

MANGO (*Mangifera indica*) AND AMBARELLA (*Spondias cytherea*) PEEL EXTRACTED PECTINS IMPROVE VISCOELASTIC PROPERTIES OF DERIVED JAMS

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ABSTRACT

Food industries in developing countries are faced with the problem of inadequate supply of additives which can be met by proper utilization of local pectin sources. Mango (*Mangifera indica*) and ambarella (*Spondias cytherea*) peels are most of the time thrown into nature or used for animal feeding. They have been reported to be a potential source of pectins which could be used to process the fruits into various products. In order to assess their feasibility to be used in jam processing, ambarella and mango (*Mango* variety) peel pectins were extracted using three different extraction conditions: HCl at 85 °C/1h, water at 70 °C/1h and oxalic acid/ammonium oxalate (OAAO) at 85 °C/1h. Compare to commercial lime pectin with degree of methoxylation (DM) 70%, phase diagrams presenting sol-gel transition of purified pectins established as sucrose concentration (40-75 %, weight/weight) versus reduced pectin concentration (0.1-1.8 %, weight/weight) were studied at pH 3. Mango and ambarella jams were prepared with and without highly methoxylated peels pectins (0.4 %; DM 60-75%) and the effect of pectins on jam firmness was studied. Prepared hot jams, with 64 % of dry matter, 60 % of sucrose and/or 0.4 % of pectin, were characterized for their gelation kinetics and mechanical spectra at 20 °C. Phase diagrams showed that at pH 3, the minimal sucrose concentration used to obtain the gel is 40 % for OAAO mango pectin, 45 % for HCl mango and OAAO ambarella pectin, and 50 % for HCl ambarella and commercial pectin. Only gelation of OAAO extracted pectins was possible at low polymer (0.2 %) and standard sucrose (60 %) concentrations. Jams prepared without pectins exhibited a weak gel behaviour ($G' = 500-1000$ Pa at 10 Hz) with those of ambarella being stronger than those of mango. Because of its good physicochemical characteristics, ambarella pulp was more suitable than mango pulp for jam processing. Mango and ambarella jams exhibited very strong gels ($G' = 2000-5000$ Pa at 10 Hz) behaviour while using OAAO extracted pectins; the viscoelastic strength of the processing fruits increases 3-6 folds. Accordingly, OAAO extracted mango and ambarella peel pectins allow to obtain jams with excellent gelling properties.

Key words: Mango, Ambarella, Pectins, Jam, Rheology

INTRODUCTION

Mango (*Mangifera indica*) and ambarella also known as golden apple (*Spondias cytherea*) are tropical fruits, which belong to the family of Anacardiaceae. In Cameroon, these fruits are widely eaten by the population between April and July where mangoes are produced with an important post-harvest loss (22 % of the production) [1]. Processing of mango and ambarella into juice, jam and puree or dried fruit are some ways of reducing the loss [2,3]. Fruit processing provides jobs and bypasses market fluctuations. It promotes income-generating activities, upgrades the overflow production, and thus generates income for the producers [4]. However, in developing countries, food processing has a number of problems such as inappropriate technology, fruit supply, packaging and food additives shortage (pectin, citric acid). In addition to this, peels which represent 20% of the fruits are used in animal feeding or thrown away, causing pollution. It has been shown that these peels are good sources of fibres, polyphenols and pectins [5,6,7].

Pectins are a family of complex polysaccharides mainly present in the primary cell walls and intercellular regions of dicotyledons [8]. Structurally, they are generally described as an alternation of “smooth” (made of homogalacturonans, HGs) and “hairy” (made of type I rhamnogalacturonans, RGs-I) regions. HG is composed of (1→4)-linked α -D-galacturonic acid (GalpA) residues that can be partly methylesterified at C₆ and possibly partly acetylated at O₂ or O₃ [9]. Citrus peels and apple pomaces are the two main sources of commercial pectins [10], while mango peels and sugar beets are considered as secondary sources [5,8]. The commercial pectins are extracted by treating the raw material with hot dilute mineral acids, mainly nitric acid [11]. These native pectins are generally highly methoxylated (DM > 50 %) and slightly acetylated [8]. They are widely used as food additives for their thickening, gelling and emulsifying properties [12].

