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Yield and Quality of Pectins Extractable from the Peels of Thai Mango Cultivars Depending on Fruit Ripeness

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Pectins, recovered from the peels of four mango (*Mangifera indica* L.) cultivars by mimicking industrial techniques, were evaluated in terms of yield, composition, macromolecular properties, and technofunctional quality. Freeze-dried peels of mature-green fruits, after major mesocarp softening, and at full ripeness were extracted using hot acid. The pectins were precipitated in propan-2-ol and their crude yields quantified as alcohol-insoluble substance. Like apple pomace, the dried peels provided hardly acetylated (DAc < 6.3%) rapid-set to ultrarapid-set high-methoxyl pectins at starch-adjusted yields of 11−21 g/100 g. However, despite similar high molecular weight fractions and galacturonic acid/rhamnose ratios, their average molecular weight was markedly reduced by a characteristic, almost monodisperse fraction of 16000−19000. Expanded galactans, indicated by galactose/rhamnose ratios of 15−24 mol/mol, probably represented arabinogalactan side-chain fragments withstanding hot-acid extraction at pH 1.5 and 2.0, as implied by arabinose/galactose ratios of 8−15 and 33−56 mol/100 mol, respectively. Limited galacturonic acid contents made the mango peel pectins less valuable than commercial apple pectins with regard to gelling capacity and thickening properties. Whereas starch and matrix glycan fragments almost completely degraded during ripening, depolymerization of pectins and galactans was insignificant. Technofunctional properties, modulated by extraction at different pH values, were ascribed to structural differences influencing macromolecular entanglements.

KEYWORDS: Exocarp; fruit maturity; gel; gelation; hot-acid extraction; mango (*Mangifera indica* L.); molecular weight distribution; pectin; peel; viscosity

INTRODUCTION

As gelling and stabilizing agents, pectins are commonly used in the food industry (*1*). Their bioactivities are of pharmacological interest (*2*). Located in the primary cell walls and middle lamella of dicotyledonous plants and noncommelinid monocotyledons, pectic substances influence the strength, porosity, and adhesion of cell walls during the plant development (*1*). As associated polysaccharides, they comprise several partly connected structural elements, especially homo- (HG) or xylogalacturonans besides the rhamnogalacturonan types I and II (RG-I, RG-II) (*3*). The (1→4)-linked α-D-galacturonosyl residues constituting HG stretches are methyl-esterified at C_6 and acetylated to different extents depending on the plant species. The RG-I backbone is formed by alternating (1→4)-linked α-D-galacturonosyl and (1→2)-linked α-L-rhamnopyranosyl residues, with the latter carrying arabinan, galactan, and arabinogalactan side chains. RG-II is a highly branched galacturonan (>7 units) with four characteristic oligosaccharide side chains. Although the HG chain lengths may be rather uniform (*4*), the size of various pectin elements is still debatable. The average molar ratio of rhamnose (Rha) to anhydrogalacturonic acid (AUA) greatly varies among plant species (*3*).

Commercial pectins are typically recovered by hot-acid extraction (pH 1−3, 50−90 °C), aiming at maximized yield [10−15% of dried apple pomace, 20−30% of dried citrus peels (*1*)] through partial hydrolysis of rhamnopyranosyl and arabinofuranosyl linkages, solubilization of ionically bound pectins, and hydrolysis of RG-II borate esters (*5*). Thus, they are rich in galacturonic acid [75−90% (*5, 6*)], but the molecules differ in their sizes, the methylation and acetylation degrees, intramolecular distribution of methyl-esterified units, and side-chain lengths (*7, 8*).

Mango (*Mangifera indica* L.) has been deemed a promising, but not yet exploited, alternative pectin source (*1, 6*). Pectin yields greatly varied (6.4−21%) among experimental extractions of peel waste from industrial mango processing (*9*−*11*). Similar

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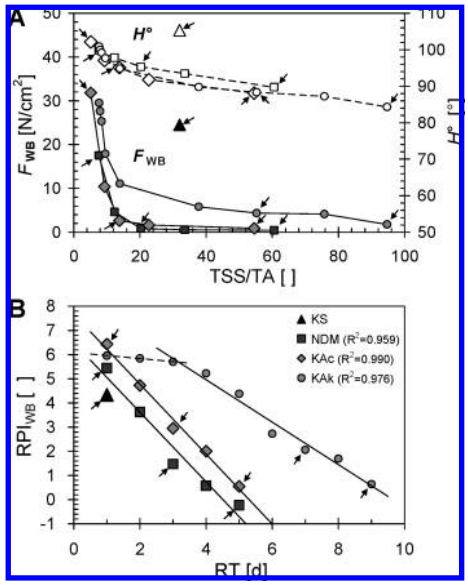

Figure 1. Mesocarp quality (**A**) and fruit ripeness (**B**) during postharvest ripening of mango fruit lots of 'Kiew Sawoei' (KS; triangles), 'Nam Dokmai #4' (NDM; squares), and 'Kaew Chuk' (KAc; rhombs) with CaC_2 as ripening accelerator (harvest 2003) and cv. 'Kaew Khiew' (KAk; circles) without CaC_2 (harvest 2004) at 25−28 °C. Arrows indicate quality and ripeness stages of the fruits used for pectin extraction. F_{WB}, mesocarp firmness (solid symbols); $H°$, hue angle (open symbols) describing mesocarp color; TSS/TA, sugar/acid ratio; RPI_{WB}, postharvest ripeness index; RT, postharvest ripening time after harvest on day 0; R^2, coefficients of determination for the linear functions between RPI_{WB} and RT describing postharvest ripening (—), partly occurring after an initial lag phase (- - -).

yields (10.1−24.5%) resulted when fruit peeling and peel drying were included in the experiment (*12*−*16*). The impacts of extraction conditions (*10*−*12*) and cultivar (*12, 13, 15, 16*) were shown. All of those pectins were highly methylated (52−86%), but structural details are scarce (*12, 16*). The AUA contents ranged from 42 to 73% after hot-acid extraction (*9*−*12, 15, 16*). Thus, the minimum galacturonic acid content (≥65%) specified for commercial pectins (*17*) was not always met. Conclusions as to extraction techniques and peel specifications are impaired by differences in scarcely specified fruit maturity and the protocols for peel preprocessing, extraction [e.g., solid/liquid ratios (*6*), extracting agents (*10*)], and precipitation, leading to contradictory observations, such as pH values recommended for extraction (*10, 11*). Moreover, exploitation of mango peels may be notably demanding, because their availability and quality are affected by different types of fruit processing. Whereas apple and citrus juice processing generates the major pectin sources in huge amounts (*1*), a great share of processed mango fruits is preserved by canning and drying on a small scale, where manual peeling ensures high flexibility of processing lines for the year-round processing of several crops. Mango fruit specifications, such as the firmness required for cutting or pulping, thermal preservation, and sensory aspects, are met by exploiting different maturities and cultivars (*18*). On the other hand, mango peels, constituting 15−18% of the total fruit mass (*19*), generate, together with seeds (13−29%) and nonutilizable pulp, large amounts of processing byproducts. Increasing mango processing has thus boosted research into value-adding waste reduction, for example, through fibers with antioxidant activity (*20*) and the joint recovery of pectins and polyphenols (*14*) from mango peels.

Because the great variation in yield and quality is a major obstacle to pectin recovery from mango peels, this study aimed at exploring to which extent the high diversity of fruit maturity in mango processing and ripening-associated pectin changes actually limit the utilization of mango peels. As the cultivar-specific ripeness stages preferred for consumption extremely vary from mature-green to full-ripe, three representative Thai mango varieties were considered. To evaluate the suitability of their peels at different maturity stages for pectin recovery, industrial hot-acid extraction was mimicked by two standard protocols on a laboratory scale. In view of the limited knowledge of the nature and functionality of mango peel pectins, yield, composition, macromolecular properties, and technofunctional quality of the isolated pectins were comprehensively characterized, besides coextractability of starch.

MATERIALS AND METHODS

Sample Material and Experimental Design. Mango fruits of cvs. 'Kaew Chuk' (KAc; ∼80 kg), 'Kiew Sawoei' (KS; ∼40 kg), and 'Nam Dokmai #4' (NDM; ∼80 kg) were obtained from two orchards in the San Sai district, Chiang Mai, Thailand, during the main harvest season in May−June 2003. Mature-green fruits were picked and ripened for 5 days at 25 ± 2 °C and 70−80% relative humidity (RH) at Chiang Mai University, Chiang Mai, Thailand, until full ripeness. Paper bags with calcium carbide (CaC_2, 15 g/kg of fruit) as a ripening accelerator were evenly distributed over the ripening boxes. Fruit samples of ∼2 kg were randomly collected for daily monitoring of postharvest ripening on the basis of the ripeness index (RPI_{WB}; eq 1) introduced previously (*21*). At selected ripeness stages, ∼20 kg of fruit per cultivar was manually peeled and destoned, while small fruit portions were processed consecutively. The peels were immediately quick-frozen in liquid nitrogen, vacuum-packed in aluminum pouches, and stored at −80 °C until freeze-drying. The mesocarp was cut into cubes of ∼1 cm^3 with stainless steel knives prior to quick-freezing. The lyophilized samples were sent deep-frozen by air freight to Hohenheim University, Stuttgart, Germany. After further lyophilization upon arrival, the brittle samples were manually crushed, vacuum-packed into PE pouches, and stored with desiccant at ∼22 °C until pectin extraction. By pre-estimating the ripening times from the linear development of RPI_{WB} (eq 1), the experiment was repeated with ∼400 kg of mangoes cv. 'Kaew Khiew' (KAk) in crop year 2004, but without acceleration of ripening by CaC_2 (*22*). For pectin extraction on a larger scale, ∼180 kg of fruit was processed per ripeness stage as described above. After storage of the quick-frozen mesocarp cubes and peel strips at −80 °C, portions of ∼20 kg were predried in a cabinet dryer at 80 °C as single layers on 56 × 99 cm trays until a moisture content of ∼25%, then vacuum-packed and stored at −20 °C until final freeze-drying, because of limited lyophilization capacity. The description below is limited to the pectins obtained from the peels. Complementarily, those of freeze-dried mesocarp are to be discussed in another scope. A commercial, unstandardized apple pectin with a degree of esterification (DE) of ∼72% (Herbstreith & Fox, Neuenbürg, Germany) was characterized for comparison (sample AP1).

