duncan's Multiple Range Test also shows that significant difference ($p < 0.05$) exists between extract yield at each plant part for distilled water and 1% NaOH (Table 2).

Table 2: Distilled water and 1% NaOH extract yield and Stiasny numbers from different parts of *T. tetraptera*

Source of extract	Solvent for extraction	Oven-dry weight of sample (g)	Weight of total dry extract (g)	Mean extract yield (%)*	Weight of dry extract (g)	Weight of precipitate (g)	Stiasny no.*
Leaf	Distilled water	4.35	0.79	18.16 ±1.15 ^{a}	0.40	0.27	67.50± 2.09 ^{b}
Bark		4.35	0.61	14.02 ±0.23 ^{b}	0.32	0.28	87.50± 0.65 ^{a}
Fruit		4.40	0.57	12.96±0.45 ^{b}	0.29	0.20	68.96± 4.06 ^{b}
Leaf	1% NaOH	4.35	1.72	39.54±3.68 ^{B}	0.86	0.29	33.72±1.36 ^{B}
Bark		4.35	3.28	75.40±5.18 ^{A}	1.13	0.61	37.42±6.06 ^{AB}
Fruit		4.40	3.39	77.05±5.69 ^{A}	1.55	0.34	21.94±1.62 ^{C}

* Means with different letters in a column are significantly different ($p < 0.05$).

ii. The Amount of Stiasny Precipitate (Tannin Content) from the Extracts

Table 2 shows that, unlike extract yield, the Stiasny numbers for extracts at the plant parts were all greater for those extracted in distilled water than those contained in 1% NaOH. For the water-soluble extracts, Stiasny number from the bark extract was the maximum followed by those for the fruits and then the leaves with their differences being significant ($p < 0.05$). Bark extracts contained in 1% NaOH also had the largest Stiasny number, while that for the fruit extract was the least. Duncan's Multiple Range Test (Table 2) shows that significant differences ($p < 0.05$) also exist between the Stiasny

numbers for the water-soluble and 1% NaOH extracts at each plant part.

DISCUSSION

Resins based on natural products such as tannin adhesives are already in industrial use. However, new challenges are arising due to the introduction of more severe standards regarding formaldehyde emission from bonded wood products alongside the increasing costs of oil-derived synthetic resins. Development and employment of adhesives of natural polyphenols (e.g. tannins) in the substitution of synthetic phenols or resins obtained from petroleum have resulted from high petroleum costs ((Dalton, 1950; 1953; Plomley *et al*., 1957; Pizzi and Mittal, 1994). Li and Maplesden (1998) demonstrated that as a renewable resource, tannins are technically able to replace phenol and resorcinol, derivatives from the petro-chemical industry, as wood adhesives. This implies that renewable industrial wastes could be essential raw materials for the production of tannin extracts for various applications such as phenol substitutes in the formulation of wood adhesives, chrome derivative substitutes in leather tanning and a source of antioxidant compounds (Vázquez *et al*., 2010). Consequently, several researches are made on extracting tannins from different parts of many plant species (Li and Maplesden, 1998). Tannin concentrations of the bark and fruit of *Acacia albida* were between 2-28%, and 30-45% and 15-16% for the bark and leaves of *A. pycantha* respectively (Anon., 2012). Roffael and Dix (1994) also reported that polyphenols (tannins) are currently used in the bonding of wood products in Germany, England, New Zealand, Australia and other developed countries. Such patronage involves further screening for organic sources (e.g. plants) with large tannin content in tannin-adhesive formulation to meet the enormous manufacturing demands, particularly for the wood composite industry.

Qualitative Test

Extract colouration, compared with the Axis Gear Standard Colour Chart (www.axisgear.ca), has been employed as a reference point in determining the presence of tannin in aqueous extracts in reaction with Iron (111) chloride. Blue to green colouration resulting from Iron (III) chloride test on plant extracts is an indication of the presence of phenolic compounds such as tannin (Darkwa and Jetuah, 1996). These are supposed to be the reactive centres in the flavonoid units (monomers), which are linked together to form condensed tannin macro-molecules (Anderson, 1967). Several solvents have been employed to extract tannins. Takano *et al*. (1989) used alcohol (i.e., methanol and ethanol) and water, Siminonescu *et al*. (1988) used alkali, while Chavanet *et al*. (2001) employed methanol and acetone at different concentrations with and without acidification and obtained maximum amount of condensed tannins from beach, green and grass peas. Screening of the whole pod extracts of *T. tetraptera* revealed the existence of several phyto-chemicals including tannins, saponins, glycosides, proteins and essential oils (Olajide Awofisayo *et al*., 2010). Qualitative analysis revealed the presence of phenolic compounds or tannins from *T. tetraptera* in both distilled water and 1% NaOH extracts with the bark having the greatest amount in both solvents. Different colourations of the extracts reveal that the amount of the phenolic compounds differs along the stems of the plant and in the different solvents. From the classification employed by Darkwa and Jetuah (1996), distilled water extracts would yield great amount of tannins, as their precipitate colouration ranged from lime (for the fruits and bark) to Army green colouration (for the leaves). Therefore, it would be expected that extractives from the leaves would contain most tannins. For the 1% NaOH extracts, those from the leaf is also expected to contain tannins, as their colour was citrus after the reaction, which is an indication of the presence of tannin.