According to Rolin [11], jams are the oldest application of pectins. These fruit products are derived from the heat processing of the fruit pulp or calyx flower with sucrose, organic acid and pectins [13]. The resulting jam has 65 % dry matter content, 50-60 % of sugar content, a pH of nearly 3.5 and total pectin content of 0.5-1 % [14]. These values vary according to the composition of the fruit used that can be suitable for typical food processing. For example, fruits such as apple and guava don't require any additional pectin to be processed into jam [12]. But mango pulps are not rich enough in pectin (3-6 mg/g) [15] compared to pawpaw (7-10 mg/g) and apple (6-16 mg/g) pulps [16]. The type of pectin used depends on the processing temperature, the texture and the pH of the final product [17]. In case of mango and ambarella jam, there is need for highly methoxylated (DM > 50 %) pectin. According to Voragen *et al.* [8], rapid set pectins (DM \approx 70-77 %) are used in the processing of sugar foods. It has been shown that oxalic acid (OAAO) extracted mango peel pectin has high DM (75-77), molar mass (630 kDa), intrinsic viscosity [7] and gelling properties [18] compared to citrus commercial pectins.

In developing countries, food industries are faced with the problem of inadequate supply of additives. This inadequacy can be met by proper utilization of local pectin

sources such as mango, ambarella and pawpaw peels. Some rheological properties of mango and ambarella jams prepared with their extracted peel pectins are presented here.

MATERIAL AND METHODS

Sampling and sample treatment

Ripe ambarella or golden apples (*Spondias cytherea*) were harvested in an Orchard near the city of Yaoundé (Cameroon) and *Mango* (locally called *Hore Wandou*) mango (*Mangifera indica*) variety in the peasant neighborhood in Ngaoundéré town (Cameroon). The peels and pulps of the fruits were removed and chopped into pieces of about 1 cm² using a stainless steel knife. The peels were then bleached in boiling water for 5 min and dried in a convection air oven at 50 °C for 2 days. The pulps were packaged in plastic bags and deep-frozen at -30 °C. The alcohol insoluble residue (AIR) was obtained by processing the dried peels five times with 85 % ethanol (solid/liquid ratio: 1/3 weight/volume) at 70 °C for 20 min and with 95 % ethanol before drying in an oven (50 °C). Prepared AIR were blended and sieved in order to obtain a powder of 0.5 mm grain size [6].

Pectin extraction and purification

Pectin was extracted using two different extraction conditions (HCl 0.03 M and oxalic acid/ammonium oxalate 0.25 %). About 100 g of AIR powder were stirred with 4 liters of HCl 0.03M (pH 1.5) or oxalic acid/ammonium oxalate at 85 °C for 1 hour. Concerning water extraction condition, the AIRs were stirred at 70 °C for 1 hour. The extracts were separated from the AIR residues by filtering through a nylon cloth and cooled. To avoid pectin hydrolysis, the pH of HCl extract was adjusted to 4.5 using NaOH 3M. Pectins were precipitated with three volumes of ethanol (95 %). The precipitated pectins were washed five times with 70 % ethanol and finally with 96 % ethanol and acetone before drying in an oven at 50 °C [19]. Pectins were purified by centrifugation (11 000 rpm) for 15 min and microfiltration followed by precipitation with three volumes of ethanol as performed by Koubala *et al.* [18].