Monitoring of Postharvest Ripening. During postharvest storage, fresh fruit quality was daily analyzed. To assess mesocarp firmness, the maximum shear load (F_{WB}, N/cm^2) needed to cut a sample cube over a cross-section of 1 × 1 cm was measured by using the Warner-Bratzler shear cell (WB) of an Instron Universal Texture Analyzer type 3365 (Instron, Canton, MA) at a crosshead speed of 200 mm/min and a load cell capacity of 0.1 kN. The color and contents of total soluble solids (TSS) and titratable acidity (TA) were determined from the ground mesocarp as detailed elsewhere (*21*), expressing TSS as sucrose (°Brix) and TA as citric acid in grams per 100 g of mesocarp. In this study, only the hue angle ($H°$) was considered among the parameters of the CIELab color space, analyzed with a colorimeter CR 300 (Minolta, Tokyo, Japan). Division of TSS by TA yielded the sugar/acid ratio (TSS/TA). From the latter and the dimensionless fruit firmness ($|F_{WB}|$), that is, the absolute value of the maximum shear load, the postharvest ripeness index (RPI_{WB}) was computed (eq 1) (*21*).

$$RPI_{WB} = \ln(100|F_{WB}|TSS^{-1}TA) \quad (1)$$

Pectin Extraction. Pectin was extracted from the dried raw material (DRM), that is, the freeze-dried peels, on a laboratory scale, using two standard protocols (EM A and EM C). Per run, 20 g of DRM was filled with distilled water to a total of 400 g. DRM samples from KAk were treated on the double scale (40 g/800 g) throughout. The suspension was boiled for 15−20 min and recooled. The pH was adjusted to 1.5 with H_2SO_4 (25% w/w; EM C) or pH 2.0 with 2 N H_2SO_4 (EM A) prior to extraction (90 °C, 2.5 h) in an oil bath. The recooled extract was manually pressed through a perlon filter cloth. After the residue had been washed with 200 mL of distilled water, the pectins were precipitated from the combined filtrates in 4 L of propan-2-ol (≥99.9% v/v) for 30 min. After two washings with propan-2-ol (2 × 2.5 L, ≥99.9% v/v), the precipitate was dried (60 °C, 1−2 h) in an oven. Four to 15 runs per extraction method were performed for each DRM sample, except for DRM from KAk (25−27 runs per variant). For each run, the yield of dried crude pectin was calculated as alcohol-insoluble substance (AIS, g/100 g of DRM). Per sample and extraction method, the AIS of all runs was pooled and ground in a centrifugal mill type ZM 1 (Retsch, Haan, Germany) to particle sizes of <0.25 mm. The starch-adjusted pectin yield ($AIS_{S\text{-}corr}$, g/100 g of DRM) was calculated (eq 2) after enzymatic quantification of coextracted starch ($starch_{AIS}$, g/100 g of AIS) by means of the respective test combination (R-Biopharm, Darmstadt, Germany). The ground AIS and the reference pectin (AP1) were characterized by analogy to a previous study (*7*).

$$AIS_{S\text{-}corr} = AIS - \frac{starch_{AIS}AIS}{100} \quad (2)$$

Chemical Pectin Characterization. As to the legal pectin specification (*17*), the galacturonide content was titrimetrically quantified in duplicate from the neutralization and saponification equivalents and expressed as galacturonic acid (M_r = 194.1 g/mol) on an ash- and moisture-free basis [$GalUA_{titr}$, g/100 g of purified AIS (AIS_p)]. The JECFA standard method (*17*) was slightly modified by dissolving the ash-free sample (AIS_p) under moderate heating with subsequent recooling to 20 °C and the use of a pH 8.1 mixed indicator. On the basis of the recovery rate after purification in acidified propan-2-ol (AIS_p/AIS, g/g), $GalUA_{titr}$ was converted into the anhydrogalacturonic acid content (M_r = 176.13 g/mol) of the original sample (AUA_{titr}, g/100 g of AIS). By analogy, its methyl ester content (M_r = 31 g/mol) was calculated ($MeOH_{titr}$, g/100 g of AIS) from the saponification equivalents. The degree of esterification (DE) resulted as the percentage of the saponification equivalents relative to the total of neutralization and saponification equivalents.

Furthermore, the anhydrouronic acid content (M_r = 176.13 g/mol) was quantified colorimetrically (AUA_c, g/100 g of AIS), using the modified *m*-hydroxydiphenyl (MHDP) assay (*23*). Following the previous adaptation to the analysis of predissolved pectins (*7*), 75 mg of AIS was dissolved in 30 mL of ultrapure water under automatic shaking (12 h) before the volume was adjusted to 50 mL. For the acid hydrolysis, 1500 μL of this solution (or its appropriate aqueous dilution) was shaken (1 h) with 5 mL of H_2SO_4 (72% w/w) at ambient temperature and made up to 50 mL. For the photometric series analysis in triplicate against a sample blank, 500 μL of hydrolysate and 3 mL of H_2SO_4 (98% w/w) with tetraborate (0.0125 mol/L) were mixed, heated (100 °C, 10 min), and recooled in an ice−water bath (2 min) before the addition of 50 μL of MHDP reagent (*23*) [sample blank, 50 μL of NaOH (0.5% w/v)]. Exactly 20 min after MHDP addition, the absorbance of the degassed sample was measured at 520 nm with a Cary 100 spectrophotometer (Varian, Mulgrave, VIC, Australia).

The methanol and acetyl contents (g/100 g of AIS) were determined by HPLC (*24*), using the 2695 Separations Module of a Waters HPLC Alliance system (Waters, Milford, MA) with a Waters 2410 refractive index (RI) detector set to 35 °C. As internal standard, lithium lactate was dissolved in alkaline propan-2-ol that was prepared by diluting 250 mL of 0.8 M NaOH with propan-2-ol (≥99.9% v/v) to 500 mL ($ISTD_{Lac}$, 5 mg/mL). After saponification of 50 mg of AIS in 1 mL of alkaline propan-2-ol and 200 μL of $ISTD_{Lac}$ under automatic shaking for 2 h at ambient temperature, the suspension was centrifuged (14000*g*, 15 min). The supernatant was cooled in an ice−water bath for 10 min, then neutralized by adding 500 μL of 1 N H_2SO_4, and continuously cooled for a further 15 min. The supernatant of the subsequent centrifugation (14000*g*, 5 min) was cooled in the ice−water bath (10 min) and filtered through a PTFE membrane filter (0.45 μm) into a vial for injection of 50 μL (20 °C). The column (Aminex HPX-87H, 300 × 7.8 mm, Bio-Rad Laboratories, Hercules, CA) was eluted at 40 °C with 0.01 N H_2SO_4 (0.6 mL/min). Samples were prepared in duplicate with two injections per vial. For calibration, 200 μL of $ISTD_{Lac}$ and 500 μL of 1 N H_2SO_4 were added to 1 mL of a mixed standard solution of methanol (120−3000 μg/mL) and acetic acid (75−1000 μg/mL) in alkaline propan-2-ol. Degrees of methylation (DMe) and acetylation (DAc) were calculated as the molar ratios of methanol (MeOH, M_r = 32.04 g/mol) and acetic acid (HAc, M_r = 60.05 g/mol) to AUA_c, respectively.

The neutral sugars were determined in duplicate by gas chromatography (GC) as their alditol acetates, using *myo*-inositol as internal standard ($ISTD_{MI}$, 2 g/L of ultrapure water). For the acid hydrolysis in a Pyrex test tube, 30 mg of AIS was wetted with 100 μL of propan-2-ol and mixed with 300 μL of H_2SO_4 (72% w/w) by means of a glass stirrer. After 60 min at ambient temperature, 5 mL of N_2-saturated, ultrapure water was added, while the glass stirrer was rinsed. The screw-capped tube was stirred on a vortex mixer, followed by hot-acid hydrolysis (121 °C, 1 h) in an electric heating block (Thermochem CH 20; Liebisch, Brackwede, Germany) and subsequent cooling in an ice−water bath (10−15 min). Upon addition of 600 μL of ammonia (25% w/w), the hydrolysate was transferred to adjust the volume to 10 mL with ultrapure water. Subsequent reduction of the sugars with sodium borohydride and acetylation of the alditols with acetic anhydride in the presence of 1-methylimidazole as catalyst, followed by the extraction of the alditol acetates from the aqueous phase with ethyl acetate produced after addition of absolute ethanol, and final GC analysis were performed as detailed elsewhere (*25*).

The moisture (g/100 g of AIS) was gravimetrically determined in duplicate as mass loss that resulted from drying of 1 g of AIS in a porcelain crucible at 105 ± 2 °C in a hot-air cabinet for 2 h (*17*) and recooling in a desiccator until constant weight. For subsequent quantification of the ash content (g/100 g of AIS), the moisture-free AIS was slowly preincinerated on an electric heating plate, followed by incineration in a muffle furnace (550 °C, 3 h). After recooling in a desiccator (30 min), the sample was wetted with 2−4 drops of ultrapure water and 4−5 drops of H_2O_2 (30% w/w) and dried in the hot-air cabinet (105 ± 2 °C, 1 h) prior to complete incineration (550 °C, 16 h) and recooling (30 min). The mass of white ash was verified after repeated incineration (550 °C, 1 h) and recooling (60 min).

Characterization of Macromolecular Pectin Parameters. Intrinsic viscosities and molecular size distributions were explored in buffers that mimicked the gel systems used for the gelation studies in terms of pH and concentration. The intrinsic viscosity ([η], mL/g) was assessed as an average parameter influenced by all polymers of an AIS sample. On the basis of the single-point relationship (eq 3, Solomon−Ciuta equation), it was computed from the specific viscosities [$\eta_{sp} = (\eta_s - \eta_o)/\eta_o$] of different AIS solutions as a mean of 10 records and verified by the Huggins plot and the Kraemer plot (*26*). The AIS contents (*c*) of five different solutions per sample were adjusted to the η_{sp} range of 0.2−1 (*26*) by appropriate dilution of a sample stock solution (c = 0.2−0.5 g/dL) with the solvent. The dynamic viscosities ($\eta = K\rho t$, mPa s) of solvent (η_o) and AIS solutions (η_s) were calculated from the flow time (t, s), measured at 20 °C for a test volume of 2 mL (2 × 3 runs for t_o and t_s, respectively) by using a Mikro−Ostwald capillary viscosimeter (capillary constant K = 0.01181 mm^2/s^2). The latter was operated in a water bath CT 050 and controlled by a viscosity analyzer AVS 400 (Schott Instruments, Mainz, Germany). The densities (ρ, g/cm^3) of AIS solutions (ρ_s) and solvent (ρ_o) were measured at 20 °C with a density meter DMA 48 (Anton Paar, Graz, Austria). The AIS was dissolved under automatic shaking (16 h) before the volume of the stock solution was adjusted to 100 mL. A 0.28 M buffer (pH 3.0 ± 0.05) of potassium acetate (KAC, 4.57 g/L) and lactic acid [LA (90%), 23.59 g/L] served as solvent.

