Available online at www.sciencedirect.com
SCIENCE DIRECT®
Carbohydrate Polymers 54 (2003) 183–192
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Effect of roasting on the carbohydrate composition of *Coffea arabica* beans

A. Oosterveld, A.G.J. Voragen, H.A. Schols*

Laboratory of Food Chemistry, Department of Agrotechnology and Food Sciences, Wageningen University, P.O. Box 8129, 6700 EV Wageningen, The Netherlands

Received 24 March 2003; accepted 8 May 2003

Abstract

Coffee beans (arabica) with different degrees of roast were sequentially extracted with water (90 °C, 1 h), water (170 °C, 30 min), and 0.05 M NaOH (0 °C, 1 h). The amount and composition of polysaccharides, oligosaccharides and monosaccharides in the extracts and residues were analyzed. The results were compared with the composition of the same batch of green arabica coffee beans. Although part of our results were already reported in rather fragmented studies, this study gives a more complete overview of the amount and composition of unextractable polymers, extractable polymers, oligomers, monomers, and their conversion into (non-sugar) degradation products as a function of their degree of roast.

It was found that most carbohydrates in the roasted coffee bean were present as polysaccharides (extractable or unextractable). The fact that only a small part of the carbohydrates in the extracts were recovered as oligomer and even less as monomers, showed that oligomers and especially monomers were converted very rapidly into Maillard and pyrolysis products. Cellulose remains unextractable and its solubility was not affected by the degree of roast. Galactomannans were also mainly present as unextractable polymers in green beans, but were solubilized to a large extent with increasing degrees of roast. The arabinogalactans in the roasted bean were highly soluble at the extraction conditions used. The arabinose as present as side-chains in the arabinogalactans were found to be more susceptible to degradation at more severe roasting conditions than the galactans. Also evidence was found that populations of arabinogalactans with very different ara:gal ratios exist in the roasted beans as well as in the green beans.

Keywords: Arabica; Coffee beans; Roasting; Arabinogalactans; Galactomannans

1. Introduction

Roasting is an essential step in coffee production for the formation of various types of 'flavour' compounds. The conversion of carbohydrates contributes significantly to the formation of these compounds (Maria, Trugo, Moreira, & Werneck, 1994; Steinhauser, Oestreich-Janzen, & Baltes, 1999). Two types of polysaccharides are the predominating carbohydrates in coffee beans and extracts thereof: arabinogalactan type II and galactomannans (Fischer, Reimann, Trovato, & Redgwell, 2001; Wolfrom, Plunkett, & Laver, 1960). The arabinogalactans consist of a main chain of 1 → 3-linked galactose branched at C-6 with side-chains containing arabinose and galactose residues (Fischer, Reimann, Trovato, & Redgwell, 1999; Fischer et al., 2001). The galactomannans in green coffee beans are composed of a backbone of 1 → 4-linked mannans with single unit galactose side-chains at C-6 (Fischer et al., 1999; Navarini et al., 1999). The most important polysaccharide conversion reactions which occur during roasting and extraction are shown in Fig. 1. The roasting process is responsible for opening the cell-wall matrix resulting in the solubilization of polysaccharides upon extraction (Leloup & Liardon, 1993). This is caused by hydrolysis reactions, which result in a decrease in molecular weight of the polysaccharides (Leloup & Liardon, 1993). Additionally, the degree of branching of the arabinogalactans and galactomannans decreases (Leloup & Liardon, 1993; Nunes & Coimbra, 2001). This may result in a decreased solubility of these polysaccharides. The ongoing hydrolysis of the polysaccharides results in a release of

* Corresponding author. Fax: +31-317-484893.
E-mail address: henk.schols@wur.nl (H.A. Schols).

0144-8617/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0144-8617(03)00164-4

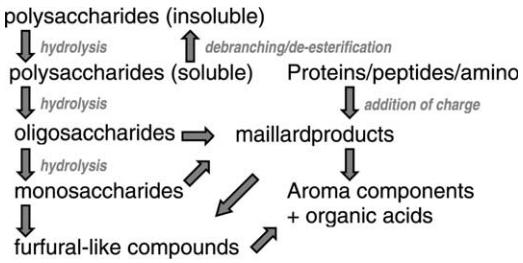

Fig. 1. Schematic representation of the polysaccharide conversion reactions which occur during roasting and extraction of coffee beans.

oligosaccharides and monosaccharides, which in their turn are converted into their degradation products (Steinhauser et al., 1999).

In the current manuscript the effect of the degree of roast on the carbohydrates present in roasted coffee beans was investigated. While in previous manuscripts the investigations towards the effect of roasting of coffee beans focussed mainly on one aspect of the degradation reactions (e.g. polysaccharide composition or release of monosaccharides), this study gives a more complete overview of the amount and composition of unextractable polymers, extractable polymers, oligomers, monomers, and the conversion into (non-sugar) degradation products in coffee beans as a function of their degree of roast.

2. Experimental

2.1. Materials

Green *Coffea arabica* beans were roasted to a degree of roast of 11% (Light), 15% (Medium), and 22% (Dark), respectively (DR; expressed as the percentage of dry weight loss of green coffee beans).

2.2. Extraction of polysaccharides from the roasted coffee beans

Ground coffee beans were Soxhlet-extracted for 6 h with petroleum ether to remove the lipids. Defatted ground coffee beans (100 g) were sequentially extracted with 2000 ml of water (90 °C, 1 h), water (170 °C, 20 min), and 0.05 M NaOH + 0.02 M $NaBH_4$ (0 °C, 1 h). All extracts were neutralized to pH 6, dialyzed, and freeze dried. The monosaccharide content of the extracts was determined before dialysis. The content of low molecular weight material (LMWM; monomers plus oligomers) was determined by filtration over a 10 kDa filter membrane. Subsequently, the filtrate was analysed.

