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Screening of Mango (*Mangifera indica* L.) Cultivars for Their Contents of Flavonol *O*- and Xanthone *C*-Glycosides, Anthocyanins, and Pectin

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With respect to their browning potential and in consideration of a combined recovery of pectin and phenolic compounds, peels of 14 cultivars and the flesh of nine cultivars of mango (*Mangifera indica* L.) fruits were analyzed for their contents of flavonol *O*- and xanthone *C*-glycosides by high-performance liquid chromatography (HPLC)−diode array detection−electrospray ionization mass spectrometry (ESI-MS). While total amounts of up to 4860 mg/kg dry matter demonstrated the peels to be a rich source of phenolic compounds, only traces could be detected in the flesh. The profile of flavonol glycosides of the peels proved to be highly characteristic and may therefore serve as a tool for authenticity control of mango puree concentrate, which is often produced from unpeeled fruits and represents an important intermediate for the production of mango nectars. Two compounds were isolated by preparative HPLC, and their structures were elucidated on the basis of ESI-MS as well as NMR spectroscopy, establishing the two compounds as rhamnetin 3-*O*-β-galactopyranoside and rhamnetin 3-*O*-β-glucopyranoside, respectively. In the peels of red-colored cultivars, cyanidin 3-*O*-galactoside and an anthocyanidin hexoside so far not reported in mango could tentatively be identified. The contents and degrees of esterification of pectins extracted from the lyophilized peels ranged from 12.2 to 21.2% and from 56.3 to 65.6%, respectively, suggesting mango peels also as a promising source of high-quality pectin.

KEYWORDS: ***Mangifera indica* (L.); mango; peels; rhamnetin glycosides; flavonols; xanthones; anthocyanins; pectin; HPLC-DAD-MS^n; NMR**

INTRODUCTION

Mango (*Mangifera indica* L., Anacardiaceae) is one of the most important tropical fruits with a global production exceeding 25 million tons in 2003 (*1*). Extensive plant breeding has generated hundreds of cultivars, the fruits of which show a pronounced diversity in size, shape, color, flavor, seed size, and composition (*2*). While fruits from the temperate zone, e.g., apples, are usually characterized by a large edible portion and moderate amounts of waste materials such as peels and seeds, considerably higher ratios of byproducts arise from tropical and subtropical fruit processing. In the case of mangos, the peels and seeds amount to 35−60% of the total fruit weight (*3*).

The composition of mango kernels and their utilization as a source of fat (*4*−*6*), natural antioxidants (*7*), starch (*8*), flour (*9*), and feed (*10*, *11*) have been investigated in a number of studies. In contrast, investigations on the composition and possible utilization of mango peels are comparatively scarce. Their use as a source of pectin was proposed by several authors (*12*−*16*); however, only a small number of different cultivars have so far been studied with respect to contents and properties of the pectin (*12*−*20*).

Our recent investigations have demonstrated that mango peels of the cultivar Tommy Atkins contain a large number of flavonol *O*- and xanthone *C*-glycosides (*21*) (**Figure 1**), corroborating the results obtained in a previous study of the phenolic profile of a commercial mango puree concentrate (*22*). These compounds might be used as natural antioxidants to replace synthetic additives or also as functional food ingredients. In view of the large number of mango cultivars of commercial importance, more information on the presence of valuable compounds would be highly desirable to draw conclusions as to their recovery from byproducts. Therefore, in the present study, a screening of mango peels of 14 different cultivars originating from Africa, Asia, Australia, and South America for their contents of flavonoids including anthocyanins and xanthones was carried out. Selected cultivars were also investigated for their polyphe-

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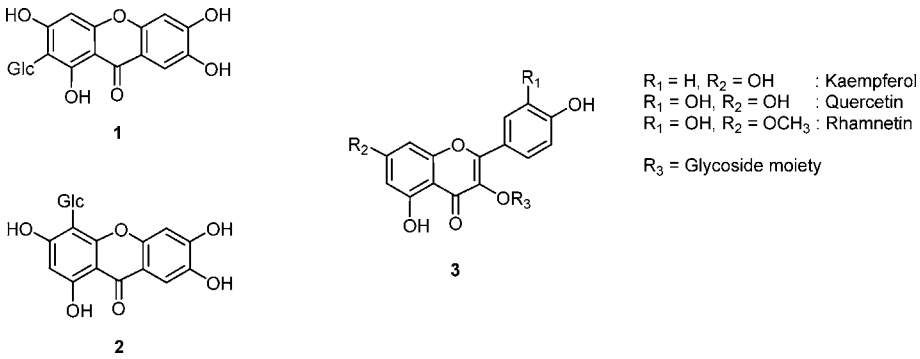

Figure 1. Structures of the xanthone *C*-glycosides mangiferin (**1**) and isomangiferin (**2**) and the general structure and substitution pattern of flavonol glycosides (**3**) detected in mango peels.

nolic contents in the flesh. During our study on the identification of mango peel phenolics, a flavonol glycoside was detected, which was tentatively identified as a rhamnetin attached to a hexose. The assignment was based on UV spectral and mass spectrometric data (*21*). However, because of the lack of reference substances, its exact structure could not be proven. Therefore, another objective of the present study was the isolation and structure elucidation of this rhamnetin glycoside by one-dimensional (1D) and two-dimensional (2D) ^{1}H NMR spectroscopy. Furthermore, the content of mango peel pectin as another valuable compound and its degree of esterification were determined.

MATERIALS AND METHODS

Standards. Standards used for identification and quantification purposes with high-performance liquid chromatography (HPLC) and MS were as follows: quercetin 3-*O*-xyloside and quercetin 3-*O*-arabinofuranoside (Plantech, Reading, United Kingdom); quercetin, quercetin 3-*O*-arabinopyranoside, and quercetin 3-*O*-arabinoglucoside (Roth, Karlsruhe, Germany); mangiferin [2-*C*-*β*-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone], quercetin 3-*O*-galactoside, quercetin 3-*O*-glucoside, quercetin 3-*O*-rhamnoside, kaempferol 3-*O*-glucoside, isorhamnetin 3-*O*-glucoside, and rhamnetin (Extrasynthese, Lyon, France); and cyanidin 3-*O*-glucoside and peonidin 3-*O*-glucoside (Polyphenols, Sandnes, Norway). Because of the limited amounts available, quercetin 3-*O*-arabinofuranoside and -pyranoside could only be used for identification purposes. Dried cranberries (*Vaccinium macrocarpon* AIT, 100 g) obtained from the local market were homogenized after the addition of 100 mL of acidified methanol (0.1% hydrochloric acid) using a Grindomix GM 200 knife mill (Retsch, Haan, Germany). The comminuted berries were mixed with 300 mL of acidified methanol (0.1% hydrochloric acid) and extracted for 1 h under stirring in a nitrogen atmosphere. The extract was centrifuged (10 min, 3480*g*), and the organic solvent was removed from the supernatant by evaporation in vacuo at 30 °C.