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln(\eta_s/\eta_o))}}{c} \quad (3)$$

Molecular size distributions were analyzed by high-performance size exclusion chromatography (HP-SEC). By detection with the 2410 RI detector of the Waters Alliance HPLC System at 30 °C, the molecular weights were determined relative to dextran after calibration with 7 DIN-accredited standards of the types 5000−670000 (Sigma-Aldrich Chemie, Munich, Germany). A series of TSK-GEL columns G6000PW$_{XL}$, G3000PW$_{XL}$, and G2500PW$_{XL}$ (300 × 7.8 mm) was used in combination with a TSK guard column PW$_{XL}$ (40 × 6.0 mm) (Tosoh Bioscience Division, Tokyo, Japan). The columns were eluted at 40 °C and a flow rate of 0.6 mL/min with a 0.294 M buffer (pH 3.0) of potassium acetate (KAC, 4.046 g/L) and lactic acid [LA (∼90%), 25.25 g/L] that contained 0.6 mM potassium citrate (KCA) as complexing agent. For the sample solutions, 50 mg of AIS was dissolved in 11.66 mg of a 1.72 mM KCA solution. Subsequently, 5 mL of a 0.704 M buffer, which consisted of KAC (9.708 g/L) and LA, 90% (60.56 g/L), was added, followed by automatic shaking (14 h) before the volume was adjusted to 20 mL with the 0.704 M KAC/LA buffer. After membrane filtration (0.45 μm), 100 μL of the AIS solution (2.5 mg/mL, in 0.294 M KAC/LA buffer containing 1 mM KCA) was injected within 14 h (20 °C) in duplicate. Analysis of the molecular size distributions was performed with the Millenium^{32} Chromatography Manager (Waters, Milford, MA).

Characterization of Technofunctional Pectin Properties. To study the flow properties of standardized AIS solutions, the viscosity of an aqueous AIS solution (2% w/w) was measured at 20 °C over a shear rate ($\dot{\gamma}$) range of 1−100 s^{-1} by using a Bohlin CVO 120 HR rheometer (Malvern Instruments, Herrenberg, Germany) with a modified (*27*) double-gap (DG 40/50) device. For sample preparation, 50.00 g of ultrapure water was boiled on a heating plate and 1 g of AIS was sprinkled into the boiling water under continuous magnetic stirring. After 25 min of stirring on the hot plate, the mass of the solution was adjusted to 50.00 g, while rinsing the stirring bar with ultrapure water. The hot sample solution was immediately filled into the device. To avoid evaporation, the free sample surface was covered with a few drops of low-viscous liquid paraffin (VWR, Darmstadt, Germany). Additionally, a covering plate with a humidified inner surface was used. After this filling procedure (5 min) and a subsequent equilibration period (120 min) without mechanical operation, the flow curve was recorded in the shear rate ramp mode based on intervals and integration times of 30 s each.

For pectin−sucrose gels (TSS = 65 ± 0.5 °Brix, pH 3.0 ± 0.04) with AIS doses (c_p) of 0.15−1 g/100 g in a KAC/LA buffer (0.25 mol/kg of gel), the setting temperatures were assayed by dynamic rheometric analyses (*7*) in duplicate, using the Bohlin CVO 120 HR rheometer with a Searle cylinder device (C 25) after partial adaptation of parameters. The gels were prepared as before (*7*). In brief, the AIS, premixed with a small portion of sucrose, was carefully dispersed at ambient temperature in the diluted buffer that resulted from 68 g of distilled water and 17 g of a KAC/LA buffer stock solution [KAC, 40.48 g/L; LA (90%), 188.05 g/L]. When the AIS was completely dissolved under heating in the presence of 1−2 drops of defoaming emulsion, the remaining part of the sugar was stepwise added to the boiling mixture. TSS was adjusted by cooking to a precalculated net weight of 170 g under stirring. Subsequently, the sample was poured into the preheated C 25 device (90 °C). To avoid evaporation and superficial incrustation, the free sample surface was covered with hot low-viscous liquid paraffin. Gel formation was monitored by measuring the storage (G') and loss (G'') moduli as well as the phase angle [δ = arctan (G''/G')] at fixed frequency (f = 1 Hz) and strain amplitude (γ = 0.015) as a function of time (t, s) during cooling from 90 to 20 °C at a constant rate ($\Delta T = -1.028 \pm 0.006$ K/min). In the sol−gel transition range, the $\delta-t$ curves were iteratively approximated by a modified logistic four-parameter model as detailed previously (*7*), using the NLIN procedure (Marquardt method) of the Statistical Analysis System (SAS) 9.1 (SAS Institute, Cary, NC). Unlike the previous study (*7*), setting times ($t_{\delta=45°}$, s) and temperatures ($T_{\delta=45°}$, °C) were not deduced from the previously defined pseudo gel points [δ(1 Hz) = 75°], but from the crossover-points of the moduli [δ(1 Hz) = 45°], despite the larger influence of the frequency on the latter, because the former were partly affected by a worse signal-to-noise ratio due to the very low viscosity of some samples in the sol state. Further curing at 20 °C and the viscoelastic properties of the gels (*7*) were not considered in this study, because slippage partly occurred during curing of some samples. Power law approximation of the dependence of $T_{\delta=45°}$ on the biopolymer concentration (*7*) was performed with Microsoft Excel 2003.

The gel properties were characterized by the breaking strengths of pectin−sucrose gels (TSS = 65 °Brix, pH 3.0 ± 0.05) with AIS doses of 0.2−0.35 g/100 g in a KAC/LA buffer (0.28 mol/kg of gel) on the basis of an empirical tension test established for the standardization of pectins and the comparative evaluation of pectin sources (*28*). By using the Herbstreith−Pectinometer type Mark III (Herbstreith & Fox), the breaking strength (BS) was recorded in device-specific units (HPE). The AIS dose required for a standardized gel (BS = 530 HPE) was calculated by interpolation as the breaking capacity of the AIS (BC$_{530HPE}$, g/100 g of gel). By dividing the sugar content of this gel (TSS) by BC$_{530HPE}$, the gelling capacity of the AIS (SBC$_{530HPE}$, g/g of AIS) was obtained as the sugar-binding capacity, that is, the amount of sugar bound by this AIS dose in a gel of 530 HPE. Multiplication of SBC$_{530HPE}$ with the AIS content of the DRM yielded the corresponding gelling capacity of the DRM extracted (SBC$_{DRM}$, g/100 g of DRM). With each AIS dose, a gel was prepared in duplicate by cooking the AIS-containing mixture on the basis of 216.0 g of sugar and 147.0 g of a 0.65 M KAC/LA buffer [KAC, 10.5 g/L; LA (90%), 54.25 g/L] to a final net weight of 338 g and subsequent hot-filling of 100 ± 1 g into each of three test cups (*28*). After 2 h of gel curing in a water bath (20 °C), BS was measured for each test cup. In terms of the procedure for dissolving the AIS and cooking until a final net weight, the method corresponded to that reported above for the oscillatory gelation analysis. TSS and pH of all gel samples were experimentally verified. For their

Table 1. Yields of Alcohol-Insoluble Substance (AIS) Extracted from the Freeze-Dried Peels of Mango Fruits (MP) 'Kiew Sawoei' (KS), 'Nam Dokmai #4' (NDM), 'Kaew Chuk' (KAc), and 'Kaew Khiew' (KAk) at Different Postharvest Ripeness Stages (RS)

		MP source							
		KS	NDM		KAc			KAk	
RS:[a]		I	II	III	I	II	III	II	III
RPI$_{WB}$:		4.34	1.48	−0.23	6.43	2.95	0.55	2.07	0.64
AIS[b] [g/100 g of MP]	C[c]	32.7 ± 0.5	16.7 ± 0.1	14.3 ± 0.3	41.7 ± 0.5	22.2 ± 0.5	16.8 ± 0.2	15.7 ± 0.2	13.8 ± 0.2
	A[c]	24.8 ± 0.9	17.0 ± 0.2	14.7 ± 0.3	33.5 ± 0.9	24.1 ± 0.5	16.8 ± 0.4	13.5 ± 0.2	13.1 ± 0.2
starch[d] [g/100 g of AIS]	C	52.6 ± 0.2	14.5 ± 1.3	5.1 ± 0.4	50.0 ± 0.3	21.2 ± 0.6	1.3 ± 0.1	18.4 ± 0.4	4.8 ± 0.2
	A	51.9 ± 0.4	15.1 ± 0.0	3.9 ± 0.5	47.1 ± 0.0	21.9 ± 0.5	1.2 ± 0.0	16.0 ± 1.4	4.5 ± 0.4
AIS$_{S\text{-}corr}$[e] [g/100 g of MP]	C	15.5 ± 0.3	14.3 ± 0.2	13.6 ± 0.3	20.8 ± 0.3	17.5 ± 0.4	16.5 ± 0.2	12.9 ± 0.2	13.1 ± 0.2
	A	12.0 ± 0.4	14.4 ± 0.2	14.1 ± 0.3	17.7 ± 0.5	18.8 ± 0.4	16.5 ± 0.4	11.4 ± 0.2	12.5 ± 0.2

[a] Ripeness stage (RS) number, corresponding to postharvest ripeness index (RPI$_{WB}$) classes of 4.3−6.5 (I), 1.4−3.0 (II), and −0.7 < 0 < 0.7 (III). [b] Total yield of extractable polymers as AIS in g/100 g of dried fruit material (DRM, here MP). [c] Extraction methods (EM A, pH 2.0; EM C, pH 1.5). [d] Starch content of the AIS according to enzymatic quantification (reference sample AP1, 0.16 ± 0.02 g/100 g of pectin). [e] Net pectin yield (AIS$_{S\text{-}corr}$) as starch-adjusted AIS in g/100 g of DRM (MP).