2.3. Analytical methods

The uronic acid contents of the extracts were determined by the automated *m*-hydroxy biphenyl assay (Thibault, 1979). The neutral sugar compositions were determined after prehydrolysis with 72% sulphuric acid, hydrolysis with 1 M sulphuric acid and conversion into alditol acetates as described previously (Oosterveld, Beldman, Schols, & Voragen, 1996).

2.4. Chromatography

High-performance size-exclusion chromatography (HPSEC) was performed on three Bio-Gel TSK columns in series (60XL–40XL–30XL) as described (Oosterveld, Beldman, Schols, & Voragen, 2000) using 0.2 M $NaNO_3$ as eluens. The effluent was partitioned in fractions of 0.24 ml using a Gilson FC-203B fraction collector. The fractions obtained by HPSEC were pooled as indicated in the corresponding figures and the sugar compositions were determined by high-performance anion-exchange chromatography (HPAEC) after hydrolysis with 2 M TFA as described by Ruiter, Schols, Voragen, & Rombouts (1992).

3. Results and discussion

3.1. Influence of the degree of roast (DR) on the carbohydrate composition of roasted arabica coffee beans

The carbohydrate content of the arabica coffee beans with different degrees of roast decreased from 41.8% w/w for light roasted coffee beans to 36.5% w/w for dark roasted coffee beans (Table 1). Taking into account the loss of dry matter as a result of the roasting process, 37 g of carbohydrates remained for light roasted coffee beans from the initial 46 g present in 100 g of green beans, while only 29 g remained in dark roasted coffee beans. This means that during roasting 20–37% of the carbohydrates is converted into degradation products, depending on the degree of roast. These results were in agreement with the results found by Redgwell, Trovato, Curti and Fischer (2003).

The carbohydrates in light roasted coffee beans consisted mainly of mannose (48 mol%), galactose (23 mol%), and glucose (15 mol%), originating from galactomannans, (arabino)galactans, and cellulose (Table 1). The effect of

Table 1
Sugar composition of light, medium, and dark roasted coffee beans (mol%)

	Green	Light	Medium	Dark
Rhamnose	1	1	1	1
Arabinose	10	7	6	5
Xylose	1	1	1	1
Mannose	42	48	51	51
Galactose	24	23	22	21
Glucose	18	15	16	18
Uronic acid	6	5	4	4
Total sugar (% w/w)	46	42	41	37
Degree of roast	0	11	15	22

roasting on the sugar composition of the coffee beans is significant. The relative content of the pectic sugars arabinose, galacturonic acid, galactose and, to a lesser extent, rhamnose in the coffee bean decreased with increasing degree of roast. On the other hand, the relative abundance of mannose and glucose in the beans increased as a result of the loss of other sugars. The recovery of the main sugars from coffee roasted beans as compared to the amount of each sugar in the initial green bean is shown in Fig. 2. Arabinose was the sugar most sensitive to degradation during roasting, with a loss of 44% for the light roasted coffee beans and 66% for the dark roasted coffee beans. Almost half of the galactose was degraded during roasting, indicating that the composition of the arabinogalactans in the coffee beans changes significantly with increasing degree of roast. Mannose was the least sensitive to the roasting conditions; Only 5% of mannose was lost for the light roasted coffee and 28% for the dark roasted coffee. Glucose also appeared to be very stable under the roasting conditions used, although an initial drop in the glucose recovery was noticed, probably as a result of the conversion of sucrose, which was found to be present in the green bean (6–7% w/w) (Mazzafera, 1999; Wolfrom et al., 1960), although this effect was not seen by Redgwell et al. (2003). The reactivity of the various sugars during roasting was seen before in roasted coffee beans (Clifford, 1985, Nunes & Coimbra, 2003; Redgwell et al., 2003).

3.2. Characterization of polysaccharides in the extracts and residues obtained from roasted coffee beans

In order to study structural differences in the individual polysaccharides present in light, medium, and dark roasted coffee beans, polysaccharide fractions were isolated by sequential extraction with water at 90 and 170 °C, and with 0.05 M NaOH. The yields and compositions of these extracts and the residues are shown in Table 2.

25–27% of the carbohydrates present in the roasted coffee beans could be extracted as polysaccharides with water at 90 and 170 °C, and with 0.05 M NaOH (Table 2). Although the amount of sugars extracted from the roasted beans was comparable for light, medium, and dark roasted coffee beans, the sugar composition of the polymeric fraction varied significantly. The extractability of the sugars had the following order: galactose > rhamnose > uronic acid > arabinose > mannose > glucose. A major part of the polysaccharides from the roasted arabica bean was recovered in the residue: 45% for the dark roasted beans to 59% for the light roasted bean.

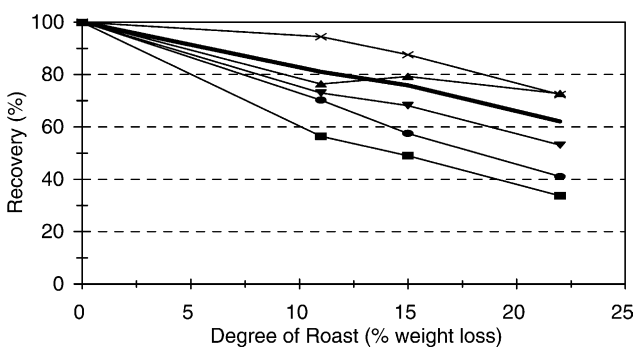

Fig. 2. Recovery of the predominant individual sugars in coffee beans as a function of the degree of roast. Green coffee beans have a degree of roast of 0. ×: mannose; ▲: glucose; ▼: galactose; ●: uronic acid; ■: arabinose. Thick line: recovery of (total) polysaccharides as a function of the degree of roast.