Phase diagram

Aqueous solutions containing different concentrations of mango and ambarella (extracted with HCl or OAAO) peel pectins were prepared. Only HCl and OAAO extracted pectin were used to study phase diagrams because of the high extraction yield obtained. Phase diagrams were performed using various quantities of sucrose (40-75 %, weight/weight) against pectin concentrations (0.1-1.8 %, weight/weight). The pH of the polysaccharide solution was adjusted using citric acid (1M). Within a tube under stirring, these solutions were heated (100 °C) for 30 min. After that, the resulting system was then cooled for 16 h [20]. The system was considered to be a sol when it flowed easily. Sol/gel transition was defined at the onset of the meniscus deformation when the tube was held horizontal. Determination of the sol-gel transition was reproducible within less than 5% marginal error.

Jam preparation and rheological measurements

Ambarella and mango jam were prepared with and without adding OAAO extracted pectin (DM 60-75%) or commercial citrus pectin (DM 70%). These DM were

determined by HPLC on a C18 column, as previously described [6]. According to results obtained from phase diagram experiments, only OAAO extracted pectins were used. The gelation kinetics and mechanical spectrum of the jams were determined with a Carri-med CSL 100 controlled stress rheometer (CSL100, 105847; Carri-Med Ltd, Dorking, Surrey, UK) using a temperature-regulated cone-plate device (radius 2 cm; angle 4°01'02'', gap 98 µm). About 18.5 g of sucrose were introduced into a screw-capped conical flask (50 ml) containing 10 g of pulp slurry (10 %, weight/volume). 0.12 g of pectin (when added) was used and 2.5 ml of citric acid (1 M) was then added to reach 0.05 M (pH 3) in the final slurry. The mixture was heated at 100 °C for 30 min while stirring. The obtained jam presents 64 % of dry matter, 60 % of sucrose and/or 0.4 % of pectin. The hot jam was poured onto the rheometer plate heated to 90 °C and the surface of the sample was covered with paraffin oil. The system was cooled to 20 °C before starting rheological measurements.

Statistical treatment

The average yields of pectins were calculated with their standard deviations. Statistical treatment measurements were performed at least in triplicate. Results were compared using analysis of variance and the Student's t-test using the SPSS version 12 software. Significance was accepted at 0.05 level of probability.

RESULTS

Extraction yield

Table 1 shows that Mango and ambarella peel pectins were recovered with a yield varying from 12 to 32 % (dry alcohol insoluble residue). The highest yields are recorded using oxalic acid/ammonium oxalate (OAAO) as extracting agent. It was noted that only few quantities of pectins are recovered with water. Any year in Cameroon, 2000 tons of pectin can be recovered from 15 000 tons of mango by-product (peels specially) using OAAO extraction condition. This can be initiated in Adamawa and Littoral regions where more than 60 % of production is found.

Phase diagrams of sucrose/pectin systems

Figure 1 presents sol/gel transition lines of five pectin/sucrose systems. HCl and OAAO ambarella and mango peel pectins were used for their high yield and compared to commercial citrus pectin. The transition lines for these five systems have the same shape but there are important differences between their coordinates (x and y axis). The minimal sucrose concentration used to obtain the gel is 40 % for OAAO mango pectin, 45 % for HCl mango and OAAO ambarella pectin, and 50 % for HCl ambarella and commercial pectins.

Sucrose (%)