Quantitative Test

i. Efficiency of Solvent and Method for Tannin Extraction

Darkwa and Jetuah (1996) and Jetuah *et al*. (2001) found 1% NaOH the most effective in extracting most phenols from *Rhizophora* spp. using Soxhlet extractor, while Dametey (2010) found water efficient for tannin extraction in *A. mangium, A. auriculiformis* bark and *Pinus oocarpa* leaves. Hong *et al*. (2009) established that hot water and methanol were effective solvents in tannin extraction from *A. magium*. High Stiasny number, which is expressed by adhesive components (Vázquez *et al*., 2010), indicates great tannin content, while a low extract yield implies that the solvent could not remove much or all the extracts in the plant material. Our investigation has demonstrated that 1% NaOH had greater extractive yield for the three positions of *T. tetraptera* but lower amount of tannin than in water, which is more efficient and had the higher Stiasny number (67.50 - 87.50%) than those of 1% NaOH (21.94 - 33.72%) although it had low extract yield of between 4.89 - 18.16% (Table 2). Tannin yields were quite lower using distilled water as the solvent for extraction than results from other researchers, which could primarily be attributed to the difference in the extraction methods. Ferreira *et al*.(2008) used autoclave for extraction using water as the solvent and obtained tannin content of 60-65%, while the Soxhlet extraction by Darkwa and Jetuah (1996) yielded tannins ranging from 59.6 - 68.9% for 1%NaOH and 7.7-28.7% for water. The quantity of tannin that reacted with aldehyde after methanol extraction using mechanical pulverization method by Nakamoto *et al*. (2005) was also 80%. These findings have established the efficiency of Soxhlet extraction

for the removal of tannin both in weight and in percentages using water as is illustrated in Table 2.

ii. Variability in Tannin Concentration within *T. tetraptera*

Generally, the bark of many trees has usually been the material considered for the extraction of the greatest amount of tannins (Yazaki and Collins, 1994; Hoong *et al.* 2009). Different yields of extract and tannin contents exist from different parts of *T. tetraptera*. The leaf had the greatest extract yield in distilled water (18.16%), followed by the bark (14.02%) and the fruit (12.96%), which were all less than the yields in 1% NaOH (39.54, 75.40 and 77.05% respectively). However, the amount of tannins present for the water-soluble extracts was higher than in 1%NaOH, especially for the bark and least for the leaf. The Stiasny numbers for the bark, fruit and leaf of *T. tetraptera* water-soluble extracts are 87.50, 68.96 and 67.50% respectively. Tannin content in the bark, fruit and leaf of *T. tetraptera* extracted in 1% NaOH estimated by their Stiasny numbers was 37.42, 21.94 and 33.72% respectively. Thus, similar to other plants, the bark of *T. tetraptera* contains more tannins than the other parts of its shoot system (Yazaki and Collins, 1994). Nevertheless, the tannin content removed from *T. tetraptera* fruit or leaf was influenced by the type of solvent employed for the extraction.