Extraction of light roasted coffee with water at 90 °C beans yielded an extract consisting mainly of polysaccharides containing mannose (39 mol%) and galactose (38 mol%). The mannose:galactose ratio of 1.0 was in agreement with the results found by Leloup and Liardon (1993) for a hot water extract obtained from roasted coffee beans by extraction for 30 min at 95 °C. However, Nunes and Coimbra (2003) found a ratio of mannose:galactose of ~0.55 for a 90 °C hot water extract. Also, some arabinose (13 mol%) and galacturonic acid (7 mol%) was present in the 90 °C extract. This sugar composition indicates the presence of galactomannans, arabinogalactans, and pectins. When comparing the polymeric fraction of the 90 °C extract from the light roasted coffee beans with those from the medium and dark roasted coffee beans, a decrease of the relative amount of arabinose, galactose, and galacturonic acid was found for coffee beans with a higher degree of roast. Also, the ratio arabinose:galactose decreased from 0.34 for the 90 °C extract from light roasted coffee beans to 0.24 for dark roasted coffee beans. The mannose content increased significantly showing that the extractability of the galactomannans in coffee beans increased with increasing degree of roast. Extraction of light roasted coffee beans with water at 170 °C yielded a polymeric fraction with a high galactose content, indicating that it contained mainly (arabino)galactans. This was in agreement with the results found by Leloup and Liardon (1993) for extraction of roasted coffee beans for 15 min at 180 °C. In comparison with the 90 °C water extract the ratio arabinose:galactose was much lower in the 170 °C water extract (0.12 versus 0.34, respectively). Apparently, arabinose is removed from the arabinogalactans at these high extraction temperatures, or a different type of galactan, containing less arabinose, is released.

In the polymeric fraction of the 170 °C extracts of the medium and dark roasted coffee beans lower relative galactose and arabinose contents were found in comparison to the light roasted coffee beans. In the extract from the medium and dark roasted coffee beans the relative mannose content was significantly higher when compared to light roasted beans (0.24 versus 0.41 and 0.83, respectively). The mannose:galactose ratio increased from 0.24 for light roasted beans to 0.41 and 0.83 for medium and dark roasted coffee beans, respectively. Our results indicate that a darker degree of roast results

Table 2
Composition of the polymeric fraction of extracts obtained from roasted Arabica coffee beans

		Sugar residues (mol%)							Sugars (%w/w)	Sugars (g/100 g beans)	Yield (% w/w)
		Rha	Ara	Xyl	Man	Gal	Glc	UA			
Light	Water, 90 °C	2	13	0	39	38	1	7	51	4.6	9
	Water, 170 °C	0	8	0	16	67	0	8	65	5.2	8
	0.05 M NaOH	0	8	0	18	63	1	10	25	0.5	2
	Residue	0	1	1	67	2	27	2	59	23.6	40
Medium	Water, 90 °C	1	10	0	43	38	1	7	54	4.9	9
	Water, 170 °C	0	7	0	25	61	1	7	67	4.7	7
	0.05 M NaOH	0	7	0	27	57	1	7	25	0.8	3
	Residue	0	1	1	66	2	28	2	57	20.5	36
Dark	Water, 90 °C	1	8	0	51	33	2	5	51	5.6	11
	Water, 170 °C	0	5	0	40	48	1	7	56	3.9	7
	0.05 M NaOH	0	6	0	30	51	6	7	20	0.6	3
	Residue	1	1	1	60	3	34	1	53	17.5	33

in an increased extractability of the (galacto)mannans. Our findings on the behaviour of galactomannans upon roasting was in agreement with Leloup, Michieli, and Liardon (1997) and Nunes and Coimbra (2003). The same effect of roasting on the sugar composition was also found for the polymeric fraction of the 0.05 M NaOH extract.

It was found that after removing the polysaccharides soluble in water at 90 °C the sugar composition of the extract obtained with water at 170 °C and with 0.05 M NaOH still depended on the degree of roast. This shows that the extraction behaviour and solubilization of unextractable polysaccharides depend on the degree of roast of the coffee beans, probably as a result of structural and architectural changes which occur in the coffee bean during roasting.

The residues had a high polysaccharide content and consisted almost exclusively of mannose and glucose, showing that mannans and cellulose are very hard to extract under the conditions used, whereas most of the arabinogalactans and pectins were solubilized. However, the decreasing mannose contents of the residues showed that the solubilization of mannans increased with increasing degree of roast.

3.3. Characterization of low molecular weight material in the extracts obtained from roasted coffee beans

In order to obtain insight in the carbohydrate conversion processes which occur during roasting and extraction of coffee beans, not only the characteristics of the polysaccharide fraction were investigated, but also the characteristics of the low molecular weight fraction which was separated by dialysis (Table 3). This fraction consisted of both oligomers and monomers.

The yields of the LMWM of 90 °C extracts of the roasted coffee beans increased from 2 to 3% w/w from light to dark roast. Especially arabinose and uronic acid were found in relatively high proportions in the LMWM of roasted beans indicating that the arabinogalactans and pectins were relatively easily degraded to oligomers and monomers during roasting. With increasing degree of roast both the relative and absolute amounts of arabinose and uronic acid of LMWM decreased in favour of mannose and galactose. This again confirms that an increase in the degree of roast also results in an increase in the galactomannan degradation.