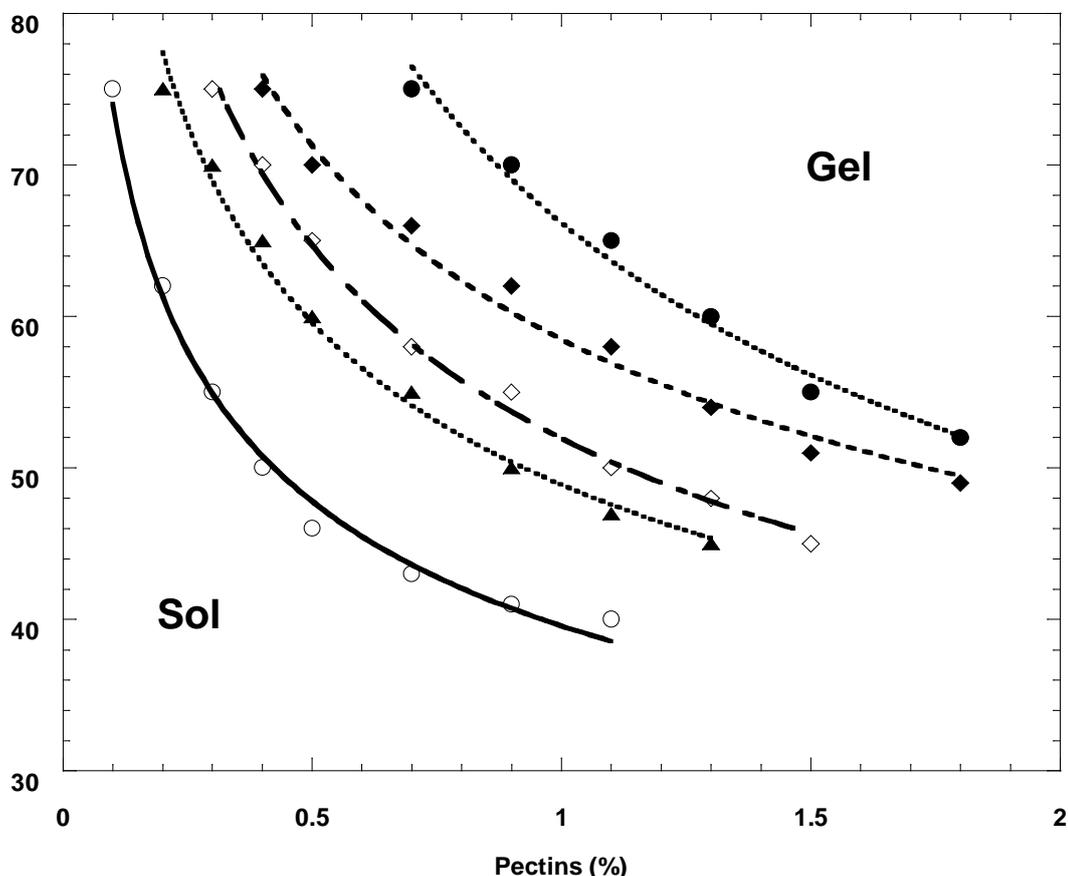


Figure 1: Phase diagrams at pH 3 of mango (OAAO: ○, HCl : ▲) and ambarella (OAAO : ◇, HCl : ●) peel pectins compared to commercial citrus pectin (◆); mango and ambarella peel pectins were extracted using OAAO or HCl

Effect of pectin on the rheological properties of jam

Jams were prepared from ripe mango and ambarella pulps with and without pectin addition. Highly methoxylated OAAO extracted mango (DM 75%) and ambarella (DM 60%) peel pectins were used and compared to commercial citrus pectin (DM 70%). The final jam had a pH of 3, a total dry matter, sucrose and pectin (in the case of addition) contents of 65 %, 60% and 0.4 % (w/w) respectively. Pectins were used at 0.4%, on the basis of results previously obtained by phase diagrams. Gelation kinetics and mechanical spectrum of prepared jams were then evaluated.

Viscoelastic properties of jams prepared without pectins

Figure 2a shows that gelation kinetics of prepared ambarella jam exhibit highest values of storage modulus (G') compare to that of mango jam. Mechanical spectrum of mango and ambarella jams presents the evolution of storage (G') and loss (G'')

moduli at various frequencies (0.01-10 Hz) (Figure 3a). G' are higher than G'' at all frequencies and there is a slight dependence of G' with frequencies.