After the residue was dissolved in 100 mL of water, 20 mL of the solution was applied on a 10 g C_{18}-Sep-Pak cartridge, which was activated with methanol and rinsed with water. Nonanthocyanin substances were subsequently eluted with 50 mL of 0.01% hydrochloric acid and 50 mL of ethyl actetate. The anthocyanins were eluted with 50 mL of acidified methanol (0.01% hydrochloric acid), and the eluate was evaporated in vacuo to dryness. The residue was dissolved with 5 mL of acidified methanol (0.01% hydrochloric acid).

Mango Samples. Twenty to twenty-five mature mango fruits of the cultivars Tommy Atkins (Brazil), Manila (Thailand), Ngowe (Kenia), R2E2 (Australia), Kent (Brazil), José (La Réunion), Mini-mango (Colombia), Haden (Peru), and Heidi (Peru) were obtained from the local market. Freeze-dried peels of Kaew, Mon Duen Gao, Maha Chanock, Nam Dokmai, and Chock Anan were obtained from Thailand. The peels were vacuum-sealed in polyethylene bags and stored at −20 °C until analysis. For isolation and structure elucidation of the rhamnetin hexoside, mango fruits of the cultivar Tommy Atkins (Peru) were obtained from the local market.

Sample Preparation. The extraction and purification of flavonol and xanthone glycosides were performed as described previously (*21*). The peels were removed with a stainless steel knife. After the separation of residual pulp from the peel with a razor blade, the peels were combined, immediately lyophilized, and finely ground using a S1/2 ball mill (Retsch). The pulp was also combined, lyophilized, and manually ground in a mortar. Aliquots of 2.5 g of the lyophilized peels and 5 g of the lyophilized pulp, respectively, were weighed into an amber glass round-bottomed flask. After the addition of 0.5 g of ascorbic acid, the flask was flushed with nitrogen, and the mixture was extracted with 50 mL of aqueous acetone (80%, v/v) for 3 h under stirring. The extract was centrifuged (10 min, 3480*g*), and the residue was extracted with 50 mL of aqueous acetone for 10 min. The organic solvent was removed from the combined supernatants by evaporation in vacuo at 30 °C. The aqueous solution was transferred into a volumetric flask and made up to 50 mL with deionized water. After microfiltration (5 μm), aliquots of 20 mL were used for further purification. Polyamide CC6 (2 g, 0.05−0.16 mm) (Macherey-Nagel, Dueren, Germany) was filled into an Econo-Pac column (BioRad, Munich, Germany) and successively conditioned with 25 mL of methanol and 50 mL of deionized water prior to application of the peel extract to the column. After it was washed with water (50 mL), the polyphenolic fraction was recovered by elution with methanol (100 mL). The eluate was evaporated to dryness, and the residue was dissolved in 0.5 mL of methanol. The solution was membrane-filtered (0.45 μm, Whatman Inc., Clifton, United States) and used for HPLC.

For isolation of the rhamnetin glycosides, the extraction was performed as previously described. A glass column (400 mm × 20 mm i.d.) was filled with 25 g of polyamide (0.05−0.16 mm; Roth) and successively conditioned with 200 mL of methanol and 1 L of deionized water. Aliquots of 650 mL of the aqueous mango peel extract were microfiltered (5 μm) and applied on the column. After they were washed with 1.5 L of deionized water, the phenolic compounds were eluted with 2 L of methanol. The eluate was evaporated to 10 mL and stored at −80 °C in a nitrogen atmosphere.

For the characterization of anthocyanins in the peels of red-colored mango fruits, 1 mL of the aqueous peel extract (before polyamide purification) was evaporated to dryness, and the residue was dissolved in 0.5 mL of acidified methanol (0.01% hydrochloric acid). The solution was membrane-filtered (0.45 μm) (Whatman Inc.) and used for HPLC.

HPLC and LC-MS Analysis. The separation of phenolic compounds was performed using an Agilent HPLC series 1100 system (Agilent, Waldbronn, Germany) equipped with ChemStation software, a model G1322A degasser, a model G1312A binary gradient pump, a model G1329/1330A thermoautosampler, a model G1316A column oven, and a model G1315B diode array detector. UV/vis spectra were recorded from 200 to 600 nm (peak width 0.2 min).

LC-MS analyses were performed with a similar HPLC system as described above connected in series with a Bruker (Bremen, Germany) model Esquire 3000+ ion trap mass spectrometer fitted with an ESI source. Negative ion (flavonols and xanthones) and positive ion (anthocyanins) mass spectra of the column eluate were recorded in the range *m*/*z* 50−1000. Nitrogen was used as the drying gas at a flow rate of 10.0 L/min and at a pressure of 60.0 psi (flavonols and

Table 1. UV Spectra and Characteristic Ions of Rhamnetin Glycosides Extracted from Peels of *M. indica* L. cv. Tommy Atkins; Data of Selected Reference Compounds (Std) Are Also Included

peak	identity	HPLC-DAD λ_{max} (nm)	$[M-H]^-$ (*m*/*z*)	HPLC-ESI(–)-MS^n experiment (*m*/*z*) (% base peak)
1	rhamnetin 3-*O*-β-galactopyranoside (compound A)	230, 257, 265sh, 297sh, 354	477	–MS^2 [477]: 315 (100), 314 (23) –MS^3 [477 → 315]: 300 (29), 193 (38), 165 (100)
2	rhamnetin 3-*O*-β-glucopyranoside (compound B)	231, 257, 265sh, 297sh, 354	477	–MS^2 [477]: 315 (100), 314 (27) –MS^3 [477 → 315]: 300 (35), 193 (29), 165 (100)
Std	isorhamnetin 3-*O*-glucoside	255, 265sh, 297sh, 354	477	–MS^2 [477]: 477 (76), 357 (18), 315 (37), 314 (100) –MS^3 [477 → 315]: 300 (100)
Std	rhamnetin	230, 256, 370	315	–MS^2 [315]: 300 (26), 193 (37), 165 (100)