For the 170 °C extracts of the roasted coffee beans the yields of the LMWM were found to vary from 1.8 to 2.5%

Table 3
Sugar composition (mol%) and yields (g per 100 g roasted coffee) of LMWM from extracts obtained from roasted coffee beans

	Rha	Ara	Xyl	Man	Gal	Glc	UA	Yield of LMWM g/100 g beans
Light 90 °C	2	17	1	30	28	7	16	2.0
Light 170 °C	1	24	0	26	38	2	10	2.4
Light 0.05 M NaOH	0	21	0	27	30	0	21	0.7
Medium 90 °C	2	18	0	24	34	6	16	1.8
Medium 170 °C	1	22	0	31	32	2	12	1.8
Medium 0.05 M NaOH	0	16	0	39	31	0	14	0.8
Dark 90 °C	1	9	0	40	38	5	8	3.0
Dark 170 °C	1	16	1	45	27	2	9	2.5
Dark 0.05 M NaOH	1	12	1	38	33	3	13	1.0

w/w. Due to the sequential extracion, it can be concluded that the LMWM fraction found in the 170 °C extracts was formed during the extraction. The relative arabinose content in LMWM had increased threefold in comparison with the initial roasted beans, indicating that especially arabinose containing oligomers and monomers were formed during extraction at 170 °C, as was also found in several other studies (Blanc, Davis, Parchet, & Viani, 1989; Leloup et al., 1997; Steinhauser et al., 1999). It was found that the relative level of arabinogalactans in the LMWM decreased with increasing degree of roast, while the galactomannan content increased significantly.

The same effect was observed for the 0.05 M NaOH extract releasing another 1% w/w of LMWM.

3.4. Characterization of monomers in the extracts obtained from roasted coffee beans

The free monomers present in the extracts obtained from light, medium, and dark roasted coffee beans were also analysed (Table 4). While the yields of the polysaccharides in the 90 °C extracts of the roasted coffee beans were approximately 4.6 g/100 g of roasted beans, and the oligosaccharide yields were approximately 2.0 g/100 g of roasted beans, the free monomer yields were much lower (28 mg/100 g of beans). Arabinose was the most abundant monomer in the 90 °C extracts, but also galactose and glucose were present in relatively high quantities. The glucose content was much lower than expected based on the sucrose content in the green beans (Wolfrom et al., 1960). Apparently, most of the sucrose was converted into sugar degradation products even at relatively mild roasting conditions. It was found that the relative arabinose and galactose content decreased somewhat with increasing degree of roast, while the glucose content increased. The free monomer levels in the 170 °C extracts were much higher than those of the 90 °C extracts (237 mg/100 g of beans). It was found that mainly mono-arabinose was present in this extract (69 mol%), while also some galactose (14 mol%) and mannose (5 mol%) was present. These results were in agreement with the results found by Blanc et al. (1989). The degree of roast only slightly affects the composition of the 170 °C extract. The free monomer content in the 0.05 M NaOH extract was only 53 mg/100 g. Arabinose was again the predominant free monomer (91 mol%) in this extract, while the galactose content was very low (2.6 mol%), and this composition was quite constant for all roasting conditions.

3.5. Molecular weight distributions of the extracts from roasted coffee beans

In order to obtain more insight in the polysaccharide populations present in the extracts obtained from light, medium, and dark roasted coffee beans, the extracts were separated based on their molecular weight by HPSEC, fractionated into four pools and analysed.

The molecular weight distributions of the 90 °C extracts show a main population eluting at 26 min. It seems that a small shoulder eluted at approximately 29 min (Fig. 3a). The intensity of this shoulder is affected by the degree of roast. It was found that fractions could be obtained quite conveniently after HPSEC, allowing us to obtain valuable information on the sugar composition of the different molecular weight populations. The neutral sugar composition of pool I of the 90 °C extract shows the presence of a large amount of galactose, glucose, and mannose (Fig. 3a, Table 5a). Especially the accumulation of all glucose in the high molecular weight material was surprising. This indicates that glucose containing polysaccharides (for instance glucomannans) are present in this population. It was found that the glucose, and also the arabinose content decreased with increasing degree of roast in the high molecular weight population. The mannose rich polymer seemed to be much more resistant upon roasting. Pool II, III, and IV consisted mainly of arabinose, galactose, and mannose. The mannose content was the highest in pool II, indicating that the mannans had a relatively high molecular weight, while galactose, and arabinose were more abundant in the low molecular weight fractions. Additionally, the ratio arabinose:galactose increased with decreasing molecular weight. The presence of high molecular weight

Table 4
Free monomer composition (mol%) of extracts obtained from roasted Arabica coffee beans

	Rha	Ara	Gal	Glc	Man	Xyl	Monomer yield (mg/100 g beans)
Light 90 °C	5	42	25	19	0	9	28
Light 170 °C	11	69	14	2	5	0	237
Light 0.05 M NaOH	0	91	3	1	5	0	53
Medium 90 °C	9	38	21	24	0	8	23
Medium 170 °C	13	65	15	2	6	0	201
Medium 0.05 M NaOH	0	96	1	0	3	0	47
Dark 90 °C	8	34	20	32	0	7	30
Dark 170 °C	14	59	19	2	7	0	191
Dark 0.05 M NaOH	0	91	3	1	5	0	48