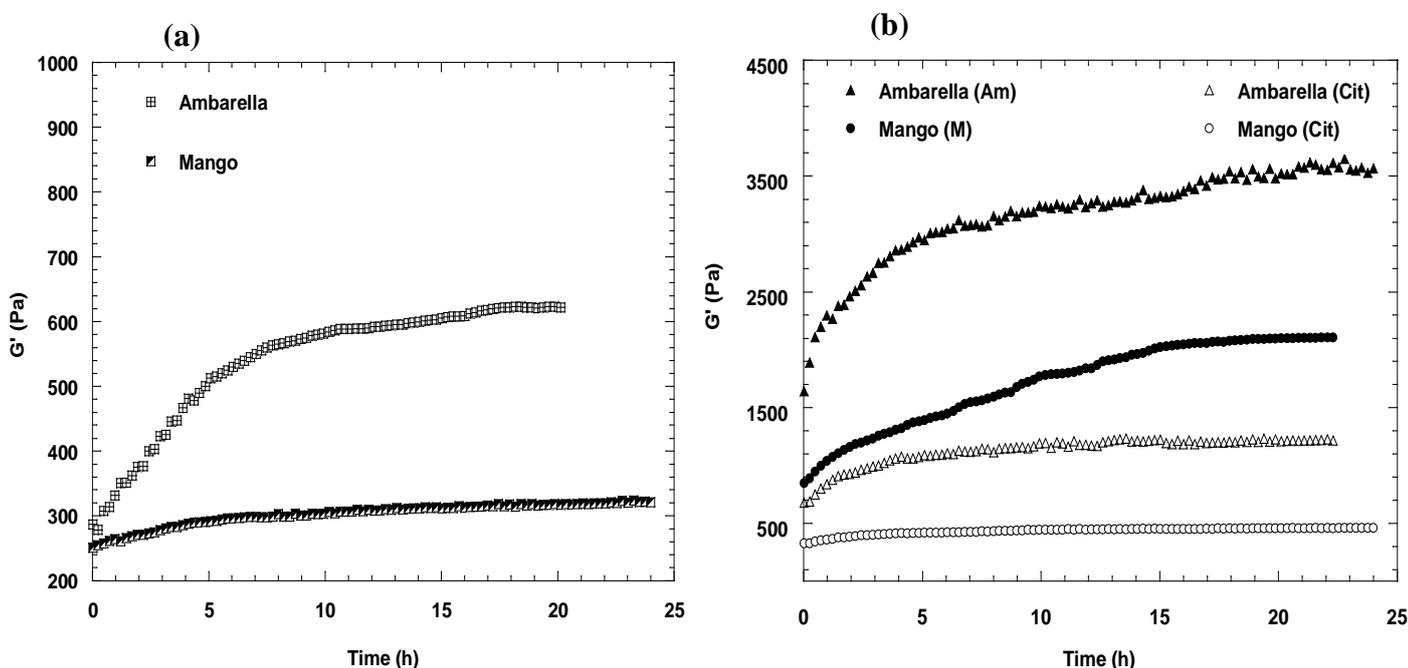


Figure 2: Gelation kinetics: Evolution of storage modulus (G') of mango and ambarella jam with time; mango and ambarella jams were prepared without *a* and with *b* pectins (0.4%). (Am), (M) and (Cit) are ambarella, Mango and commercial Citrus pectins, respectively

Viscoelastic properties of jams prepared with pectins

Figure 2b describes gelation kinetics of mango and ambarella jams prepared with OAAO extracted peel pectins compared to commercial citrus pectin. G' values of ambarella jam increase till 3500 Pa, which are higher than values recorded for mango jam. The use of mango and ambarella peel pectins increases 5-6 fold the values of storage modulus. The Mechanical spectrum of jams prepared with (Figure 3b) and without (Figure 3a) pectins shows the same shape, but significant differences ($p < 0.05$) are observed at the levels of recorded values of storage (G') and loss (G'') moduli and of G''/G' ratio or gap value between G'' and G' . For example, concerning jams prepared without pectins and at 10 Hz frequency, recorded values of G' (900-1000 Pa) are lower than values (2000-5000 Pa) obtained with jams prepared using pectins.