Table 2. ^{1}H and ^{13}C NMR Spectral Data of Rhamnetin 3-*O*-β-Galactopyranoside and Rhamnetin 3-*O*-β-Glucopyranoside in Pyridine-d_5 (δ [ppm])

	rhamnetin 3-*O*-β-galactopyranoside (compound A)		rhamnetin 3-*O*-β-glucopyranoside (compound B)	
	^{1}H	^{13}C[a]	^{1}H	^{13}C[a]
position	δ, multiplicity (J)	δ	δ, multiplicity (J)	δ
2		157.9		157.6
3		135.4		135.2
4		*b*		178.5
5		162.0		162.4
6	6.53, *d* (2.3)	98.0	6.54, *d* (1.9)	98.0
7		165.7		165.7
7-OCH_3	3.74, *s*	55.2	3.75, *s*	55.4
8	6.48, *d* (2.3)	91.8	6.49, *d* (1.9)	92.0
9		156.9		156.9
10		105.7		105.7
1′		122.0		121.9
2′	8.47, *d* (2.1)	117.4	8.44, *d* (1.9)	117.3
3′		146.7		146.6
4′		150.5		150.6
5′	7.30, *d* (8.4)	115.9	7.31, *d* (8.4)	115.9
6′	8.11, *dd* (2.1, 8.4)	122.1	8.09, *dd* (1.9, 8.4)	122.2
1″	6.13, *d* (7.9)	104.6	6.25, *d* (7.1)	103.4
2″	4.80, *dd* (7.8, 9.3)	72.7	4.33, *m* (overlapped)	75.7
3″	4.28, *dd* (3.4, 9.3)	74.8	4.33, *m* (overlapped)	78.1
4″	4.60, *bd* (3.2)	69.2	4.19, *bt* (9.4)	70.8
5″	4.15, *bt* (6.2)	77.0	4.03, *ddd* (2.5, 5.3, 9.4)	78.3
6″	4.40, *dd* (6.3, 10.9) 4.30, *dd* (5.9, 10.9)	61.3	4.41, *dd* (2.5, 11.8) 4.25, *dd* (5.3, 11.8)	62.0

[a] Carbons were assigned by GHSQC and GHMQC experiments. Proton assignment is based on ^{1}H, 1D TOCSY, GCOSY, ROESY, and DPFGNOE spectra. [b] Not detectable via $^4J_{C,H}$ because of limited sample amount.

xanthones), 11.0 L/min and 65.0 psi (anthocyanins), or 12.0 L/min and 70.0 psi (rhamnetin hexoside), respectively. The nebulizer temperature was set at 365 °C (*21*, *23*). Collision-induced dissociation spectra were obtained with a fragmentation amplitude of 1.0 V using helium as the collision gas (1.1×10^{-5} mbar).

Individual compounds were identified by their retention times and UV/vis and mass spectra (*21*) and quantified using a calibration curve of the corresponding standard compound. When reference compounds were not available, the calibration of structurally related substances was used including a molecular weight correction factor (*24*). All determinations were performed in duplicate.

Flavonol and Xanthone Analysis. The column used for HPLC was a 150 mm × 3.0 mm i.d., 4 μm Synergi Hydro-RP (Phenomenex, Torrance, CA), with a 4.0 mm × 2.0 mm i.d. C18 ODS guard column, operated at a temperature of 25 °C. The mobile phase consisted of 2% (v/v) acetic acid in water (eluent A) and of 0.5% acetic acid in water and acetonitrile (50:50, v/v; eluent B). The gradient program was as follows: 0−25% B (15 min), 25−30% B (35 min), 30−80% B (10 min), and 80 to 0% B (0.5 min). The injection volume for all samples was 4 μL. Simultaneous monitoring was performed at 320 (xanthones) and 370 (flavonols) nm at a flow rate of 0.6 mL/min (*21*).

Anthocyanin Analysis. The column used was a 250 mm × 4.6 mm i.d., 5 μm C18 Aqua (Phenomenex), with a 4.0 mm × 3.0 mm i.d. C18 ODS guard column, operated at a temperature of 25 °C. The mobile phase consisted of 87% (v/v) water, 10% formic acid, and 3% acetonitrile (eluent A) and 40% water, 10% formic acid, and acetonitrile 50% (eluent B). The gradient program was as follows: 10−25% B (10 min), 25−31% B (5 min), 31−40% B (5 min), 40−50% B (10 min), 50−100% B (10 min), and 100 to 10% B (5 min). The injection volume for all samples was 50 μL. Monitoring was performed at 520 nm at a flow rate of 0.8 mL/min (*23*).

Isolation and Structure Elucidation of Rhamnetin Glycosides. *Preparative HPLC (1).* The preparative isolation of the rhamnetin glycosides was performed on a HPLC system consisting of a LC-CaDI 22-14 control unit, two HPLC compact pumps (Bischoff, Leonberg, Germany), a SPD-10AV VP UV/vis detector (Shimadzu, Kyoto, Japan), and a dynamic mixing chamber (Knauer, Berlin, Germany). A Phenomenex C18 Aqua column (250 mm × 21.2 mm i.d., particle size 5 μm, pore size 125 Å) fitted with a SecurityGuard Cartridge (10 mm × 10 mm i.d., ODS) (Phenomenex) was used as the stationary phase at room temperature. The mobile phase consisted of 0.5% (v/v) formic acid in water (eluent A) and 60% (v/v) acetonitrile in water (eluent B). The gradient program was as follows: 30−80% B (10 min), 80−90% B (5 min), 90−100% B (3 min), and 100 to 30% B (2 min). The flow rate was 9 mL/min, and monitoring was performed at 370 nm. Aliquots of 1 mL of the concentrated eluate were applied per injection, and the effluent was collected from 14 to 15 min. The eluate was neutralized with aqueous ammonia and reduced to 5 mL in vacuo.

LC-MS Analyses. The column used was a 250 mm × 4.6 mm i.d., 5 μm C18 Aqua (Phenomenex), with a 4.0 mm × 3.0 mm i.d. C18 ODS guard column, operated at a temperature of 25 °C. The mobile phase consisted of 2% (v/v) acetic acid in water (eluent A) and of 0.5% acetic acid in water and acetonitrile (50:50, v/v; eluent B). The separation was carried out isocratically (40% eluent B) at a flow rate of 1.0 mL/min. The injection volume was 10 μL, and monitoring was performed at 370 nm.

Preparative HPLC (2). The preparative separation of individual rhamnetin glycosides was performed with the same preparative HPLC system as described above. The mobile phase consisted of 2% (v/v) acetic acid in water (eluent A) and of 0.5% acetic acid in water and acetonitrile (50:50, v/v; eluent B). The separation of rhamnetin glycosides was achieved isocratically (37% eluent B) at a flow rate of 17.0 mL/min. Monitoring was performed at 370 nm.

Aliquots of 1 mL of the concentrated eluate obtained from the first preparative HPLC procedure were applied per injection, and the effluent was collected from 103 to 108 min for compound **1** and from 110 to 115 min for compound **2**. The solutions were neutralized with aqueous ammonia and reduced to 5 mL in vacuo. For final purification, Chromabond C18 (6 mL, 1000 mg) SPE columns were successively conditioned with 10 mL of acetonitrile and 10 mL of water. After the samples were applied, the column was washed with 20 mL of water. The rhamnetin glycosides were eluted with 25 mL of acidified acetonitrile (pH 3, trifluoroacetic acid). The eluates were evaporated to dryness in vacuo, and the residues were stored at −80 °C in a nitrogen atmosphere.