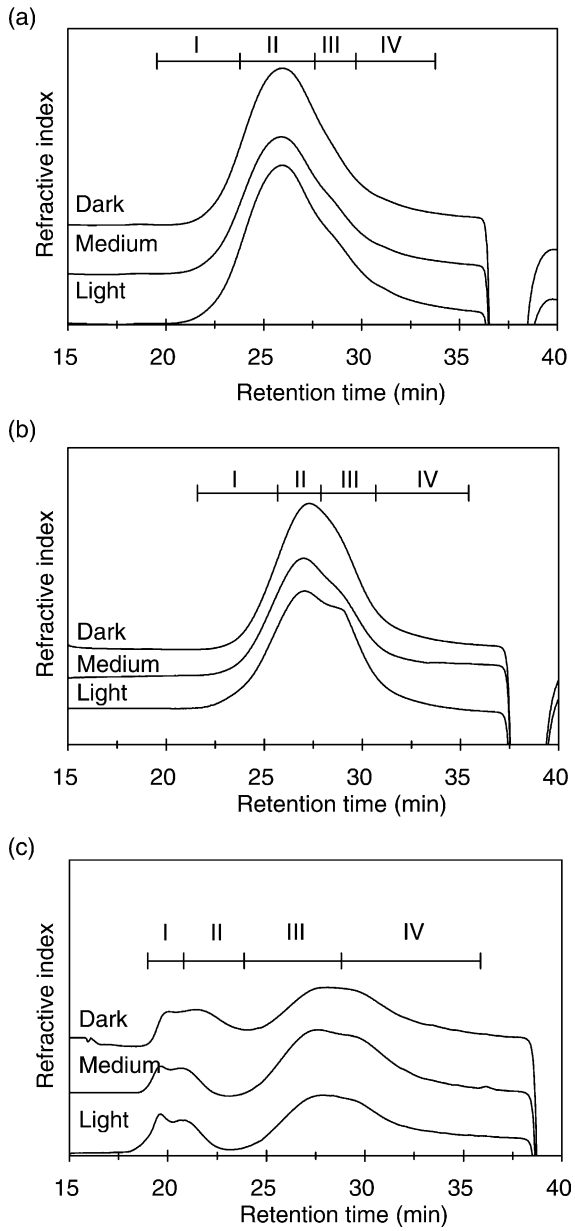

Fig. 3. Molecular weight distributions (HPSEC) of (a) water extracts (90 °C); (b) water extracts (170 °C); and (c) 0.05 m NaOH extracts from light, medium, and dark roasted coffee beans.

Table 5
Sugar composition of HPSEC pools from light, medium, and dark roasted coffee beans (mol%)

		Rha	Ara	Gal	Glc	Man
(a) *Water extracts (90 °C)*						
Light	Pool I	3	9	39	23	27
	Pool II	4	12	36	2	47
	Pool III	6	15	40	3	36
	Pool IV	4	22	42	7	26
Medium	Pool I	2	9	37	21	31
	Pool II	2	11	35	2	50
	Pool III	2	12	40	2	43
	Pool IV	3	18	48	4	28
Dark	Pool I	1	5	40	8	45
	Pool II	1	6	28	3	61
	Pool III	2	8	34	3	53
	Pool IV	2	13	37	4	43
(b) *Water extracts (170 °C)*						
Light	Pool I	3	4	76	9	8
	Pool II	0	9	85	0	6
	Pool III	0	12	71	0	17
	Pool IV	0	12	63	0	25
Medium	Pool I	5	5	77	2	11
	Pool II	0	8	75	1	16
	Pool III	0	7	65	0	28
	Pool IV	0	11	65	0	24
Dark	Pool I	0	3	77	4	17
	Pool II	0	5	57	1	36
	Pool III	0	4	48	3	46
	Pool IV	0	5	46	4	45
(c) *0.05 M NaOH extracts*						
Light	Pool I	5	6	33	0	55
	Pool II	0	4	36	0	60
	Pool III	4	22	70	0	4
	Pool IV	3	27	57	0	12
Medium	Pool I	0	4	51	0	45
	Pool II	1	2	38	0	59
	Pool III	0	27	66	0	7
	Pool IV	0	22	62	0	16
Dark	Pool I	0	8	45	0	47
	Pool II	0	10	63	0	26
	Pool III	0	8	80	3	8
	Pool IV	0	11	68	0	21

galactans with a low arabinose content and low molecular weight galactans with high arabinose contents is not consistent with the idea that only one type of arabinogalactans with a high molecular weight and high arabinose substitution was present in the green bean. Therefore, these results indicate that different types of arabinogalactans are present in the coffee bean cell wall which differ in their arabinose substitution and molecular weight and behaviour during roasting.

The extracts obtained at 170 °C contained a main population eluting at approximately 27.5 min, with a shoulder at 29 min. This shoulder also disappeared with increasing degree of roast. These extracts were fractionated into four pools, as shown in Fig. 3b. Galactose was the most abundant sugar in pool I (Table 5b). The arabinose:galactose ratio was very low in this pool. Galactose was also the most abundant sugar in pool II, III, and IV, but the arabinose and mannose content increased with decreasing molecular weight. Similar findings were found by Leloup and Liardon (1993) and Leloup et al. (1997).

For the 0.05 M NaOH extracts a number of populations could be distinguished (Fig. 3c): two high molecular weight populations eluted at 19 and 21 min, as well as a population which eluted at approximately 27.5 min, with a slight shoulder at 30 min. The populations eluting at 19 and

27.5 min became less distinct with increasing degree of roast. Based on the arabinose:galactose ratio in the pools (Table 5c) and assuming that the galactomannans present had a low gal:man ratio, a clear distinction could be made between high molecular weight arabinogalactans (pool I and II), having a low arabinose substitution, and low molecular weight arabinogalactans with a higher arabinose substitution (Pool III and IV). It could also be observed that both pool I and II, and pool IV had a relatively high mannose content. This may indicate that two galactomannan populations were present in the green coffee beans or that the lower molecular weight population originated from degradation of the high molecular weight population.

3.6. Overview of the carbohydrates present in roasted coffee beans as a function of the degree of roast

Based on a comparison of the results described in Sections 3.1–3.5 an overview was made of the carbohydrates present in roasted coffee beans. From this the percentage of carbohydrates present as unextractable polymers, extractable polymers, oligomers or monomers was calculated as a function of the degree of roast (Table 6). In such a presentation also the degradation of sugars will become visible.

Additionally, the recoveries of arabinogalactans, galactomannans, pectic backbone, and cellulose as unextractable or extractable polymer, oligomer, monomer, or degradation products is presented as a function of the degree of roast (Fig. 4) as calculated from the results given in Table 6, assuming that the galactose:mannose ratio in the galactomannans was 1:20. The cellulose recovery was based on the polymeric and oligomeric fraction.