Table 2. Composition of the Alcohol-Insoluble Substance (AIS) Extracted from the Freeze-Dried Peels of Mango Fruits (MP) 'Kiew Sawoei' (KS), 'Nam Dokmai #4' (NDM), 'Kaew Chuk' (KAc), and 'Kaew Khiew' (KAk) at Different Postharvest Ripeness Stages (RS) Relative to That of a Commercial Pectin from Apple Pomace (AP1): Mass Balance[a]

	AP1		KS (MP)	NDM (MP)		KAc (MP)			KAk (MP)	
RS:[b]	na		I	II	III	I	II	III	II	III
RPI_{WB}:	na		4.34	1.48	−0.23	6.43	2.95	0.55	2.07	0.64
moisture	6.7 ± 0.3	C[c]	5.5 ± 0.2	na	5.6 ± 0.1	4.7 ± 0.0	5.3 ± 0.0	5.1 ± 0.1	5.0 ± 0.0	4.3 ± 0.1
		A[c]	4.3 ± 0.0	5.3 ± 0.0	5.1 ± 0.0	5.0 ± 0.1	5.2 ± 0.1	5.0 ± 0.1	4.9 ± 0.1	4.6 ± 0.0
ash	3.7 ± 0.1	C	3.9 ± 0.0	na	11.0 ± 0.0	3.8 ± 0.0	6.3 ± 0.2	8.9 ± 0.0	11.9 ± 0.0	16.2 ± 0.2
		A	5.6 ± 0.1	9.1 ± 0.0	12.3 ± 0.0	4.5 ± 0.0	5.8 ± 0.0	9.9 ± 0.0	13.7 ± 0.2	17.0 ± 0.3
ANS[d]	16.9 ± 0.1	C	72.9 ± 0.2	50.3 ± 0.0	37.0 ± 0.1	76.4 ± 0.1	51.2 ± 0.1	27.8 ± 0.2	50.7 ± 0.2	35.9 ± 0.1
		A	74.9 ± 0.1	51.6 ± 0.1	43.1 ± 0.1	75.8 ± 0.0	54.1 ± 0.0	38.2 ± 0.1	54.8 ± 0.2	41.0 ± 0.1
AUA_c	84.9 ± 2.2	C	16.5 ± 0.1	31.8 ± 1.1	37.8 ± 0.9	20.2 ± 0.2	36.0 ± 0.8	50.2 ± 1.7	31.0 ± 1.1	32.6 ± 0.6
		A	12.8 ± 0.2	23.4 ± 0.7	28.8 ± 0.6	16.8 ± 0.1	35.4 ± 1.3	35.3 ± 1.2	27.4 ± 0.7	29.5 ± 1.5
MeOH[e]	12.4 ± 0.2	C	2.50 ± 0.07	3.74 ± 0.04	4.77 ± 0.07	2.96 ± 0.06	5.04 ± 0.09	6.89 ± 0.14	4.08 ± 0.05	4.60 ± 0.08
		A	2.40 ± 0.08	3.57 ± 0.05	4.23 ± 0.02	2.77 ± 0.01	4.16 ± 0.05	6.15 ± 0.08	3.31 ± 0.08	3.92 ± 0.02
Ac[e]	1.76	C	0.30	0.41	0.36	0.38	0.59	0.46	0.41	0.40
		A	0.28	0.46	0.38	0.35	0.60	0.48	0.36	0.39
total (1)	126.3	C	101.6	86.2[f]	96.5	108.3	104.4	99.4	103.0	93.9
		A	100.3	93.3	93.9	105.1	105.3	95.0	104.4	96.4
AUA_{titr}	64.5 ± 0.1	C	11.6 ± 0.1	26.4 ± 1.3	30.4 ± 0.5	20.2 ± 1.0	29.7 ± 0.9	44.2 ± 0.1	26.5 ± 0.1	34.7 ± 0.1
		A	14.5 ± 0.2	23.4 ± 0.2	27.9 ± 0.5	15.4 ± 0.6	26.4 ± 0.1	38.1 ± 0.5	23.0 ± 0.6	27.3 ± 0.1
$MeOH_{titr}$	8.17 ± 0.02	C	1.23 ± 0.01	3.13 ± 0.20	3.68 ± 0.10	2.63 ± 0.16	3.60 ± 0.15	5.58 ± 0.11	3.40 ± 0.01	4.38 ± 0.02
		A	1.89 ± 0.06	2.99 ± 0.03	3.66 ± 0.11	1.96 ± 0.09	3.51 ± 0.02	5.20 ± 0.08	3.12 ± 0.12	3.63 ± 0.01
total (2)	99.9	C	95.1	79.8[f]	87.5	107.6	96.0	91.6	97.4	95.4
		A	101.2	92.3	92.1	102.6	95.1	96.4	99.5	93.5

[a] Mean content ± standard error (SE) in g/100 g of AIS (Ac, SE ≤ 0.01 g/100 g). na, not analyzed. [b] Ripeness stage (RS) number, corresponding to postharvest ripeness index (RPI_{WB}) classes of 4.3−6.5 (I), 1.4−3.0 (II), and −0.7 < 0 < 0.7 (III). [c] Extraction methods (EM A, pH 2.0; EM C, pH 1.5). [d] Including the glucose content of starch (cf. **Table 1** and ribose (AIS from MP, not detectable−0.187 g/100 g; AP1, 0.083 ± 0.005 g/100 g). [e] Quantified by HPLC. [f] Without ash and moisture content. na, not analyzed; ANS, total content of neutral sugars, calculated as their anhydro forms; AUA_c, colorimetric anhydrogalacturonic acid content; MeOH, methoxyl content (as methanol); Ac, acetyl content (as acetic acid); AUA_{titr}, titrimetric anhydrogalacturonic acid content; $MeOH_{titr}$, titrimetric methyl ester content; total (1), mass balance based on the contents of moisture, ash, ANS, AUA_c, MeOH, and Ac; total (2), mass balance based on the contents of moisture, ash, ANS, AUA_{titr}, and $MeOH_{titr}$.

normalization to constant AUA levels, BC_{530HPE} and SBC_{530HPE} were related to the AUA_{titr} content of the AIS and expressed as $BC_{530HPE}(AUA_{titr})$ [in g of AUA/100 g of gel] and $SBC_{530HPE}(AUA_{titr})$ [in g of sugar/g of AUA], respectively.

RESULTS AND DISCUSSION

Availability of Peels from Cultivars Studied. With 1.7 million tonnes of mango produced in 2004, Thailand is one of the leading producers of this fruit crop (*29*). The mountainous northern region contributes ∼21% of the total Thai mango production (*30*). Peel waste mainly arises from cv. 'Kaew' (*31*), which is prevalent in local processing, including the phenomenologically distinguished variants under study [KAc (*31*); KAk (*32*)]. High-quality niche products are made from cv. 'Nam Dokmai', for example, the variant studied (NDM) (*32*). Besides, NDM is the prevailing dessert fruit eaten fully ripe, whereas fresh 'Kaew' fruits may be consumed mature-green and ripe and 'Kiew Sawoei' (KS) fruit (*32*) is preferred mature-green and half-ripe.

Ripeness Stages of Fruits Used for Pectin Extraction. After harvest, the mature-green 'Kaew' fruits of both crop years (KAc, KAk) showed the same mesocarp firmness and hue (**Figure 1A**). Despite uniform TSS (9.1−11.0 °Brix) and sugar/acid ratios (TSS/TA = 5.1−7.7), they were 1.8 times firmer than the NDM fruits. Consistent with their preferred consumption ripeness, the KS fruits already had a TSS/TA of 32 at 11.1 °Brix and medium firmness. Boosted by CaC_2 according to widespread local practice (*22*), softening of NDM and KAc fruits mainly occurred within the first 2−3 days, while TSS rose to 18−20 °Brix and TSS/TA to ∼20, with the mesocarp hue changing from greenish yellow ($H° = ∼100°$) to bright yellow ($H° = 92−95°$) (**Figure 1A**). Subsequently, the mesocarp turned orange-yellow ($H° < 90°$), while acid degradation markedly raised TSS/TA to 50−60 at nearly constant TSS and F_{WB}. Without CaC_2 application, the KAk fruits softened more slowly, mainly during the three days after an initial lag phase. TSS/TA at full ripeness was thus much higher. KAk and KAc mesocarp, though, displayed the same color change relative to rising TSS/TA, substantiating the unbalanced acceleration of softening induced by CaC_2 at the expense of fruit quality (*22*). The inadvisable use of CaC_2 was thus limited to the first year. As indicated by arrows in **Figure 1A**, pectins were extracted from mature-green fruits [ripeness stage (RS) I], after major softening (RS II), and at full ripeness (RS III). The ripeness index (RPI_{WB}) (eq 1) linearly decreased postharvest from ∼4.3−6.4 at RS I to <0.7 at RS III (**Figure 1B**), reflecting the initial lag phase and slower softening of KAk. Despite the differences in firmness and TSS/TA among the fruit batches, the stage after major softening was empirically defined by a RPI_{WB} class of 1.4−3.0 (RS II) and full ripeness by a RPI_{WB} class of $-0.7 < 0 < 0.7$ (RS III).

Yields of the Pectins Extractable from Mango Peels. The crude pectin yields (AIS) from peels of mature-green fruits (RS I) were notably high (25−42 g/100 g of DRM; KS and KAc in **Table 1**; NDM peel not analyzed at RS I). After major fruit

Table 3. Molar Sugar Composition[a] of the Starch-Free Alcohol-Insoluble Substance ($AIS_{S\text{-}corr}$) Recovered from the Freeze-Dried Peels of Mango Fruits (MP) 'Kiew Sawoei' (KS), 'Nam Dokmai #4' (NDM), 'Kaew Chuk' (KAc), and 'Kaew Khiew' (KAk) at Different Postharvest Ripeness Stages (RS) Relative to That of a Commercial Pectin from Apple Pomace (AP1)