NMR Analysis. NMR data were obtained on a Varian Deutschland GmbH (Darmstadt, Germany) Unity Inova 500 MHz spectrometer. The ^{1}H and ^{13}C chemical shifts were referenced to solvent signals at $\delta\delta_{H/C}$

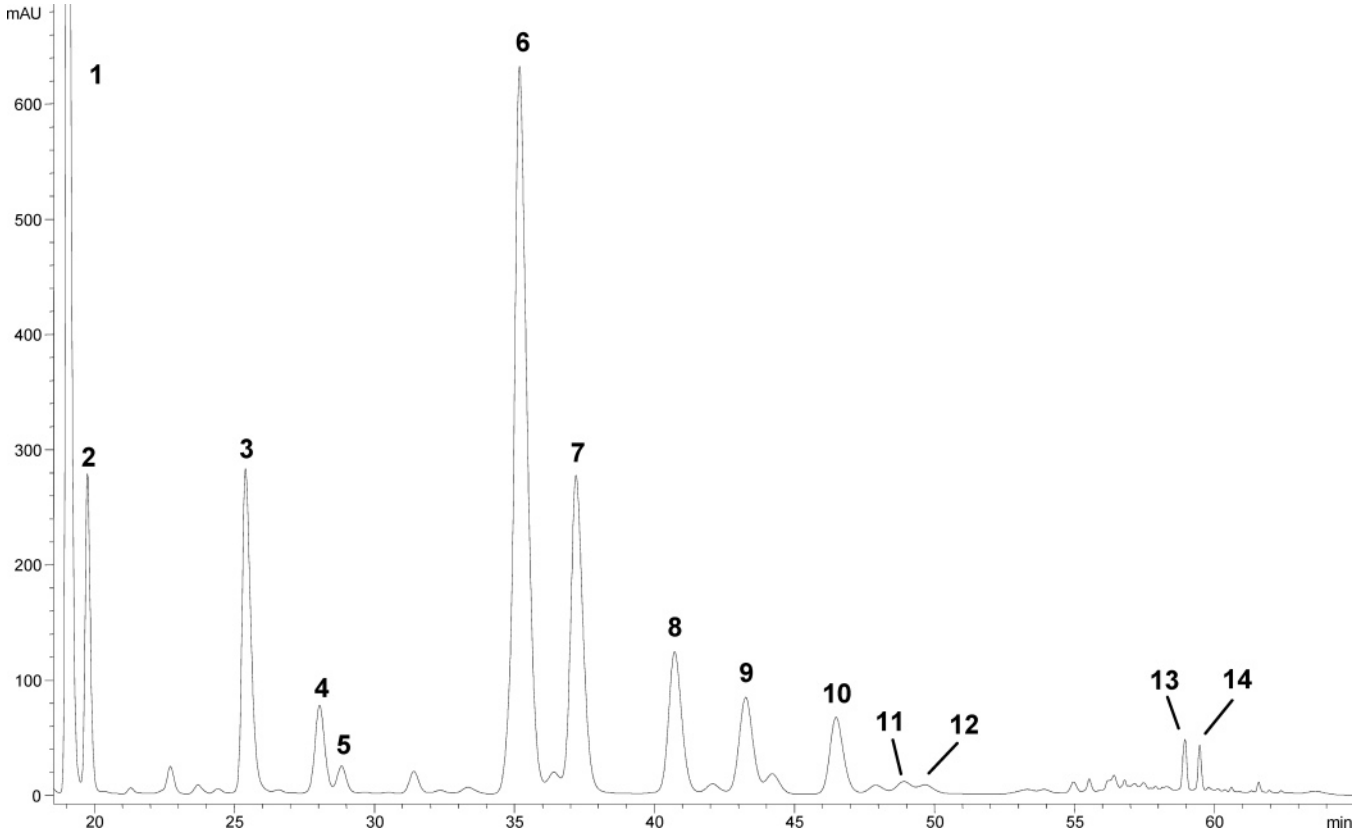

Figure 2. Separation of flavonol *O*- and xanthone *C*-glycosides extracted from mango peels (cv. Ngowe) by HPLC (370 nm). Peak assignments: 1, mangiferin; 2, isomangiferin; 3 and 4, mangiferin gallate and isomangiferin gallate (tentatively identified); 5, quercetin 3-*O*-diglycoside; 6, quercetin 3-*O*-galactoside; 7, quercetin 3-*O*-glucoside; 8, quercetin 3-*O*-xyloside; 9, quercetin 3-*O*-arabinopyranoside; 10, quercetin 3-*O*-arabinofuranoside; 11, quercetin 3-*O*-rhamnoside; 12, kaempferol 3-*O*-glucoside; 13, rhamnetin 3-*O*-galactoside and rhamnetin 3-*O*-glucoside; and 14, quercetin (aglycone).

8.71/149.8 (pyridine-d_5) relative to that of TMS. All 1D (^{1}H, DPFG-NOE) and 2D (DQFCOSY, GHSQC, GHMQC, G = gradient enhanced) NMR measurements were performed using standard Varian pulse sequences. ^{1}H−^{13}C correlation spectra were recorded by GHSQC (J_{C-H} = 140 Hz) for the determination of proton-bearing carbons and GHMQC ($^nJ_{C-H}$ optimized for 8 Hz) for multibond correlations (HMBC). ROESY experiments were carried out with 0.5 s mixing time.

Pectin Analysis. Ten grams of the lyophilized peels was weighed into an Erlenmeyer flask. After the addition of 390 g of water, the sample was heated at 100 °C under stirring and afterward allowed to cool. The solution was adjusted to pH 1.5 using aqueous sulfuric acid (25%), covered with a watch glass, and heated at 90 °C in a water bath for 2.5 h. After it was cooled, the solution was centrifuged (20 min, 3941*g*). The pectin was precipitated by adding the supernatant to 3.5 L of ethanol (88%) and filtered through a perlon filter cloth after 30 min. The precipitate was washed with 1.5 L of ethanol (88%), pressed, and lyophilized. Pectin yields were determined gravimetrically. The lyophilizate was microscopically tested for the presence of starch after adding KI/I_2 solution.

For determination of the degree of esterification, 0.5 g of the lyophilized and ground pectin and 15 mL of acidified aqueous ethanol [5 mL of hydrochloric acid (25%) in 100 mL of aqueous ethanol (60%)] were stirred for 10 min. The solution was vacuum-filtered through an Econo-Pac column (BioRad, Munich, Germany) and washed six times with 5 mL of acidified aqueous ethanol. The residue was subsequently washed with 25 mL of ethanol (60%) and 20 mL of ethanol (96%). The pectin was transferred into an Erlenmeyer flask, and 2 mL of ethanol was added (96%). After the addition of 100 mL of water, the solution was stirred in a water bath at 20 °C until the pectin was completely dissolved. The solution was automatically titrated to pH 8.1 with a solution of 0.1 N sodium hydroxide using a 702 SM Titrino titrator (Metrohm, Herisau, Switzerland). For saponification of the methoxylated galacturonic acids, 20 mL of 0.5 N sodium hydroxide solution was added and the solution was kept for 15 min. Subsequently, 20 mL of 0.5 N hydrochloric acid was added and the solution was automatically titrated to pH 8.1 with 0.1 N sodium hydroxide solution.