In the light roasted coffee beans the unextractable polysaccharides represented the predominant carbohydrate fraction: 36% w/w of the carbohydrates initially present in the green bean (Table 6). The extractable polysaccharides represented 21% w/w of the carbohydrates present in the light roasted coffee bean. The oligosaccharides plus monosaccharides were the smallest fraction and accounted for 11% w/w of the polysaccharides. From these figures, it can be calculated that 19% of sugars have been degraded.

A darker roasting of the coffee beans predominantly resulted in a conversion of polysaccharides into sugar degradation products (Table 6b and c; 38% w/w of all carbohydrates). Surprisingly, a darker roast lead to a decrease in the amount of extractable polysaccharides, although it was expected that roasting would lead to solubilisation of polysaccharides upon extraction. Additionally, a small increase in the amount of monomers plus oligomers was found. These results suggest that the conversion of monomers plus oligomers to degradation products is much faster than the reaction of extractable polysaccharides to oligosaccharides. Therefore, the solubilization of unextractable polysaccharides goes together with an even higher degradation of the extractable polymers and an increase in degradation products.

Table 6
Percentage of individual sugars of light roasted coffee beans that was recovered as unextractable polymer, extractable polymer, oligomer, monomer, or that was converted into degradation products

	Rha	Ara	Xyl	Man	Gal	Glc	UA	Total
(a) *Light (DR = 11)*								
Unextractable	6	3	32	54	3	64	13	36
Polymer	20	24	5	12	48	1	30	21
90 °C	17	13	3	9	15	1	13	
170 °C	3	10	2	4	31	0	16	
0.05 M NaOH	0	1	1	0	3	0	2	
Monomer + Oligomer	13	23	3	7	14	2	26	11
90 °C	8	7	2	3	5	2	12	4
170 °C	5	13	1	3	8	1	9	5
0.05 M NaOH	0	3	0	1	2	0	5	1
Monomer	61	55	6	0	0	0		
90 °C	0	0	1	0	0	0		
170 °C	6	4	0	0	0	0		
0.05 M NaOH	0	1	0	0	0	0		
Degradation products	56	44	52	6	27	24	30	19
Not analysed	6	7	9	21	8	10	2	13
Sum	100	100	100	100	100	100	100	100
(b) *Medium (DR = 15)*								
Unextractable	30	4	29	49	3	67	10	35
Polymer	16	20	5	15	42	1	25	19
90 °C	13	12	2	10	16	1	12	
170 °C	2	7	2	5	23	0	12	
0.05 M NaOH	0	1	1	1	3	0	1	
Monomer + Oligomer	11	17	1	6	12	2	22	9
90 °C	8	7	1	2	5	1	10	
170 °C	3	8	0	3	5	0	8	
0.05 M NaOH	0	3	0	2	20	0	4	
Monomer	61	44	4	1	3	0		
90 °C	1	0	4	0	0	0		
170 °C	6	3	0	0	0	0		
0.05 M NaOH	0	1	0	0	0	0		
Degradation products	58	51	54	12	32	21	43	24
Not analysed	_3	8	11	17	12	10	0	14
Sum	100	100	100	100	100	100	100	100
(c) *Dark (DR = 22)*								
Unextractable	16	2	30	34	3	68	5	28
Polymer	16	14	4	21	33	2	22	14
90 °C	13	9	2	13	15	2	11	
170 °C	2	4	2	7	15	0	9	
0.05 M NaOH	0	1	1	1	3	1	1	
Monomer + Oligomer	12	16	7	12	17	3	20	13
90 °C	6	5	0	6	9	2	8	
170 °C	4	8	4	5	5	1	8	
0.05 M NaOH	2	2	2	2	3	0	5	
Monomer	6	4	0	0	0	0		
90 °C	0	0	0	0	0	0		
170 °C	5	2	0	0	0	0		
0.05 M NaOH	0	1	0	0	0	0		
Degradation products	61	66	58	28	47	27	59	38
Not analysed	−4	3	2	5	0	0	−5	7
Sum	100	100	100	100	100	100	100	100

The amount of the individual sugar in the *green* coffee bean is set to 100%. The weight loss during roasting was included.