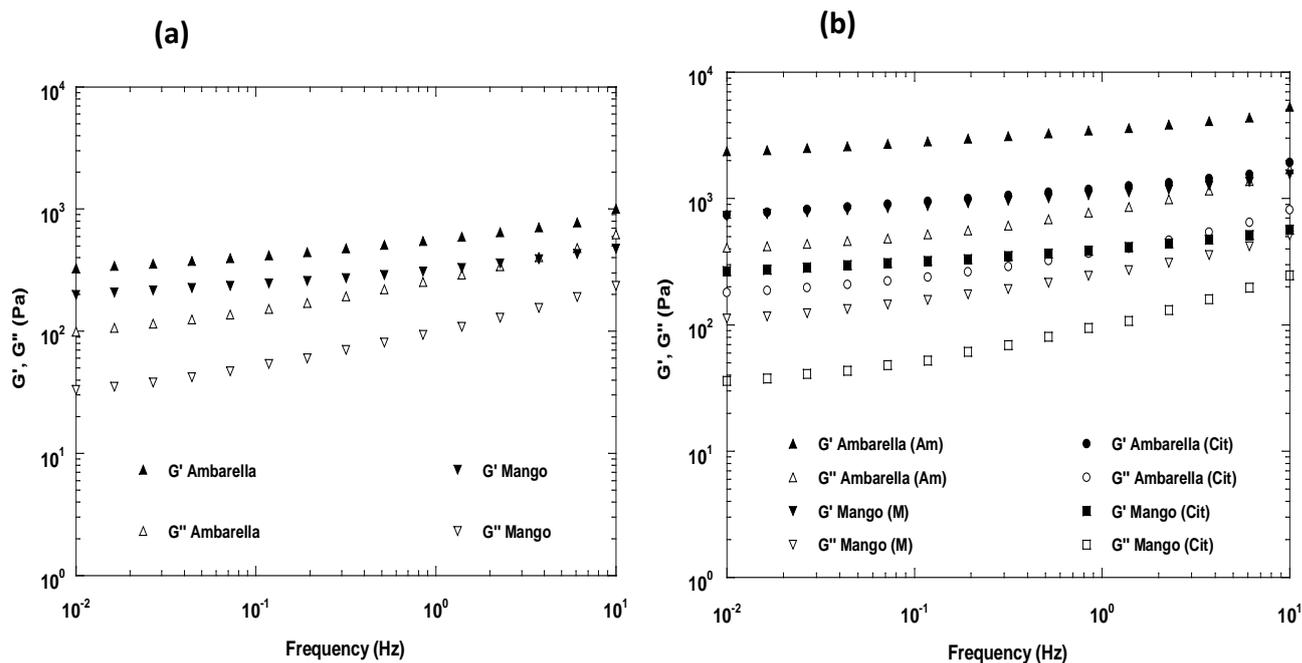


Figure 3: Effect of pectin used on frequency sweep of mango and ambarella jam; mango and ambarella jams were prepared without *a* and with *b* pectins (0.4%). Am, M and Cit are ambarella, mango and commercial citrus pectins used, respectively

DISCUSSION

Concerning jam prepared without pectin, recorded value of storage modulus is higher than that of loss modulus showing the evidence of gel formation. But, the low gap value between G'' and G' (40-200 Pa) observed in the frequency range explored, showed that these jams exhibit weak gels behavior. This suggests the need of pectin in ambarella and mango jam processing. If ambarella jam is stronger than mango jam, it can be suggested that ambarella pulp is more suitable than mango to be processed into jam. Differences observed in jam firmness are mainly due to the chemical composition of the pulp. Compare to mango, ambarella pulp exhibits high uronic acid (21 mg/g) content and low pH (3.9) [21]; meaning that preparation of ambarella jam will need less pectin than that of mango. Despite the high pH value and low uronic acid content, Iagher *et al.* [22] showed that pectic polysaccharides extracted from mango pulp exhibited high viscosity and could be potential as a thickening additive in food applications. Differences between jams gel strength or their viscosity were also observed between pineapple, orange, pawpaw and banana jams [23] and between *Améliorée*, *Keitt* and *Palmer* mango jams [24].