RESULTS AND DISCUSSION

Isolation and Structure Elucidation of the Rhamnetin Hexoside. Because preliminary NMR analysis of the compound obtained from the first preparative HPLC procedure revealed the presence of two rhamnetin glycosides, further purification steps were necessary. For this purpose, an analytical stationary phase with hydrophilic endcapping was applied, resulting in the separation of two compounds. Both compounds displayed identical UV spectra and pseudomolecular ions of *m*/*z* 477 [M − H]$^-$. As shown in **Table 1**, fragments of *m*/*z* 315 and 314, respectively, were obtained in the MS^2 experiment, indicating the presence of a methoxylated flavonol aglycone, i.e., rhamnetin or isorhamnetin. As already discussed in our recent publication (*21*), methoxylated flavonol glycosides can be distinguished by means of mass spectrometry because they differ in their fragmentation of flavonoid aglycones in the MS^3 experiment. From **Table 1**, it can be seen that the two rhamnetin glycosides isolated from mango peels generated a fragment of *m*/*z* 165 as the most abundant ion in the MS^3 experiment, which exactly matches the fragmentation profile of the rhamnetin aglycone standard in the MS^2 experiment. In contrast, the predominant fragment ion of isorhamnetin 3-glucoside was shown to be *m*/*z* 300.

For unambiguous structure elucidation by NMR spectroscopy, the rhamnetin glycosides were individually recovered by preparative HPLC. The two compounds eluted after 106 and 113 min, respectively. Pyridine-d_5 as the solvent allowed nearly the complete assignment of all protons and carbons by 1D and

Table 3. Contents (mg/kg Dry Matter) of Flavonol and Xanthone Glycosides in the Peels of Different Mango Cultivars

	Tommy Atkins	Manila	Ngowe	R2E2	Kent	José	Mini-mango
mangiferin	1263.2 ± 197.2	43.5 ± 9.8	775.8 ± 11.7	82.9 ± 4.2	13.9 ± 1.5	983.6 ± 50.1	449.9 ± 37.7
isomangiferin[a]	40.3 ± 0.8	11.5 ± 1.2	184.7 ± 5.9	19.0 ± 0.3	4.0 ± 0.3	45.5 ± 1.9	13.3 ± 0.9
mangiferin gallate[b]	87.3 ± 1.5	7.8 ± 0.7	377.4 ± 19.8	ND	ND	25.2 ± 2.0	31.6 ± 1.8
isomangiferin gallate[b]	12.3 ± 0.6	3.0 ± 0.1	127.1 ± 2.0	ND	ND	ND	ND
quercetin -diglycoside[c]	55.1 ± 0.7	145.9 ± 0.0	29.7 ± 0.1	ND	ND	40.3 ± 2.8	ND
quercetin 3-*O*-gal	1217.3 ± 18.0	430.6 ± 18.4	797.6 ± 11.8	116.5 ± 8.8	944.5 ± 38.3	1467.7 ± 42.3	1147.1 ± 55.1
quercetin 3-*O*-glc	882.0 ± 4.2	282.5 ± 12.9	359.1 ± 6.3	124.4 ± 5.9	890.0 ± 39.8	1045.3 ± 41.6	767.8 ± 46.8
quercetin 3-*O*-xyl	239.5 ± 3.8	39.2 ± 2.9	100.9 ± 1.7	17.8 ± 0.4	150.7 ± 8.2	278.6 ± 8.4	10.2 ± 0.0
quercetin 3-*O*-ara*p*[d]	163.5 ± 2.8	27.6 ± 1.2	70.7 ± 0.5	8.8 ± 0.3	91.6 ± 3.4	191.8 ± 7.5	3.5 ± 0.3
quercetin 3-*O*-ara*f*[d]	152.4 ± 2.7	17.9 ± 1.2	56.8 ± 2.2	8.2 ± 0.5	84.8 ± 3.8	119.6 ± 3.5	ND
quercetin 3-*O*-rha	38.2 ± 1.7	15.6 ± 0.6	20.6 ± 0.8	5.3 ± 0.3	58.1 ± 3.5	116.4 ± 4.3	ND
kaempferol 3-*O*-glc	77.3 ± 5.3	16.8 ± 1.1	24.1 ± 1.3	11.2 ± 1.1	30.6 ± 1.8	171.7 ± 8.8	ND
rhamnetin 3-*O*-gal/glc[e]	215.6 ± 4.9	14.6 ± 1.7	22.6 ± 0.4	5.4 ± 0.0	70.6 ± 3.4	374.4 ± 11.1	49.8 ± 1.4
quercetin	ND[f]	1.7 ± 0.2	6.7 ± 0.4	ND	3.3 ± 0.1	ND	19.3 ± 0.5
total	4444.0 ± 198.3	1058.1 ± 25.1	2953.8 ± 27.6	399.4 ± 11.5	2342.0 ± 56.4	4860.2 ± 80.0	2442.5 ± 81.6

	Haden	Heidi	Kaew	Mon Duen Gao	Maha Chanock	Nam Dokmai	Chok Anan
mangiferin	11.2 ± 0.1	108.9 ± 3.5	313.6 ± 4.4	68.0 ± 2.3	973.9 ± 106.9	78.1 ± 2.8	1297.1 ± 140.1
isomangiferin[a]	21.0 ± 0.8	8.0 ± 0.3	28.6 ± 3.6	10.6 ± 0.6	54.7 ± 2.5	14.3 ± 1.6	41.2 ± 0.0
mangiferin gallate[b]	ND	ND	43.0 ± 1.3	8.7 ± 0.3	166.1 ± 27.5	24.1 ± 1.0	89.9 ± 4.4
isomangiferin gallate[b]	ND	ND	ND	ND	22.3 ± 3.0	ND	ND
quercetin -diglycoside[c]	ND	25.9 ± 3.6	6.1 ± 0.1	10.1 ± 0.5	ND	38.8 ± 0.9	ND
quercetin 3-*O*-gal	1309.1 ± 26.0	1275.7 ± 34.0	76.5 ± 0.2	121.3 ± 2.7	396.1 ± 35.1	185.2 ± 0.1	146.1 ± 2.7
quercetin 3-*O*-glc	912.7 ± 20.5	814.5 ± 16.0	77.4 ± 0.9	83.0 ± 2.6	339.0 ± 38.4	103.7 ± 0.0	92.4 ± 2.3
quercetin 3-*O*-xyl	179.1 ± 4.5	225.7 ± 4.4	14.7 ± 1.1	16.9 ± 0.0.5	42.2 ± 4.7	14.0 ± 0.0	19.1 ± 0.5
quercetin 3-*O*-ara*p*[d]	104.9 ± 5.1	131.9 ± 3.4	7.6 ± 0.1	10.2 ± 0.2	28.6 ± 4.4	8.3 ± 0.0	9.6 ± 0.2
quercetin 3-*O*-ara*f*[d]	70.5 ± 0.8	123.5 ± 2.6	6.8 ± 0.1	5.5 ± 0.1	19.8 ± 2.1	6.1 ± 0.0	8.2 ± 0.3
quercetin 3-*O*-rha	52.7 ± 0.6	41.6 ± 0.5	4.2 ± 0.0	4.6 ± 0.2	20.6 ± 3.1	5.9 ± 0.3	4.2 ± 0.1
kaempferol 3-*O*-glc	43.7 ± 1.1	73.0 ± 1.2	9.9 ± 0.2	6.7 ± 0.1	36.5 ± 4.1	3.6 ± 0.6	20.9 ± 2.1
rhamnetin 3-*O*-gal/glc[e]	228.6 ± 2.7	57.4 ± 3.4	ND	6.2 ± 0.5	20.4 ± 2.9	3.6 ± 0.0	ND
quercetin	2.8 ± 0.0	11.9 ± 1.7	ND	2.8 ± 0.3	ND	ND	ND
total	2936.4 ± 33.9	2897.8 ± 38.6	588.5 ± 6.0	354.4 ± 4.5	2120.2 ± 122.5	485.6 ± 3.6	1728.7 ± 140.2