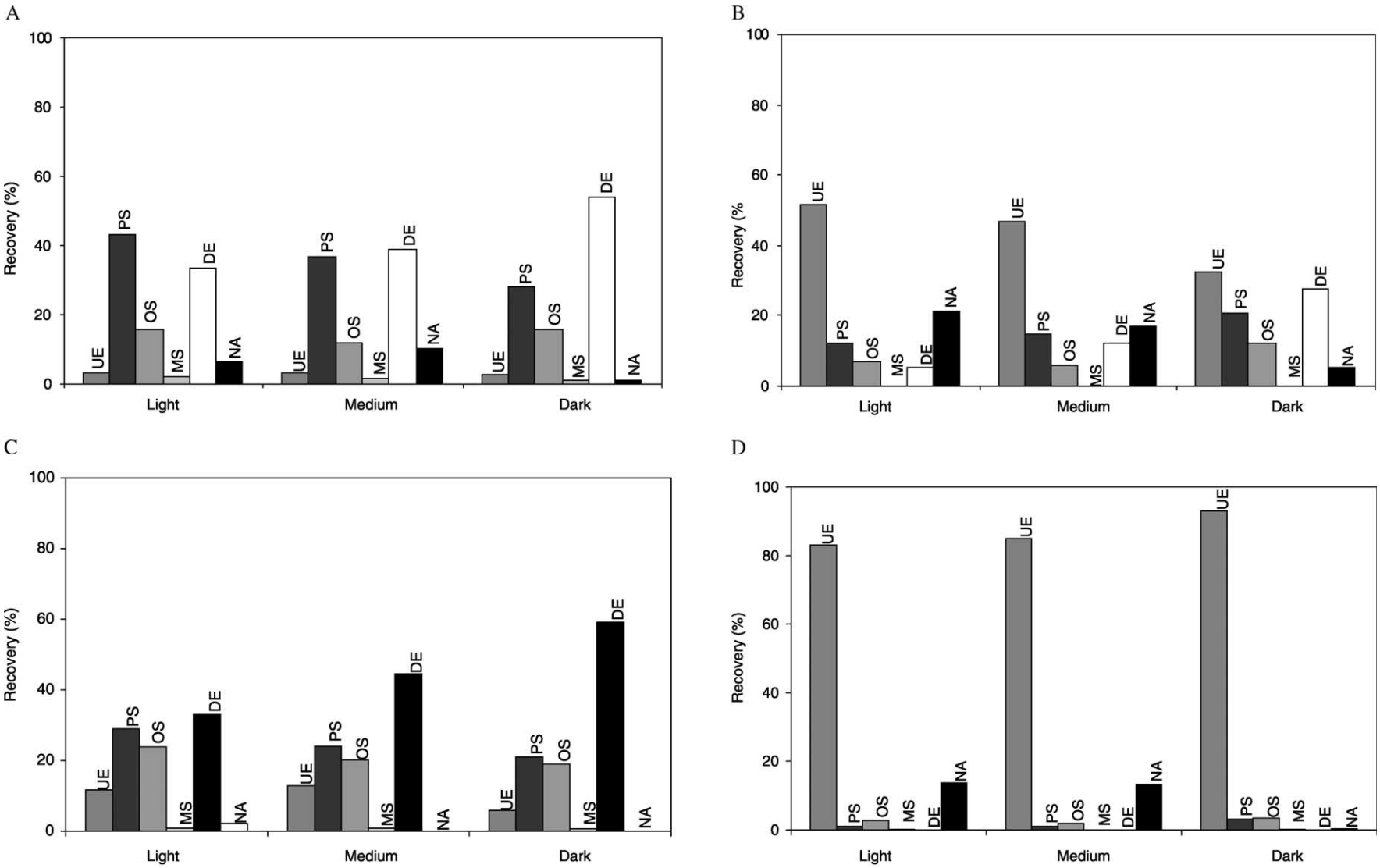

Fig. 4. Recoveries of arabinogalactans (A), galactomannans (B), pectic backbone (C), and cellulose (D) as unextractable polymer (UE), extractable polymer (PS), oligomer (OS), monomer (MS), or degradation products (De) as a function of the degree of roast. NA: not analysed.

However, large differences exist between individual polysaccharides in their reactivity at roasting conditions.

Based on the mannose recoveries shown in Table 6a, it can be concluded that the (galacto)mannans in the light roasted coffee beans were mainly present as unextractable polysaccharides (Fig. 4). Only 12% of the mannose was found in the extractable fractions and only small amounts of mannose were present as mono and oligosaccarides or were not longer recovered as intact sugars. Roasting significantly increased the solubility of the galactomannans (Table 6b and c; Fig. 4): a large decrease in the amount of unextractable mannans was found in favour of an increase in extractable polysaccharides, mono and oligosaccharides and degradation products.

In contrast with the galactomannans, only a very small percentage of the arabinogalactans in light roasted coffee beans were present as unextractable polysaccharides (Table 6a; Fig. 4). The major part of the arabinogalactans were extractable polysaccharides, while another major part was converted into sugar degradation products. Our results show that the debranching of the arabinose side-chains occurs more rapidly than the hydrolysis of the galactan backbone. Additionally, it was found for the extractable polysacharides that large differences exist in the degree of arabinosylation of the arabinogalactans. At least two distinct populations were found: a high Mw arabinogalactan population with a low degree of arabinosylation and a lower Mw arabinogalactan population with a high degree of arabinosylation. In spite of the polysaccharide degradation reactions, which were observed in this study we rationalise that these differences already existed in the green coffee bean. More intense roasting conditions resulted in a loss of extractable polymeric arabinogalactans in favour of a higher amount of sugar degradation products (Table 6b and c).

The backbone of the pectin present in the light roasted coffee bean, made up of uronic acid and rhamnose, was found to be highly extractable (Table 6a; Fig. 4). Large proportions of extractable polymeric fragments of the pectic backbone were present. Also a large part of the pectic backbone was already converted into sugar degradation products in the light roasted bean. Based on the high percentage of sugar degradation products for rhamnose, it is assumed that the rhamnogalacturonan backbone was more easily degradable under the light roasting conditions than the homogalacturonans. More severe roasting conditions showed in particular a conversion of the homogalacturonans to sugar degradation products (Table 6b and c).

The cellulose was found to be highly unextractable, based on the glucose recoveries (Table 6a; Fig. 4). Only very small proportions of cellulose were present as extractable carbohydrates. An increasing degree of roasting had very little effect on the solubility of the cellulose (Table 6b and c).

Xylose was either present in unextractable polysaccharides or as sugar degradation products (Table 6a). This indicated that xylose is present in polysaccharides, with a different reactivity towards roasting. It has been suggested that degradation of xyloglucans as a result of roasting, and that the subsequent loosening of the cell wall may form an important mechanism for the increased extractability of polysaccharides after roasting (Oosterveld, Harmsen, Voragen, & Schols, 2002). However, conclusive evidence for this phenomena is not yet obtained.

4. Concluding remarks

The overview of the carbohydrates present in coffee beans as a function of the degree of roast as given in this investigation shows large differences for different types of polysaccharides. In general it was found that depending on the type of polysaccharide present in the green bean, most carbohydrates were present as unextractable or extractable polysaccharides. The fact that only very small amounts of the carbohydrates were recovered as oligomer and even less as monomers, shows that both oligomers and monomers are converted very rapidly into sugar degradation products.