	AP1		KS (MP)	NDM (MP)		KAc (MP)			KAk (MP)	
RS:[b]	na		I	II	III	I	II	III	II	III
RPI_{WB}:	na		4.34	1.48	−0.23	6.43	2.95	0.55	2.07	0.64
AUA_c	483 ± 13	C[c]	198 ± 5	211 ± 8	226 ± 8	229 ± 5	260 ± 10	289 ± 10	215 ± 9	194 ± 5
		A[c]	151 ± 8	157 ± 5	170 ± 5	180 ± 7	258 ± 12	203 ± 10	185 ± 7	175 ± 9
AUA_{titr}	367 ± 0.3	C	139 ± 3	175 ± 9	182 ± 6	229 ± 12	214 ± 10	255 ± 3	184 ± 3	207 ± 4
		A	171 ± 9	157 ± 3	165 ± 5	165 ± 9	192 ± 6	219 ± 8	155 ± 6	162 ± 3
Glc[d]	9.4 ± 0.1	C	134 ± 5	52 ± 10	22 ± 3	160 ± 5	67 ± 6	13 ± 1	65 ± 3	28 ± 1
		A	127 ± 8	38 ± 1	24 ± 3	135 ± 5	70 ± 5	18 ± 1	71 ± 11	27 ± 3
Gal	46.5 ± 0.6	C	107 ± 3	183 ± 3	162 ± 5	138 ± 3	138 ± 4	127 ± 2	155 ± 3	146 ± 3
		A	108 ± 5	169 ± 3	161 ± 4	137 ± 5	126 ± 4	138 ± 5	154 ± 4	148 ± 3
Ara	27.2 ± 0.6	C	13 ± 0	14 ± 0	17 ± 1	18 ± 0	20 ± 1	17 ± 0	16 ± 0	19 ± 0
		A	57 ± 3	56 ± 1	67 ± 2	60 ± 2	56 ± 2	77 ± 3	60 ± 2	61 ± 1
Rha	15.4 ± 0.0	C	6.5 ± 0.4	8.0 ± 0.2	6.8 ± 0.4	7.2 ± 0.2	9.3 ± 0.3	8.3 ± 0.1	7.5 ± 0.2	8.6 ± 0.2
		A	5.6 ± 0.3	8.2 ± 0.2	8.9 ± 0.2	6.4 ± 0.3	7.9 ± 0.2	9.0 ± 0.3	6.9 ± 0.2	7.7 ± 0.3
Man	0.9 ± 0.0	C	3.4 ± 0.5	2.2 ± 0.1	2.2 ± 0.1	2.5 ± 0.1	2.7 ± 0.3	1.9 ± 0.0	2.3 ± 0.0	2.2 ± 0.0
		A	3.2 ± 0.2	2.1 ± 0.0	2.0 ± 0.1	2.9 ± 0.1	2.6 ± 0.1	2.4 ± 0.1	2.4 ± 0.1	2.3 ± 0.0
Xyl	11.2 ± 0.5	C	2.9 ± 0.1	1.7 ± 0.0	1.5 ± 0.0	1.9 ± 0.1	2.0 ± 0.1	1.7 ± 0.0	2.1 ± 0.1	1.6 ± 0.1
		A	2.9 ± 0.2	1.8 ± 0.0	1.3 ± 0.0	2.7 ± 0.1	2.7 ± 0.1	1.7 ± 0.1	2.0 ± 0.1	1.6 ± 0.1
Fuc	0.9 ± 0.0	C	0.5 ± 0.1	0.4 ± 0.0	0.3 ± 0.0	0.4 ± 0.0	0.6 ± 0.1	0.5 ± 0.0	0.4 ± 0.0	0.4 ± 0.0
		A	0.6 ± 0.0	0.6 ± 0.0	0.5 ± 0.0	0.7 ± 0.0	0.8 ± 0.0	0.7 ± 0.0	0.6 ± 0.0	0.5 ± 0.0

[a] Mean ± standard error in mmol/100 g $AIS_{S\text{-}corr}$. na, not analyzed. [b] Ripeness stage (RS) number, corresponding to postharvest ripeness index (RPI_{WB}) classes of 4.3−6.5 (I), 1.4−3.0 (II), and −0.7 < 0 < 0.7 (III). [c] Extraction methods (EM A, pH 2.0; EM C, pH 1.5). [d] Without glucose included in starch. AUA_c, galacturonic acid (colorimetric); AUA_{titr}, galacturonic acid (titrimetric); Glc, glucose; Gal, galactose; Ara, arabinose; Rha, rhamnose; Man, mannose; Xyl, xylose; Fuc, fucose.

softening (RS II), they dropped to 14−24 g/100 g (KAk, NDM, KAc), followed by a further decrease to 13−17 g/100 g at RS III. However, this decline mainly resulted from starch degradation. Coextracted starch constituted 47−53 g/100 g in AIS of peels at RS I and only 15−22 g/100 g at RS II (**Table 1**). Regardless of CaC_2 application, starch degraded to residual levels of 1.2−5.1 g/100 g in AIS of peels at RS III. The starch-adjusted net pectin yields ($AIS_{S\text{-}corr}$) lay in the ranges of 11.4−13.1 (KAk at RS II−III), 13.6−14.4 (NDM at RS II−III), 12.0−15.5 (KS at RS I), and 16.5−20.8 g/100 g of DRM (KAc at RS I−III), irrespective of ripeness stage and extraction mode (**Table 1**). Despite similar firmness of NDM and KAc mesocarp at RS II and III (**Figure 1A**), $AIS_{S\text{-}corr}$ of KAc peels was much higher. Conversely, the peels of the softest fruits (NDM at RS II and III) were comparable to those of the clearly firmer KAk fruits as to $AIS_{S\text{-}corr}$. Although coextraction of starch was usually not considered in previous studies apart from qualitative starch detection (*13*), $AIS_{S\text{-}corr}$ complied with the pectin yields from mango peels of cultivars from Africa (*12, 13, 16*), Australia (*13*), India and Pakistan (*10, 11, 15*), and South America (*13, 14*). Yields reported for 'Kaew' and 'Nam Dokmai' peels (*13*) were confirmed by the faintly higher $AIS_{S\text{-}corr}$ of KAc and NDM.

The extracting agent hardly influenced the net yield of peel pectin and coextraction of starch. The more acidic agent (method C at pH 1.5) was clearly more efficacious in pectin solubilization from peels of mature-green fruits (KS and KAc at RS I) (**Table 1**), consistent with other studies (*10*). However, respective differences in $AIS_{S\text{-}corr}$ were minor to insignificant at RS II and III. The less acidic agent (method A at pH 2.0) even seemed to slightly favor the recovery from the KAc peels at RS II. Thus, opposing observations (*11*) were also partly confirmed. Unlike the crude pectin yield, the impact of fruit maturity on $AIS_{S\text{-}corr}$ was marginal (**Table 1**). As to the net pectin yields of hot-acid extraction (11−21%), mango peels thus came closer to apple pomace than to citrus peels (*6*). Higher yields of up to 24.5% were found only for peels blanched in ethanol prior to drying (*16*), but lower yields of 6.4% (*9*) and 10−15% (*12*) also occurred, despite the overall beneficial effect of an ethanolic peel pretreatment (*9*), which improves purity by the removal of ethanol-soluble components, including sugars, and inactivates enzymes without leaching soluble pectin fractions.

Purity of Mango Peel Pectins. Total neutral sugars (ANS), ash, moisture, and the titrimetrically quantified anhydrogalacturonic acid (AUA_{titr}) and methoxyl ester ($MeOH_{titr}$) contents of the commercial unstandardized apple pectin (AP1) added up to a complete mass balance [total (2), **Table 2**]. Indeed, the corresponding mass balance [total (1)] of AP1 indicated overestimation of both AUA_c by the colorimetric MHDP assay and methanol (MeOH) by HPLC analysis. However, comparable results were obtained for the AIS of mango peels, as shown by the average molar ratios of 1.10 for AUA_c/AUA_{titr} and 1.16 for $MeOH/MeOH_{titr}$. Apart from the components studied, acid-extracted mango peel pectins may contain 1.1−3.3% protein (*16*). With levels <6.7%, the moisture contents of AP1 and the AIS of mango peels were far below the tolerated maximum (*17*). The ash contents of AIS from peels at RS I were comparable to that of AP1, but they increased with fruit ripeness within a total range of 3.8−17.0 g/100 g (**Table 2**). Due to coextracted starch (**Table 1**), the total neutral sugars (ANS) accounted for up to 76% in AIS from peels at RS I (**Table 2**). However, AUA_c was even low (35−50 g/100 g) compared to ANS (38−28 g/100 g) when starch was minimal (1.3 g/100 g, KAc at RS III). Purer pectins (AUA_c = 69−71 g/100 g, ANS = 20−16 g/100 g) were gained by hot-acid extraction from the alcohol-insoluble residue

Table 4. Structural Indices[a] of the Alcohol-Insoluble Substance (AIS) Extracted from the Freeze-Dried Peels of Mango Fruits (MP) 'Kiew Sawoei' (KS), 'Nam Dokmai #4' (NDM), 'Kaew Chuk' (KAc), and 'Kaew Khiew' (KAk) at Different Postharvest Ripeness Stages (RS) Relative to That of a Commercial Pectin from Apple Pomace (AP1): Esterification, Side-Chain, and Backbone Indices

	AP1		KS (MP)	NDM (MP)		KAc (MP)			KAk (MP)	
RS:[b]	na		I	II	III	I	II	III	II	III
RPI_{WB}:	na		4.34	1.48	−0.23	6.43	2.95	0.55	2.07	0.64
$GalUA_{titr}$ [g/100 g of AIS_p]	81.2 ± 0.1	C[c]	15.7 ± 0.1	37.2 ± 1.8	44.7 ± 0.7	27.0 ± 1.3	40.5 ± 1.3	60.6 ± 0.2	42.5 ± 0.1	49.7 ± 0.2
		A[c]	19.4 ± 0.2	35.0 ± 0.4	44.7 ± 0.8	20.4 ± 0.7	36.8 ± 0.2	57.4 ± 0.7	34.4 ± 0.9	42.3 ± 0.1
esterification indices										
DE [%]	72.0 ± 0.2	C	60.3 ± 0.2	67.5 ± 1.1	68.9 ± 0.9	74.0 ± 0.9	68.8 ± 0.7	71.7 ± 1.2	73.0 ± 0.4	71.8 ± 0.1
		A	74.1 ± 1.5	72.6 ± 0.1	74.5 ± 0.9	72.5 ± 0.6	75.4 ± 0.0	77.5 ± 0.2	77.2 ± 0.9	75.7 ± 0.4
DMe [%]	80.4 ± 2.3	C	83.1 ± 2.5	64.7 ± 2.3	69.3 ± 2.0	80.6 ± 1.8	76.9 ± 2.1	75.5 ± 3.0	72.4 ± 2.7	77.8 ± 2.0
		A	102.9 ± 3.4	83.8 ± 2.9	80.9 ± 1.7	90.6 ± 0.4	64.6 ± 2.5	95.9 ± 3.5	66.4 ± 2.3	73.1 ± 3.6
DAc [%]	6.1 ± 0.2	C	5.3 ± 0.0	3.8 ± 0.1	2.8 ± 0.1	5.5 ± 0.1	4.8 ± 0.1	2.7 ± 0.1	3.9 ± 0.1	3.6 ± 0.1
		A	6.3 ± 0.1	5.7 ± 0.2	3.9 ± 0.1	6.2 ± 0.0	5.0 ± 0.2	4.0 ± 0.2	3.9 ± 0.1	3.9 ± 0.2
side-chain indices										
Ara/Rha [mol/mol]	1.8 ± 0.0	C	2.0 ± 0.1	1.8 ± 0.0	2.4 ± 0.1	2.5 ± 0.1	2.2 ± 0.0	2.1 ± 0.0	2.1 ± 0.0	2.2 ± 0.0
		A	10.2 ± 0.3	6.8 ± 0.1	7.5 ± 0.0	9.3 ± 0.1	7.1 ± 0.0	8.5 ± 0.1	8.8 ± 0.0	7.9 ± 0.2
Gal/Rha [mol/mol]	3.0 ± 0.0	C	16.4 ± 0.9	23.0 ± 0.2	23.6 ± 1.2	19.2 ± 0.5	14.9 ± 0.2	15.4 ± 0.1	20.8 ± 0.3	17.0 ± 0.1
		A	19.3 ± 0.5	20.6 ± 0.3	18.1 ± 0.0	21.4 ± 0.2	16.0 ± 0.1	15.2 ± 0.1	22.4 ± 0.0	19.2 ± 0.6
Ara/Gal [mol/100 mol]	58.4 ± 1.5	C	12.3 ± 0.2	7.7 ± 0.0	10.3 ± 0.0	12.8 ± 0.1	14.5 ± 0.1	13.5 ± 0.1	10.2 ± 0.1	12.9 ± 0.1
		A	52.9 ± 0.4	33.2 ± 0.1	41.4 ± 0.1	43.7 ± 0.1	44.6 ± 0.1	56.1 ± 0.2	39.2 ± 0.1	41.1 ± 0.1
backbone indices (of $AIS_{S\text{-}corr}$)										
HG_{max}[d] [mmol/100 g]	468 ± 13	C	191 ± 5	203 ± 8	220 ± 8	222 ± 5	250 ± 10	281 ± 10	208 ± 9	186 ± 5
		A	145 ± 8	148 ± 5	161 ± 5	174 ± 7	250 ± 12	194 ± 10	178 ± 7	168 ± 9
$RG\text{-}I_{max}$[e] [mmol/100 g]	30.7 ± 0.1	C	13.1 ± 0.8	15.9 ± 0.3	13.7 ± 0.8	14.4 ± 0.4	18.5 ± 0.7	16.6 ± 0.2	14.9 ± 0.4	17.2 ± 0.3
		A	11.2 ± 0.6	16.4 ± 0.3	17.9 ± 0.4	12.8 ± 0.5	15.8 ± 0.5	18.1 ± 0.6	13.7 ± 0.3	15.4 ± 0.5
BBP_{HG}[f] [%]	93.8	C	93.6	92.7	94.1	93.9	93.1	94.4	93.3	91.5
		A	92.8	90.0	90.0	93.1	94.1	91.5	92.8	91.6
$BBP_{RG\text{-}I}$[g] [%]	6.2	C	6.4	7.3	5.9	6.1	6.9	5.6	6.7	8.5
		A	7.2	10.0	10.0	6.9	5.9	8.5	7.2	8.4