[a] Quantified as mangiferin. [b] Quantified as mangiferin (including molecular weight correction factor). [c] Quantified as Q 3-*O*-arabinoglucoside. [d] Quantified as Q 3-*O*-xyloside. [e] Quantified as isorhamnetin 3-*O*-glucoside. [f] ND, not detected.

Table 4. Contents (mg/kg Dry Matter) of Flavonol and Xanthone Glycosides in the Flesh of Selected Mango Cultivars

	compound	content (mg/kg dry matter)
Haden	mangiferin	16.2 ± 2.7
	quercetin 3-*O*-gal	6.6 ± 0.4
	quercetin 3-*O*-glc	5.6 ± 0.0
José	mangiferin	19.4 ± 0.2
Tommy Atkins	mangiferin	4.6 ± 0.1
R2E2	mangiferin	4.3 ± 0.6
Mini-mango	mangiferin	3.0 ± 0.5
Kent	ND[a]	
Heidi	ND	
Manila	ND	
Ngowe	ND	

[a] ND, not detected.

2D NMR spectroscopy including ^{1}H, DPFGNOE, 1D TOCSY, GCOSY, ROESY, GHSQC, and GHMQC. ^{1}H and ^{13}C NMR data of both rhamnetin glycosides are given in **Table 2**. These data and comparison with literature data (*25*) identified the flavonoid moiety of both compounds as rhamnetin. The observed vicinal coupling constants of $J = 7.9$ Hz and $J = 7.1$ Hz for the anomeric protons of **A** and **B**, respectively, suggested a $\beta\beta$-linkage to the aglycone. In the ^{1}H NMR spectra of **A** and **B**, a significant difference could be detected in the region of the sugar protons (4−5 ppm). Two small coupling constants and strong ROE values between 3″-H/4″-H as well as 4″-H/5″-H in **A** indicated a galactopyranosyl moiety, whereas vicinal coupling constants of $J \approx 9$ Hz between these protons established a glucopyranosyl moiety in **B**. Comparison of the ^{13}C shifts with literature data of quercetin 3-*O*-galactoside and 3-*O*-glucoside (*26*−*28*) confirmed the presence of a galactose moiety in compound **A** and of a glucose moiety in compound **B**.

On the basis of mass spectrometry and UV and NMR spectral data, compounds **A** and **B** could unambiguously be identified as rhamnetin 3-*O*-β-galactopyranoside and rhamnetin 3-*O*-β-glucopyranoside, respectively. Although these rhamnetin glycosides have been reported in other plants, complete ^{1}H and ^{13}C NMR characterization could so far not be found in the literature. Because of the limited sample amount, the absolute configuration of the hexoses could not be elucidated.

According to Harborne and Baxter (*29*), 22 rhamnetin glycosides have been described so far. However, to our knowledge, this is the first report on the occurrence of rhamnetin 3-*O*-β-galactopyranoside and 3-*O*-β-glucopyranoside in mango peels.

Flavonols and Xanthones. The separation of polyphenols in a peel extract of the cultivar Ngowe is shown in **Figure 2**. Because their characterization has recently been reported in detail (*21*), UV/vis and mass spectrometric data are not given in the present communication. Mangiferin, isomangiferin, quercetin 3-*O*-galactoside, -3-*O*-glucoside, -3-*O*-xyloside, -3-*O*-arabinopyranoside, -3-*O*-arabinofuranoside, -3-*O*-rhamnoside, kaempferol 3-*O*-glucoside, and quercetin were unambiguously identified. The compounds **3** and **4** were tentatively identified as mangiferin gallate and isomangiferin gallate. Compound **5** was assigned to a quercetin 3-*O*-diglycoside. Peak **13** consists of rhamnetin 3-*O*-galactoside and -3-*O*-glucoside. As described above, their separation could only be achieved under isocratic conditions. The contents of flavonol and xanthone glycosides in the peels of 14 mango cultivars are shown in **Table 3**. Mangiferin was the predominant compound in the cultivars