It was found that after removal of the water soluble polysaccharides with water of 90 °C a large amount of polysaccharides could be solubilized with water of 170 °C. And the amount and composition of the material extracted in this way clearly depended on the degree of roast. This not only confirms that roasting solubilizes part of the polysaccharides, it also shows that the structure of the insoluble polysaccharides is changed in such a way that they can be extracted much easier when using more severe extraction conditions.

Cellulose was found to be highly unextractable and not affected by the degree of roast, while galactomannans were also highly unextractable, but were solubilized to a large extent with increasing degrees of roast. The arabinogalactans were found to have a high solubility, especially at higher temperatures. For the first time evidence was found that different populations of arabinogalactans exist in the coffee bean; high molecular weight arabinogalactans with a low arabinose substitution and low molecular weight arabinogalactans with a higher arabinose substitution. The arabinose side-chains in the arabinogalactans were found to be more susceptible to higher roasting conditions than the galactans.

With this study more insights have been obtained in the structure of polysaccharides in coffee beans and the degradation reactions, which occur as a function of the degree of roast. While in previous manuscripts the investigations towards the effect of roasting of coffee beans focussed mainly on one distinct aspect of the degradation reactions, in this paper we aimed to give a more complete overview of the changes, which occurred in all carbohydrate fractions during roasting.

References

Blanc, M. B., Davis, G. E., Parchet, J.-M., & Viani, R. (1989). Chromatographic profile of carbohydrates in commercial soluble coffees. *Journal of Agricultural and Food Chemistry*, *37*, 926–930.

Clifford, M. N. (1985). Chemical and physical aspects of green coffee and coffee products. In M. N. Clifford, & K. C. Wilson (Eds.), *Coffee: Botany, Biochemistry and Production of Beans and Beverage* (pp. 305–374). Westport, CT: Croom Helm/Avi.

Fischer, M., Reimann, S., Trovato, V., & Redgwell, R. J. (1999). Structural aspects of polysaccharides from Arabica coffee. Fischer et al. ASCI 18e Colloque. *Helsinki*, 91–94.

Fischer, M., Reimann, S., Trovato, V., & Redgwell, R. J. (2001). Polysaccharides of green Arabica and Robusta coffee beans. *Carbohydrate Research*, *330*, 93–101.

Leloup, V., Liardon, R., (1993). Analytical characterization of coffee carbohydrates. *ASIC 15e Colloque*, Montpellier, pp. 863–865.

Leloup, V., Michieli, J. H. d., Liardon, R., (1997). Characterisation of oligosaccharides in coffee extracts. *ASIC 17e colloque*, Nairobi, 120–127.

Maria, C. A. B. D., Trugo, L. C., Moreira, R. F. A., & Werneck, C. C. (1994). Composition of green coffee fractions and their contribution to the volatile profile formed during roasting. *Food Chemistry*, *50*, 141–145.

Mazzafera, P. (1999). Chemical composition of defective coffee beans. *Food Chemistry*, *64*, 547–554.

Navarini, L., Gilli, R., Gombac, V., Abatangelo, A., Bosco, M., & Toffanin, R. (1999). Polysaccharides from hot water extracts of roasted *Coffea arabica* beans: isolation and characterization. *Carbohydrate Polymers*, *40*, 71–81.

Nunes, F. M., & Coimbra, M. A. (2001). Chemical characterization of the high molecular weight material extracted with hot water from green and roasted arabica coffee. *Journal of Agricultural and Food Chemistry*, *49*(4), 1773–1782.

Nunes, F. M., & Coimbra, M. A. (2002). Chemical characterization of galactomannans and arabinogalactans from two arabica coffee infusions as affected by the degree of roast. *Journal of Agricultural and Food Chemistry*, *50*, 1429–1434.

Oosterveld, A., Beldman, G., Schols, H. A., & Voragen, A. G. J. (1996). Arabinose and ferulic acid rich pectic polysaccharides extracted from sugar beet pulp. *Carbohydrate Research*, *288*, 143–153.

Oosterveld, A., Beldman, G., Schols, H. A., & Voragen, A. G. J. (2000). Characterization of arabinose and ferulic acid rich pectic polysaccharides and hemicelluloses from sugar beet pulp. *Carbohydrate Research*, *328*, 185–197.

Oosterveld, A., Harmsen, J. S., Voragen, A. G. J., & Schols, H. A., (2003). Extraction and characterization of polysaccharides from green and roasted Coffea Arabica beans, *Carbohydrate Polymers*, *52*, 285–296.

Redgwell, R. J., Trovato, V., Curti, D., & Fischer, M. (2002). Effect of roasting on degradation and structural features of polysaccharides in Arabica coffee beans. *Carbohydrate Research*, *337*, 421–431.

Ruiter, G. A. d., Schols, H. A., Voragen, A. G. J., & Rombouts, F. M. (1992). Carbohydrate analysis of water-soluble uronic acid containing polysaccharides with high-performance anion-exchange chromatography using methanolysis combined with TFA hydrolysis is superior to four other methods. *Analytical Biochemistry*, *207*, 176–185.

Steinhauser, U., Oestreich-Janzen, S., & Baltes, W. (1999). Die Röstkaffee-Flüssigextraction zur Herstellung von Löslichem Kaffee in Modelversuch II. Zeitlicher Verlauf des überganges van Saüren, Kolenhydraten sowie 5-Hydroxymethyl-2-furfural (HMF) in den Flüssigextract. *Deutsche Lebensmittel-Rundschau*, *95*(11), 447–453.

Thibault, J.-F. (1979). *Lebensmittel Wissen schaft und Technologie*, *21*, 247–251.

Wolfrom, M. L., Plunkett, R. A., & Laver, M. L. (1960). Carbohydrates of the coffee bean. *Journal of Agricultural and Food Chemistry*, *8*(1), 58–65.