iii. Bark-to-Leaf Tannin Concentration Ratio

Bark-to-leaf percentage tannin ratio, as stated by Moore (1995) in determining the bark to leaf tannin concentration of herbs**,** established that the bark contained more tannins than the leaves. Distilled water and 1% NaOH bark extracts for *T. tetraptera* were 87.50% and 37.42% respectively; those of the leaves were 67.50% and 33.72% respectively. Darkwa and Jetuah (1996) used extracting solvents such as petroleum ether, ethanol, water and 1% NaOH in determining the variation in tannin concentration from three different locations of *Rhizophora* spp. They obtained 63.2% and 62.9% for bark and leaf respectively but found variation in tannin content to be dependent on the solvent type such that 1% NaOH extracted tannin most. Dametey (2010), however, found the bark of *Pinus oocarpa* to contain more tannins (0.195 g) than its leaves (0.056 g), *P. caribaea* bark also had 0.149 g and 0.054 g for the leaves, *A. mangium* bark with 0.196 g and 0.098 g for leaves as, while and *A. auriculiformis* bark had 0.102 g and leaves having 0.045 g in 1% NaOH. Generally, hardwoods have higher tannins than softwoods; Bianco and Savolainen (1994) reported that hardwoods like oak or mahogany have a higher tannin concentration than softwoods with 1.6 ± 0.3 mg g^{-1} for fir (softwood), to 80 ± 30 mg g^{-1} for oak (hardwood). Anon. (2002) reported that hydrolysed tannins are mostly limited to dicotyledons, which also have much limited production that they seem to be of little chemical and economic interest in tannin-resin production. Our investigation shows that the hardwoods have great tannin production potential, which necessitates their screening for more polyphenols. Tannin extraction has been analyzed to establish the influence of solvent type. This would assist the plywood manufacturing industries in the production of tannin-based adhesives with the inexpensive solvent (e.g. water) instead of the high cost synthetic resins. In modern times, 80% of all commercial bark tanning is done with highly concentrated extracts of Quebracho, Chestnut or Mimosa. These extracts are typically 30% tannin or more, whereas naturally occurring tannin is closer to 10% to 12% of the material (http://www.braintan.com/barktan/2tannins.htm).

Extraction yields in the range of 26.1-56.4% together with extract Stiasny numbers higher than 84 demonstrated the potential of chestnut shell extracts in the formulation of adhesives and as sources of antioxidant compounds. Under a range of operating conditions, extracts with tannin content higher than 10% (and tannin/soluble solids ratio higher than 0.6) could be used as tanning agents (Vázquez *et al*., 2010). Browning (1975) and Ferreira *et al.* (2008) reported that 30-40% tannin concentration from any part of a tree species is commercially worth exploring. There is capacity for *T. tetratepra* bark and fruit extracts in obtaining not only high extraction yields but also high quality tannin extracts with economically feasible water extraction processes, which would be heavily fortified with urea, UF, PF and RF for the manufacture of tannin-based adhesives with encouraging results. Formaldehyde is generally the aldehyde used in the preparation, setting, and curing of tannin adhesives. It is normally added to the tannin extract solution at the required pH, preferably in its polymeric form of para-formaldehyde, which is capable of fairly rapid de-polymerization under alkaline conditions, and as urea–formalin concentrates (Pizzi, 2003). For the past two decades, there has been a revival of the use of renewable resources due to their broad availability and especially as an appealing source of energy as well as the limited fossil fuel reserves. Thus, it is anticipated that an integral utilization of crops and the use of waste streams in certain industries will grow in importance leading to a more sustainable way of producing materials such as tannin-adhesive production (Vázquez et al., 2010). Results from the present study shows that tannin extracts from T. tetratepra is very promising as an adhesive since the Stiasny number for its water-soluble bark extract is greater than 84 stipulated as the ideal for chestnut by Vázquez et al. (2010). The yield of tannins obtained by extracting Leucaena leucocephala (ipil-ipil tree) barks using a 6-stage counter-current method at 80^{o} C was 71% based on the Oven-dry weight of the bark. The tannin formaldehyde adhesive prepared from the

spray-dried tannin extract exhibited glue shear strength superior to the commercial formaldehyde resin (Manas, 1979). Resins based on natural products such as tannin adhesives are already in industrial use. The interest is centred on the formulation of adhesives in which the total content of natural material is increased coupled with the total elimination of formaldehyde, which could be achieved using glyoxal, a non-volatile non-toxic aldehyde, which has been already tested in lignin and tannin adhesives for particleboards (Vázquez et al., 2010).

CONCLUSIONS

This work indicates that tannin is present in T. tetraptera bark, leaf, and fruit. Extract yield was greater in 1% NaOH, which ranged from 39.54% (from the leaf) to 77.05% (from the fruit) than in distilled water with an extract yield between 12.96% (from the fruit) to 18.16% (from the leaf). Nevertheless, of the two extraction solvents, distilled water was more effective in removing tannins, which was expressed by higher Stiasny number of 67.50 to 87.50% in the various plant parts than those contained in 1% NaOH with lower Stiasny numbers (21.94 to 37.42%). For commercial purposes, it is possible to obtain high tannin content from the bark of T. Tetraptera, which is available all year round and neglected by timber industries, using a much accessible and comparatively cheap solvent (i.e., water). This can be used in the formulation of tannin-adhesive, while its bonding strength is examined together with those extracted from its leaves and fruits for a number of industrial applications. This would contribute in increasing the raw material base for cheaper and more sustainable production of adhesives using tannins than the over-reliance on fossilized or petroleum-derived phenols in Phenol-Formaldehyde resins.

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