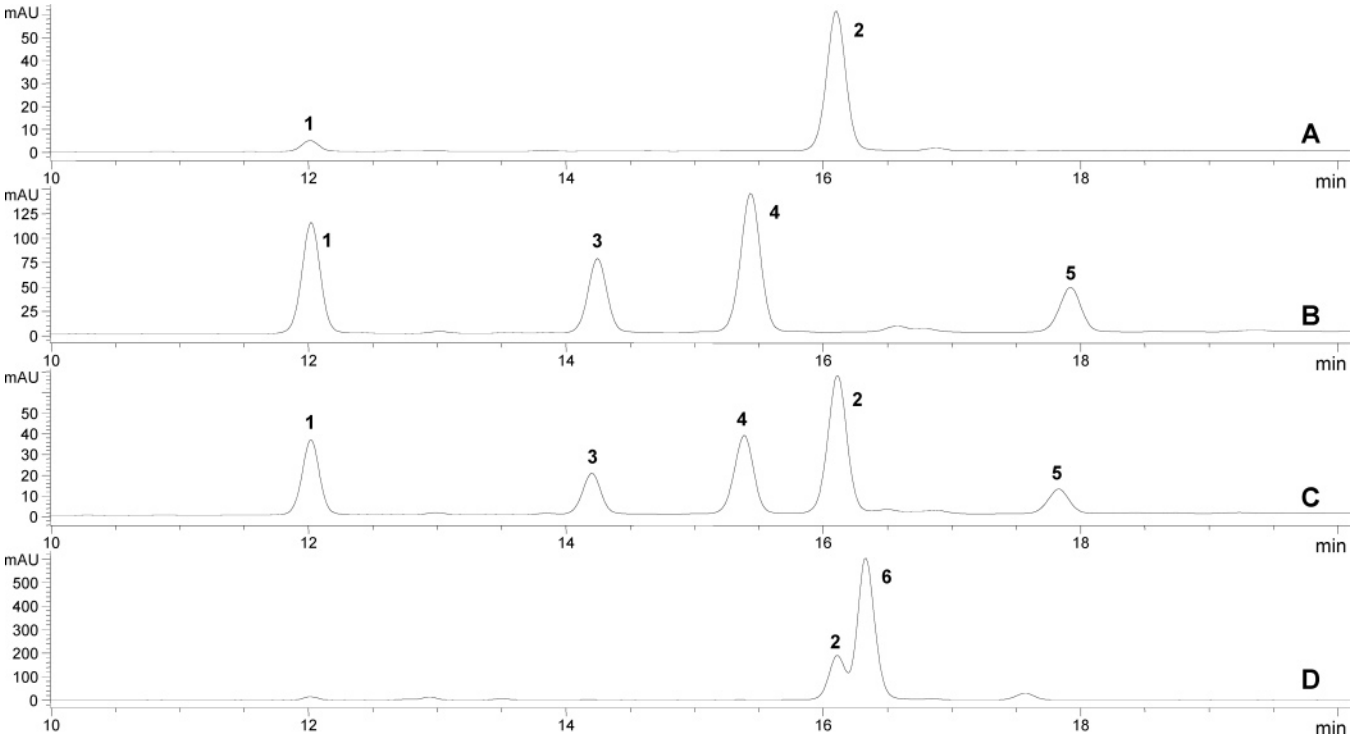

Figure 3. HPLC separation of anthocyanins (520 nm). (A) Mango peel extract (cv. Tommy Atkins), (B) cranberry extract, (C) mango peel extract spiked with cranberry extract, and (D) mango peel extract spiked with peonidin 3-*O*-glucoside standard. Peak assignments: 1, cyanidin 3-*O*-galactoside; 2, unknown anthocyanidin hexoside; 3, cyanidin 3-*O*-arabinoside; 4, peonidin 3-*O*-galactoside; 5, peonidin 3-*O*-arabinoside; and 6, peonidin 3-*O*-glucoside.

Table 5. Contents of Anthocyanins of Peels from Red-Colored Mango Cultivars (μg/kg Dry Matter)

	cyanidin 3-*O*-galactoside[a]	anthocyanidin hexoside[b]	total content
Tommy Atkins	234 ± 15	3485 ± 290	3719 ± 291
R2E2	ND[c]	211 ± 7	211 ± 7
Kent	85 ± 4	422 ± 2	507 ± 5
José	4 ± 2	279 ± 20	283 ± 20
Haden	206 ± 10	1488 ± 15	1694 ± 18
Heidi	1165 ± 99	1755 ± 90	2920 ± 134

[a] Quantified as cyanidin 3-*O*-glucoside. [b] Quantified as peonidin 3-*O*-glucoside. [c] ND, not detected.

Chok Anan, Tommy Atkins, Maha Chanock, and Kaew, with the contents ranging from ~300 to 1300 mg/kg on a dry matter basis. Considerably smaller amounts were found in the cultivars Haden and Kent. As compared to mangiferin, the contents of its isomer isomangiferin and of the galloylated derivatives were usually much lower within a given cultivar. In the majority of samples investigated, quercetin 3-*O*-galactoside was the predominant compound, amounting from ~120 (Mon Duen Gao) to almost 1470 (José) mg/kg. Only in the case of the cultivars R2E2 and Kaew was quercetin 3-*O*-glucoside present in slightly higher amounts. Most strikingly, the amounts of individual quercetin monoglycosides usually decreased in the order quercetin 3-*O*-galactoside > -3-*O*-glucoside > -3-*O*-xyloside > -3-*O*-arabinopyranoside > -3-*O*-arabinofuranoside > -3-*O*-rhamnoside. An identical profile has already been found in our previous studies (*21*, *22*) and therefore appears to be highly characteristic of mango. Because these findings have now been confirmed in a more comprehensive screening of mango cultivars, it becomes evident that the profile of flavonol glycosides is particularly useful for authenticity control, especially since intermediates such as mango puree may also be produced without peeling. Total amounts of identified flavonols and xanthones ranged from ~360 (Mon Duen Gao) to 4860 (José) mg/kg. These results demonstrate that mango peels are a rich source of phenolic compounds; however, significant differences between the cultivars were found.

Selected cultivars were also investigated for their polyphenolic contents in the flesh. Such studies are of interest both from a nutritional and from a technological point of view, since the flesh represents the major part of the edible portion of the fruit and mangos are known to be particularly prone to browning. From **Table 4**, it can be seen that only in five of the nine cultivars investigated were flavonol and xanthone glycosides detectable at all. However, as compared to the peels, only very small amounts of mangiferin were present. In the cultivar Haden, quercetin 3-*O*-galactoside and -3-*O*-glucoside were also found. These findings are consistent with previous reports that during mango fruit development total polyphenolics are higher in the peel than in the flesh at all stages (*30*). However, the question is raised as to which phenolic compounds are responsible for browning reactions in the flesh. According to Prabha and Patwardhan (*31*), gallic acid is the substrate of polyphenol oxidase in the fruit pulp, whereas ellagic acid is the predominant substrate in mango peel. Our previous investigations have shown that both gallic acid and gallotannins were present in a commercial mango puree concentrate; however, at that time, it could not conclusively be clarified whether these compounds originate from the peels or from the flesh (*22*). We have also demonstrated that the peels were rich in gallotannins, while the flesh proved to be a poor source of these compounds (*32*). Although no evidence for the presence of ellagic acid and ellagitannins has so far been obtained, it cannot be ruled out that small amounts of gallic acid in the flesh and of ellagic acid in the peels may contribute to enzymatic browning. These investigations are a subject of our current research program.

Anthocyanins. Among the 14 cultivars investigated in the present study, Tommy Atkins, R2E2, Kent, José, Haden, and Heidi showed a red-colored skin and were therefore also