The use of highly methoxylated pectin increases the gel strength of the prepared mango and ambarella jams. The high increase of storage modulus (G') of jams prepared with pectins can be explained by the action of these polysaccharides in gelation process which results from the junction zone formation between homogalacturonan chains in the presence of sugar and acid. These junction zones are

stabilized by interchain hydrogen bonds between the carboxylic group of uronic acid and by hydrophobic interactions between methylester groups [25]. Mango and ambarella jams prepared with commercial pectin exhibit low value of G' (Figure 2b). Thus at pH 3, OAAO extracted mango and ambarella peel pectins gellify better than commercial citrus pectin in jams. The use of mango and ambarella peel pectins in jams allows one to obtain good strong true gels. This was also observed by Madhav and Pushpalatha [26] who noted that most of the jellies made using pectin from mango peel and banana peel were found to have good quality regarding their setting time and consistence. This difference in gelling pattern is mainly due to the physicochemical properties of extracted pectin [18]. The extraction condition also has an effect on the gelling property of the extracted pectin. Sirisakulwat *et al.* [27] observed that acid extraction condition made the mango pectins less suitable as to gelling capacity. Contrary to OAAO, acid extraction condition reduce the length of rhamnogalacturonan I side chains by depolymerising arabinan and galactan polymers. The fruit-sugar product was very strong with ambarella jam prepared using OAAO pectin from the same fruit. This is due to the beneficial effect of the high organic acid (ascorbic, citric, malic and oxalic) content of ambarella pulp [28]. Instead of using pectin in sugar-fruit preparations, Singh *et al.* [23] proposed different combinations of fruits to obtained jam with a good gelling strength. But these combinations may affect the sensory properties of the prepared jam which can be or not accepted by the consumers.

CONCLUSION

Because of their best physicochemical properties, ambarella pulps are more suitable than mango pulp for jam processing; meaning that ambarella jam preparation needs less pectin than that of mango. The use of OAAO pectin in fruit processing increases (3-6 folds) the visco-elastic strength of the prepared jams. Sensory properties of the resulting jams are currently being investigated.

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Table 1: Effect of HCl, water and oxalic acid/ammonium oxalate (OAAO) on the extraction yield of mango and ambarella peel pectins

Extraction condition and source of pectins		Extraction Yield		
		Dry AIR (g/100g)	Dry peels (g/100g)	Fruit (mg/g)
HCl 0.03 M	<i>Mango</i>	26.33 ± 0.72 ^b	16.10 ± 0.44 ^b	5.61 ± 0.02 ^c
	<i>Ambarella</i>	19.35 ± 0.58 ^d	11.76 ± 0.35 ^d	6.72 ± 0.02 ^b
pH 1.5	<i>Mango</i>	12.51 ± 0.86 ^f	7.65 ± 0.52 ^f	2.62 ± 0.02 ^d
	<i>Ambarella</i>	15.62 ± 0.54 ^e	9.49 ± 0.33 ^e	5.41 ± 0.02 ^c
Water	<i>Mango</i>	31.76 ± 1.66 ^a	19.41 ± 1.01 ^a	6.73 ± 0.04 ^b
	<i>Ambarella</i>	22 ± 0.31 ^c	13.37 ± 0.19 ^c	7.59 ± 0.03 ^a
OAAO	<i>Mango</i>			
	<i>Ambarella</i>			

Mean values from triplicate measurements ± standard deviation. Values in the same column followed by different superscripts are significantly different (p < 0.05). AIR: alcohol insoluble residue.

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