[a] Mean ± standard error. na, not analyzed. [b] Ripeness stage (RS) number, corresponding to postharvest ripeness index (RPI_{WB}) classes of 4.3−6.5 (I), 1.4−3.0 (II), and −0.7 < 0 < 0.7 (III). [c] Extraction methods (EM A, pH 2.0; EM C, pH 1.5). [d] Estimated maximum units of the total homogalacturonan backbone (HG) calculated from the AUA_c and Rha contents in mmol/100 g of $AIS_{S\text{-}corr}$ ($HG_{max} = AUA_c - Rha$). [e] Estimated maximum units of the total rhamnogalacturonan-I backbone (RG-I) calculated from the Rha content in mmol/100 g of $AIS_{S\text{-}corr}$ ($RG\text{-}I_{max} = 2 \cdot Rha$). [f] Maximum homogalacturonan (HG) percentage of the pectin backbone [$BBP_{HG} = 100(AUA_c - Rha)/(AUA_c + Rha)$]. [g] Maximum rhamnogalacturonan-I (RG-I) percentage of the pectin backbone [$BBP_{RG\text{-}I} = 100(2 \cdot Rha)/(AUA_c + Rha)$]. $GalUA_{titr}$, titrimetric galacturonic acid content (g/100 g of AIS_p, i.e., of non-destarched AIS after acidic purification before titration); DE, degree of esterification; DMe, degree of methylation; DAc, degree of acetylation; Ara, arabinose (mmol/100 g of AIS); Rha, rhamnose (mmol/100 g of AIS); Gal, galactose (mmol/100 g of AIS).

of a hot-ethanolic peel pretreatment (*12*). In **Table 3**, the molar sugar composition is compiled on a starch-free base ($AIS_{S\text{-}corr}$). Without artificial starch degradation (*1*), the galacturonic acid contents ($GalUA_{titr}$; **Table 4**), as per JEFCA specification (*17*) (M_r = 194.1 g/mol) on an ash- and moisture-free basis (AIS_p) after AIS purification in acidic alcohol, were below the legal minimum (65 g/100 g of AIS_p). Even in almost starch-free AIS, $GalUA_{titr}$ was limited to 57−61 g/100 g of AIS_p.

Composition of Mango Peel Pectins. The molar AUA_c contents on a starch-free basis (**Table 3**) corresponded to mass percentages of 34−51 and 27−45 g/100 g of $AIS_{S\text{-}corr}$ for the mango peel pectins gained at pH 1.5 and 2.0, respectively. The increased acidity (method C) clearly facilitated pectin isolation due to hydrolysis of the highly acid-labile arabinofuranosyl linkages. Arabinose (Ara) in AIS extracted at pH 2.0 (7.4−10.2 g/100 g of $AIS_{S\text{-}corr}$) was 2.8−4.5 times higher than in samples obtained at pH 1.5. By contrast, the contents of the other neutral sugars were hardly affected by the extracting agent (**Table 3**), including the molar ratio of AUA_c to rhamnose (Rha) (AUA_c/Rha = 23−35 at pH 1.5 and 19−33 at pH 2.0). The neutral sugars detected (**Table 3**) may imply a simplifying backbone model that consists of HG and RG-I, ignoring any occurrence of RG-II, although minor RG-II fractions might even be found in acid-extracted pectins (*4*). Assuming that all Rha residues detected were part of RG-I and the galacturonic acid units (AUA_c) are allotted either to HG or RG-I, the amounts of those backbone elements were estimated as HG_{max} and $RG\text{-}I_{max}$ in terms of the maximal number of their constituting residues (**Table 4**). Accordingly, the backbones consisted of 5.6−10% $RG\text{-}I_{max}$ and 90−94.4% HG_{max} ($BBP_{RG\text{-}I}$ and BBP_{HG} in **Table 4**). Although AP1 contained more AUA and Rha, AP1 and the mango peel pectins were equal in $BBP_{RG\text{-}I}$ and BBP_{HG}, but the obvious overestimation of AUA_c increased the molar AUA_c/Rha ratio of AP1 to 32. For the pectin samples studied and further mango peel pectins (*16*), this ratio was in the range reported for apple and citrus pectins (*3, 7*). However, pectins extracted by hot acid from the alcohol-insoluble residue of mango peels revealed much higher ratios (64−94) (*12*).

The low AUA_c contents of $AIS_{S\text{-}corr}$ were entailed by notably high galactose (Gal) levels equating to 44−108% of AUA_c (**Table 3**). Irrespective of fruit ripeness and extracting agent, the mass percentages of Gal ranged from 17−18 through 20−22 and 24−25 to 26−30 g/100 g of $AIS_{S\text{-}corr}$ for peel pectins of KS, KAc, KAk, and NDM, respectively. If all Gal residues detected were ascribed to galactans with one chain branching off from each Rha unit, long and/or highly ramified galactan side chains of 15−24 residues on the average would occur according to the molar Gal/Rha ratios (**Table 4**). From the

Table 5. Molecular Properties of the Alcohol-Insoluble Substance (AIS) Extracted from the Freeze-Dried Peels of Mango Fruits (MP) 'Kiew Sawoei' (KS), 'Nam Dokmai #4' (NDM), 'Kaew Chuk' (KAc), and 'Kaew Khiew' (KAk) at Different Postharvest Ripeness Stages (RS) Relative to Those of a Commercial Pectin from Apple Pomace (AP1)

	AP1		KS (MP)	NDM (MP)		KAc (MP)			KAk (MP)	
RS:[a]	na		I	II	III	I	II	III	II	III
RPI_{WB}:	na		4.34	1.48	−0.23	6.43	2.95	0.55	2.07	0.64
$[\eta]$ [mL/g]	537 ± 3[b]	C[c]	na	169 ± 1	184 ± 1	na	234 ± 2	284 ± 2	202 ± 2	234 ± 2
		A[c]	na	186 ± 2	204 ± 2	na	232 ± 2	266 ± 2	212 ± 2	247 ± 3
overall molecular weight distribution (total integration range *R*)[d]										
$M_{w,R}$ [× 10^3]	1177	C	na	335	375	301	494	573	438	503
		A	na	553	468	951	809	614	608	563
$M_{n,R}$ [× 10^3]	33.1	C	na	9.87	9.67	10.8	11.6	12.7	8.30	7.70
		A	na	13.0	10.7	17.7	14.8	12.1	9.41	8.06
D_R	35.7	C	na	34.0	38.8	27.9	42.6	45.1	52.8	65.3
		A	na	42.6	43.9	53.6	54.8	50.7	64.6	69.9
molecular weight distribution of the high molecular weight domain (zone 1)[d]										
$M_{w,1}$ [× 10^3]	1387	C	na	883	912	693	1014	1058	1065	1183
		A	na	1321	1225	1598	1514	1313	1568	1499
$M_{n,1}$ [× 10^3]	290	C	na	193	213	157	212	251	209	249
		A	na	258	250	282	299	279	278	294
D_1	4.78	C	na	4.56	4.28	4.41	4.77	4.22	5.09	4.75
		A	na	5.11	4.90	5.67	5.06	4.71	5.64	5.10
molecular weight distribution of the nearly monodisperse fraction in zone 2[d]										
$M_{w,2}$ [× 10^3]	28.0	C	na	21.1	21.8	21.9	20.7	21.7	20.2	19.9
		A	na	21.2	20.7	22.4	20.4	20.3	20.4	20.0
$M_{p,2}$ [× 10^3]	−	C	na	18.5	19.2	15.9	15.8	18.2	16.2	16.9
		A	na	19.4	19.2	18.1	17.1	18.0	17.8	18.3
$M_{n,2}$ [× 10^3]	17.9	C	na	15.6	16.2	14.7	14.7	16.5	14.5	14.9
		A	na	16.4	16.0	16.3	15.3	15.2	15.6	15.3
D_2	1.56	C	na	1.35	1.34	1.49	1.41	1.32	1.39	1.33
		A	na	1.29	1.30	1.37	1.33	1.33	1.31	1.31

[a] Ripeness stage (RS) number, corresponding to postharvest ripeness index (RPI_{WB}) classes of 4.3−6.5 (I), 1.4−3.0 (II), and −0.7 < 0 < 0.7 (III). na, not analyzed. [b] Mean ± standard error. [c] Extraction methods (EM A, pH 2.0; EM C, 1.5). [d] Molecular weights M_w, M_n, and M_p relative to dextrans. na, not analyzed; $[\eta]$, intrinsic viscosity (0.28 M KAC/LA buffer, pH 3.0); M_w, weight-average molecular weight ($CV_{lg(Mw)}$ < 0.5%); M_n, number-average molecular weight ($CV_{lg(Mn)}$ < 0.5%); D, polydispersity (CV_D 0.07−13.9%); $M_{p,2}$, molecular weight at the peak detected in zone 2 ($CV_{lg(Mp)} \leq 0.25\%$).