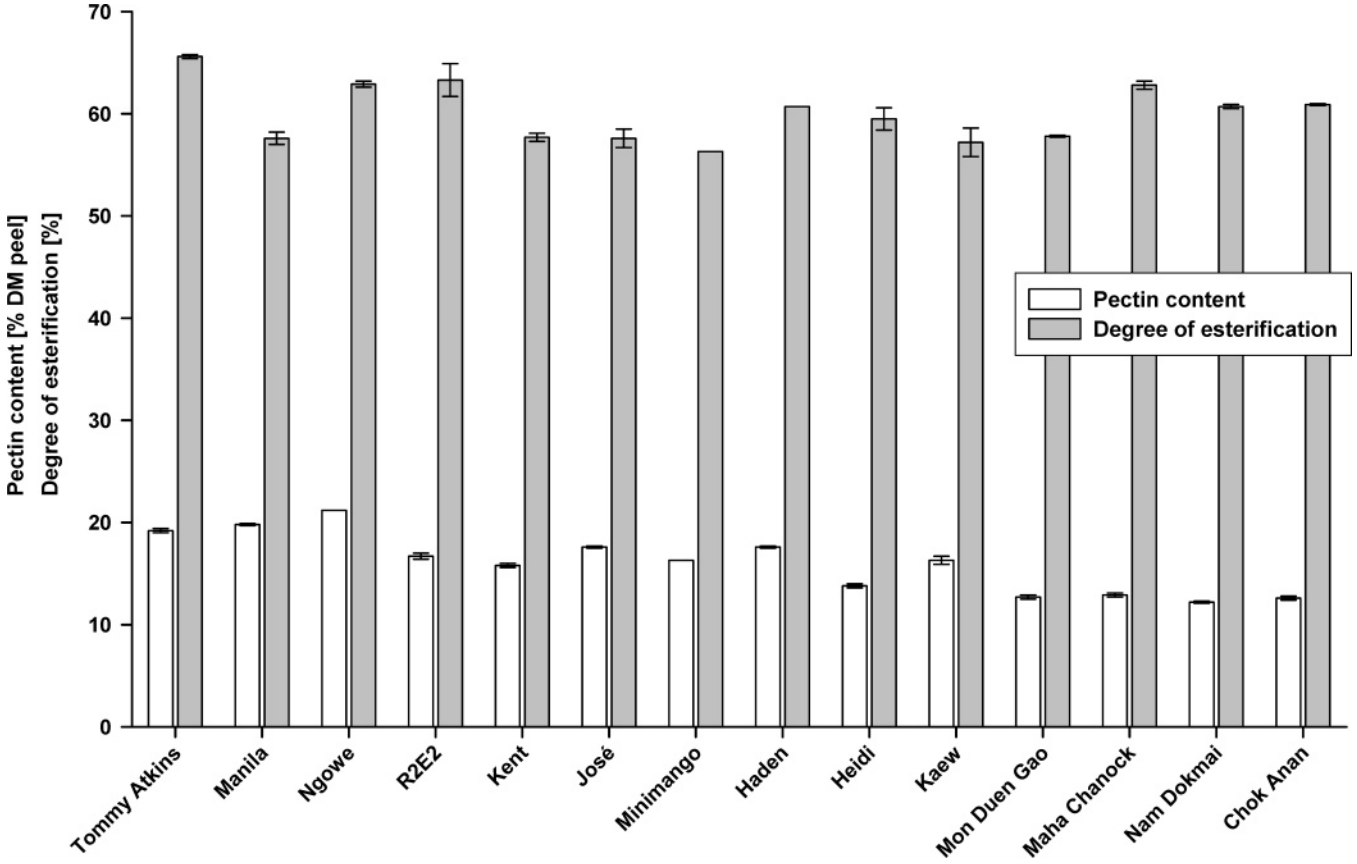

Figure 4. Pectin content and degree of esterification in peels of selected mango cultivars.

examined for their anthocyanin profile and content. The separation of the anthocyanins from an extract of Tommy Atkins peels is shown in **Figure 3A**. Peak 1 showed an $[M]^+$ ion of *m*/*z* 449 and a fragment ion of *m*/*z* 287 in the MS^2 experiment. The collision-induced fragmentation of the $[M]^+$ ion of peak 2 (*m*/*z* 463) yielded a fragment ion of *m*/*z* 301. On the basis of their mass spectra, these compounds were tentatively identified as cyanidin and peonidin hexosides, respectively. For further characterization, a Tommy Atkins peel extract was spiked with cyanidin and peonidin 3-*O*-glucoside standard substances and a cranberry (*V. macrocarpon*) extract, since cranberries are a rich source of cyanidin and peonidin 3-*O*-galactoside and -arabinoside (*33*). Through coelution experiments with the cyanidin 3-*O*-galactoside of the cranberry extract, peak 1 could be identified as cyanidin 3-*O*-galactoside (**Figure 3B**,**C**). To our knowledge, this marks the first report on the presence of cyanidin 3-*O*-galactoside in mango. The spiking experiments with the cranberry extract and peonidin 3-*O*-glucoside standard (**Figure 3C**,**D**), respectively, revealed that peak 2 could neither be assigned to peonidin 3-*O*-galactoside nor to peonidin 3-*O*-glucoside, which is in contrast to the findings of Proctor and Creasy (*34*) who identified peonidin 3-*O*-galactoside in mango fruit. Therefore, preparative isolation and structural elucidation of this compound by NMR spectroscopy are currently under way. From **Table 5**, it can be seen that the total anthocyanin contents of the peels of red-colored mango cultivars ranged from 211 (R2E2) to 3719 (Tommy Atkins) μg/kg dry matter, with the unknown anthocyanidin hexoside being present in higher amounts in all samples. As compared to other sources such as grape pomace (*23*), it becomes evident that mango peels are a very poor source of anthocyanins.

Pectin. Pectin contents of the lyophilized peels ranged from 12.2 (Nam Dokmai) to 21.2% (Ngowe) (**Figure 4**), which is in agreement with previous studies where contents between 13 and 25% were reported (*12*−*14*, *17*−*20*). Remarkably, in four of the six Thai mango cultivars, relatively low pectin contents were determined. Starch was not detectable in the pectin samples. Pectins of all cultivars investigated showed a high degree of esterification, ranging from 56.3 to 65.6%. Values reported in the literature varied from 62 to 86% (*12*, *17*−*20*), which might be explained by differences in ripeness degree or in the pectin extraction process, especially in the time−temperature regime applied. As compared with dried apple pomace and citrus peels, which contain approximately 10−15 and 20−35% pectin (*35*) with a degree of esterification of 70−88 and 70−74% (*36*, *37*), respectively, mango peels are a promising source of high-quality pectin. However, for industrial exploitation, immediate drying of peels is a prerequisite to avoid microbial spoilage, deesterification, and depolymerization of pectin, respectively. Furthermore, standardized extraction processes need to be established to warrant uniform quality.

In conclusion, the results of the present study demonstrate that mango peels are a rich source of polyphenolics, which may be used as natural antioxidants or as functional food ingredients. In this context, the cultivars José, Tommy Atkins, Ngowe, Haden, and Heidi have been shown to be most attractive; however, apart from cultivar-dependent differences, other factors such as ripening degree may also affect polyphenol contents. With respect to the pectin content and quality, Ngowe, Manila, and Tommy Atkins appear to be the most promising cultivars. As mentioned in a previous report (*21*), the increasing tendency to maximize apple juice yields by the use of depolymerizing enzymes may result in a scarcity of apple pomace as a source of pectin. Mango peels may represent a promising alternative to apple pomace, especially since they are available in large amounts. For these reasons and in continuation of our recent

investigations on apple pomace utilization (*38*), a process for the recovery of pectin and polyphenolics from byproducts of mango fruit processing is currently being developed.

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