neutral sugars of the peel pectins of other mango cultivars (*12, 16*), lower Gal/Rha ratios of 8−16 were recalculated. Commercial apple and citrus pectins, including AP1 (**Table 4**), revealed Gal/Rha ratios of only <3.3 (*7*), similar to the RG-I isolated from the acid-extracted fraction of citrus peel cell wall material (*4*). Among the cold-water-soluble cell wall polysaccharides of mango pulp (cv. 'Alphonso'), the major IEC fraction, an acidic polysaccharide of 1818−1000 kDa, comprised AUA, Gal, Ara, and Rha at recomputed ratios of 5.8/7.7/6.8/1 (mature-green fruit) and 3.2/4.5/4.5/1 (ripe fruit) (*33*). Permethylation studies indicated arabinogalactan side chains, involving nonreducing terminal Gal and Ara units, 1,5-linked arabinan chains partly branched at O-3, and 1,4-linked galactan chains partly substituted at O-6 and O-3/O-6. However, Rha was only found as nonreducing terminal unit, which may result from pectin solubilization through complete side-chain loss of RG-I during ripening (*34*). ^{13}C NMR detection of α-arabinofuranosyl and β-galactopyranosyl residues supported the presence of water-soluble arabinans and galactans in mango pulp (*35*). Besides two rhamnogalacturonans, a neutral arabinogalactan-type polymer ranked among the major fractions of EDTA-soluble mango pulp pectins (*36*). Consistently, hot-water extraction of alcohol-insoluble mango peel residues yielded pectins notably rich in Gal and Ara (AUA/Gal/Ara/Rha ∼ 15/19/7/1 and 23/11/12/1), when compared to hot-acid extraction (*12*).

Apart from starch degradation (**Table 1**), fruit ripening included a decline of nonstarch glucose (Glc) (**Table 3**). Between RS I and II, when softening was most vigorous (**Figure 1A**), Glc fell by 48−58% (KAc). With a further drop by 37−58% (NDM) up to 74−80% (KAc), this loss was even more pronounced between RS II and III. Depolymerization of matrix glycans is deemed to correlate most closely with softening (*34*). Consistently, abundance and molecular weight of the alkali-soluble hemicellulose fractions of mango pulp, mainly comprising various xyloglucans, greatly declined during ripening (*33*). Xylose (Xyl)-rich 1,4-linked β-glucans (Glc/Xyl = 3.8) were distinguished from an extensively branched fraction (Glc/Xyl = 13.1) with additional 1,3-linked Glc residues. Due to the early onset of xyloglucan degradation during maturation (*34*), respective polymer fragments were obviously extracted by hot acid from the peel of mature-green fruits, but gradually degraded during ripening.

The mango peels yielded high-methoxyl pectins irrespective of fruit ripeness (**Table 4**). The titrimetrically assayed degree of esterification (DE) of samples extracted at pH 1.5 ranged from 60 to 74%, slightly higher values resulted from the more gentle extraction at pH 2.0 (73−78%). Methanol quantification by HPLC and colorimetric AUA_c analysis partly suggested even higher degrees of methylation (DMe; **Table 4**). Nevertheless, high average methylation in a DMe range of ∼70−80% reported

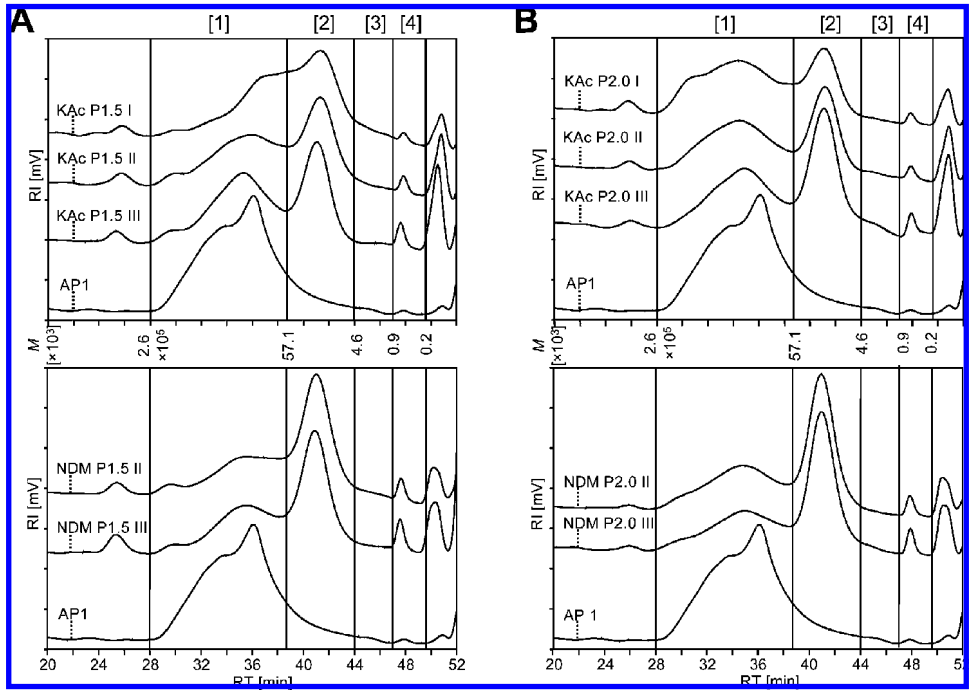

Figure 2. Molecular weight distribution of a commercial pectin from apple pomace (AP1) and AIS samples extracted at (**A**) pH 1.5 (method C) and (**B**) pH 2.0 (method A) from freeze-dried peels (P) of mango fruits 'Kaew Chuk' (KAc) and 'Nam Dokmai #4' (NDM) of different ripeness (stages I−III, cf. **Table 1**). Molecular weights are relative to dextran standards. The full calibration range comprised four zones (1−4) that were empirically defined according to the characteristic peaks observed in zones 2 and 4 for all profiles of mango peel AIS studied.

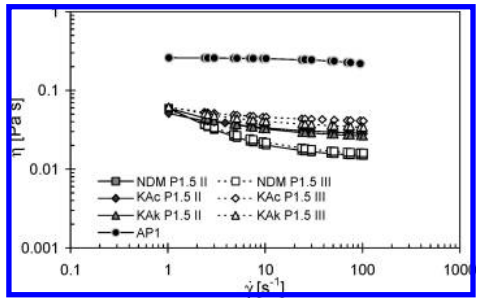

Figure 3. Flow properties of a commercial pectin from apple pomace (AP1) and AIS samples extracted at pH 1.5 (method C) from freeze-dried peels (P) of mango fruits 'Nam Dokmai #4' (NDM), 'Kaew Chuk' (KAc), and 'Kaew Khiew' (KAk) of different ripeness (stages II−III, cf. **Table 1**): viscosities $\eta(\dot{\gamma})$ of aqueous standard pectin solutions (2% w/w) at 20 °C and shear rates ($\dot{\gamma}$) of 1−100 s^{-1}.

for peel pectins from other mango cultivars (*10, 11, 15, 16*) was confirmed. Pectin methylesterase (PME) activities, greatly decreasing in ripening mango pulp, were much lower, but rather constant in the peel (*37*). By contrast, the average degree of acetylation (DAc) slightly decreased during ripening (**Table 4**). However, the mango peel pectins concurred in their low DAc (2.7−6.3%) with the acid-extracted samples from other cultivars (*12*) and apple pectins (*7*).

Molecular Properties of Mango Peel Pectins. Despite the analysis in different solvents, the intrinsic viscosity of AP1 was within the range reported for commercial pectins of similar DE (*7*) and a less methylated lime pectin (*12*), but 1.9−3.2 times higher than those of mango peel AIS (**Table 5**). By contrast, the more expanded coil dimensions of acid-extracted pectins from alcohol-insoluble mango peel residues (*12*), which were indicated by high [η] levels of 649−715 mL/g, might be ascribed to more intensive electrostatic repulsion (*26*) due to higher AUA_c contents (69−71 g/100 g) and lower DMe (52−57%) and the use of a less acidic solvent. In fact, the intrinsic viscosities of the 13 samples in **Table 5** correlated with their molar AUA_{titr} contents (Pearson's correlation coefficient $r = 0.93$) despite their suppressed polyelectrolyte character at pH 3. From RS II to III, the intrinsic viscosity of mango peel AIS always rose significantly (**Table 5**). The overall low [η] of these samples might thus rather be attributed to the presence of branched neutral polysaccharide elements than to a low average molar mass of pectin molecules. However, this was not simply an effect of coextracted starch, because the intrinsic viscosities of the almost starch-free samples (KAc at RS III; **Table 1**) were also ≤284 mL/g.

Consistently, an almost monodisperse fraction with a peak molecular weight ($M_{p,2}$) of ∼18 kDa (**Table 5**) was typical of all AIS samples from mango peel (fraction 2; **Figure 2**), irrespective of starch contents, fruit ripeness, and extraction mode. This fraction, representing 35−55% of the total integrated peak area, greatly reduced their average molecular weights ($M_{w,R}$, $M_{n,R}$) relative to that of AP1 (**Table 5**). However, AP1 and the mango peel pectins comprised similar high molecular weight fractions (fraction 1; **Figure 2**), chiefly after mango peel extraction at pH 2 ($M_{w,1}$, $M_{n,1}$ in **Table 5**). The extraction method caused by far the greatest differences in the molecular weight distributions of the pectins from peels at RS I (**Figure 2**). Improved pectin solubilization at pH 1.5 through intensified hydrolysis of arabinofuranosyl linkages led to an apparent increase in the average molecular weight of fraction 1 during ripening ($M_{w,1}$, $M_{n,1}$ in **Table 5**). Unlike the degradation of starch and matrix glycans (**Tables 1** and **3**), ripening-induced pectin depolymerization was not detected, complying with the high DMe and fairly low activities of polygalacturonase (PG) and PME in mango peel (*37*).

Functional Properties of Mango Peel Pectins. The technofunctional study was limited to AIS gained at RS II and III (RPI_{WB} < 3), when starch had naturally degraded to 1−22 g/100 g (**Table 1**). The fraction of mango peel AIS with a peak molecular weight ($M_{p,2}$) of ∼18000 led to low viscosities of

Table 6. Technofunctional Properties of the Alcohol-Insoluble Substance (AIS) Extracted from the Freeze-Dried Peels of Mango Fruits (MP) 'Kiew Sawoei' (KS), 'Nam Dokmai #4' (NDM), 'Kaew Chuk' (KAc), and 'Kaew Khiew' (KAk) at Different Postharvest Ripeness Stages (RS) Relative to Those of a Commercial Pectin from Apple Pomace (AP1)

	AP1		KS (MP)	NDM (MP)		KAc (MP)			KAk (MP)	
RS:[a]	na		I	II	III	I	II	III	II	III
RPI_{WB}:	na		4.34	1.48	−0.23	6.43	2.95	0.55	2.07	0.64
viscosity of an aqueous standard AIS solution (2% w/w) at 20 °C										
η(3 s^{-1}) [mPa s]	258.5 ±7.3[b]	C[c]	na	31.8 ±0.5	33.4 ±0.4	na	39.7 ±3.1	51.3 ±5.2	41.2 ±0.1	48.0 ±0.2
		A[c]	na	33.4 ±0.5	40.3 ±1.6	na	47.5 ±3.0	58.6 ±1.0	45.1 ±2.6	55.3 ±2.0
η(30 s^{-1}) [mPa s]	244.6 ±6.3[b]	C	na	16.6 ±0.0	17.8 ±0.7	na	30.5 ±0.6	43.1 ±4.3	28.8 ±0.7	37.0 ±0.5
		A	na	21.7 ±0.1	24.7 ±0.5	na	39.5 ±1.9	52.0 ±0.2	37.1 ±2.0	46.5 ±1.9
gelling capacity of the AIS and the dried raw material (DRM), respectively										
$BS_{0.3\%}$ [HPE]	982 ± 10[b]	C	na	238 ± 2	267 ± 3	na	379 ± 2	497 ± 7	266 ± 3	366 ± 3
		A	na	121 ± 2	151 ± 5	na	205 ± 3	276 ± 2	162 ± 3	190 ± 3
BC_{530HPE} [g/100 g]	0.17	C	na	0.56	0.47	na	0.36	0.31	0.54	0.40
		A	na	0.79	0.61	na	0.54	0.44	0.92	0.63
SBC_{530HPE} [g/g of AIS]	392	C	na	115	139	na	178	210	121	164
		A	na	82	107	na	121	148	70	104
SBC_{DRM} [g/100 g]	na	C	na	1930	1995	na	3954	3524	1912	2250
		A	na	1389	1569	na	2906	2476	952	1362
normalized gelling capacity of the AIS relative to the AUA_{titr} content of the standardized gel with 530 HPE										
BC_{530HPE} (AUA_{titr}) [g/100 g]	0.11	C	na	0.15	0.14	na	0.11	0.14	0.14	0.14
		A	na	0.19	0.17	na	0.14	0.17	0.21	0.17
SBC_{530HPE} (AUA_{titr}) [g/g of AUA]	607	C	na	438	458	na	600	476	459	471
		A	na	349	383	na	457	388	307	381

[a] Ripeness stage (RS) number, corresponding to postharvest ripeness index (RPI_{WB}) classes of 4.3−6.5 (I), 1.4−3.0 (II), and −0.7 < 0 < 0.7 (III). na, not analyzed. [b] Mean ± standard error. [c] Extraction methods (EM A, pH 2.0; EM C, pH 1.5). na, not analyzed; η(3 s^{-1}) and η(30 s^{-1}), viscosity at a shear rate of 3 and 30 s^{-1}, respectively; $BS_{0.3\%}$, breaking strength of gels with an AIS dose of 0.3% (w/w) in Herbstreith−Pectinometer units (HPE); BC_{530HPE}, breaking capacity of the AIS as gram of AIS required for 100 g of gel with 530 HPE; SBC_{530HPE}, sugar-binding capacity of the AIS as gram of sugar bound per gram of AIS in a gel of 530 HPE; SBC_{DRM}, gelling units (GU) of the dried raw material (DRM) as its sugar-binding capacity in gram of sugar bound by 100 g of DRM in a gel of 530 HPE; $BC_{530HPE}(AUA_{titr})$, normalized breaking capacity of the AIS (g of AUA/100 g of gel with 530 HPE); $SBC_{530HPE}(AUA_{titr})$, normalized sugar-binding capacity of the AIS (g of sugar/g of AUA for a gel of 530 HPE).

the aqueous AIS solutions (2% w/w), which were shear-thinning throughout the shear rate range studied (**Figure 3**). By contrast, the very viscous solution of AP1 displayed Newtonian flow until a shear rate of ∼10 mPa s, followed by faint shear-thinning. Because shear-thinning was weakest at 30 s^{-1} for both dissolved AP1 and mango peel AIS, the nearly constant viscosities at this shear rate [η(30 s^{-1}); **Table 6**] were most suitable for comparing the samples. They highly correlated with the intrinsic viscosities of the 13 pectins studied ($r = 0.98$) and likewise rose from RS II to RS III. Compared to KAc and KAk pectins, those of NDM peels developed clearly lower viscosities. Unlike the former, they showed lower average molecular weights ($M_{w,R}$, $M_{w,1}$; **Table 5**) and more Gal (**Table 3**), despite similar Gal/Rha ratios of KAk pectins (**Table 4**).

The NDM peel pectins also yielded the weakest gels at an AIS dose of 0.3 g/100 g of gel ($BS_{0.3\%}$; **Table 6**). However, very similar doses of NDM and KAk peel AIS were required for a standard gel of 530 HPE (BC_{530HPE}). The fraction with a $M_{p,2}$ of ∼18000 made the mango peel pectins inferior to AP1 in their gelling capacities. Among the mango peel pectins, the AIS obtained at pH 1.5 from ripe KAc peel (RS III), having most AUA (**Table 3**) and one of the lowest Gal/Rha ratios (**Table 4**), showed the highest sugar-binding capacity (SBC_{530HPE}), although revealing only 54% of the AP1 gelling capacity. However, when BC_{530HPE} and SBC_{530HPE} were normalized to the galacturonic acid levels of the 530 HPE-standard gels on the basis of AUA_{titr} of the pectins, this functional weakness of the mango peel pectins was shown to be largely caused by their lower AUA_{titr} contents as a dilution effect. AP1 and the pH 1.5-extracted AIS of KAc peel at RS II even had the same normalized sugar-binding capacity (∼600 g/g of AUA), requiring an AUA dose of only 0.11 g/100 g of a 530 HPE-gel (**Table 6**). The other AIS samples gained at pH 1.5 were already sufficient at the 1.3−1.4-fold AUA-normalized doses [$BC_{530HPE}(AUA_{titr})$].

Extraction at pH 1.5 was conducive to the gelling capacity of mango peel AIS. Less acidic extraction favored the thickening properties (**Table 6**). Both effects may be ascribed to improved retention of arabinofuranosyl linkages at pH 2 (**Table 3**), leading to high Ara/Rha (7−9 mol/mol) and Ara/Gal ratios (33−56 mol/100 mol) of peel AIS at RS II−III (**Table 4**). Branched arabinan side chains of RG-I and arabinogalactans contribute to thickening through macromolecular entanglements, but sterically disturb the formation of extended HG junction zones in sugar−acid gels. Because side-chain entanglements also reduce the mobility of the pectin molecules during the onset of gelation, junction zone formation at high temperatures is facilitated (*7*). Consistently, the gelling samples of mango peel AIS displayed high setting temperatures (**Figure 4A**), despite poor gel strengths (**Table 6**). The dependencies of the setting temperature on the AIS content of the gel (**Figure 4A**) and its recalculated AUA_{titr} content (**Figure 4B**), respectively, were approximated by empirical power laws, similar to the setting behavior of commercial pectins (*7*). However, this regression model was not applicable to the setting temperatures that vigorously rose with increasing doses of AIS gained at pH 2 from KAk peel. According to the high DE of AP1 and the pH 1.5 samples of KAk (72−73%) and the even higher DE of KAk AIS obtained at pH 2 (76−77%), rapid setting of the former group and ultrarapid setting of the latter were expected (*6, 15*), but became

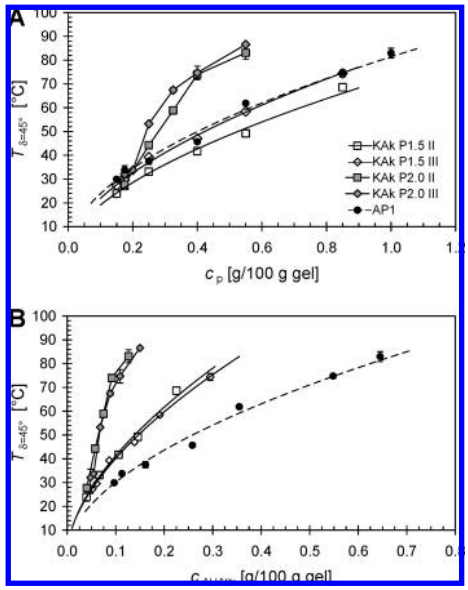

Figure 4. Gelation of a commercial pectin from apple pomace (AP1) and AIS samples extracted at pH 1.5 or 2.0 from freeze-dried peels (P) of mango fruits 'Kaew Khiew' (KAk) of different ripeness (stages II−III, cf. **Table 1**): setting temperatures ($T_{\delta=45°}$) of standard gels (65 °Brix, pH 3.0) as a function of (**A**) rising pectin (AIS) doses of the gels (c_p) and (**B**) the computed anhydrogalacturonic acid contents of the gels ($c_{AUAtitr}$) resulting from the AUA_{titr} contents of the pectin (AIS) sample (cf. **Table 2**). Exponents (n) and coefficients of determination (R^2) of empirical power law approximations were $n = 0.5331$, 0.5803, and 0.5732 and $R^2 = 0.985$, 0.994, and 0.994 for AP1, KAk P1.5 II, and KAk P1.5 III, respectively.

discernible only at high AIS doses (**Figure 4A**) (*7*). The setting behavior detected after normalization on the basis of AUA_{titr} of the pectins (**Figure 4B**) conformed to the hypothesized increase in entanglements indicated by the Gal/Rha and Ara/Rha ratios rising from AP1 to KAk AIS extracted at pH 1.5 and from the more acidic to the less acidic-extracted KAk AIS, respectively (**Table 4**). The coinciding curves reflected the similar side-chain indices of KAk AIS found at both ripeness stages.

In conclusion, the mango peels studied proved to be similar to apple pomace as to net yields and major structural average parameters of their pectins. However, limited AUA contents made the mango peel pectins less suitable as to gelling capacity and thickening properties. Expanded (arabino-)galactans and the characteristic fraction with a $M_{p,2}$ of ~18000 crucially affected the technofunctional properties. During postharvest ripening, depolymerization of pectins and galactans was insignificant, whereas pectin solubilization in mango peels may be facilitated by the loss of whole RG-I side chains.

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