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Amidation of highly methoxylated citrus pectin with primary amines

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Abstract

Partially amidated pectin derivatives (*N*-alkyl pectinamides) were prepared from highly methoxylated citrus pectin by treatment with different primary amines in methanol. The characterisation of reaction products was made by elemental analysis, photometry and diffuse reflectance FTIR spectroscopy. *N*-alkyl pectinamides (secondary amides) had two intense infrared bands (amide I and amide II) shifted to lower wave numbers in comparison with the corresponding bands of commercial amidated pectins (primary amides). In some cases aminolysis of HM pectin caused the appearance of infrared bands from *N*-substituents. Multiple Gaussian decomposition of the characteristic bands in an IR spectrum in the region of 1850–1500 cm^{-1} were applied for evaluation of the degrees of amidation and methylation. The aminolysis of pectins appears to be an interesting way to produce pectin derivatives with new properties. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: HM citrus pectin; LM amidated pectins; Amino-de-alkoxylation (aminolysis); *N*-alkyl pectinamides; FTIR (DRIFT) spectroscopy

1. Introduction

Pectins are plant polysaccharides that are widely used in the food industry. They are basically polymers of partially methyl esterified (1→4) linked α-D-galacturonic acid. Chemical modification of pectins can influence their chemical and technological properties. Amidated pectins are important pectin derivatives with good gelling properties at low-sugar conditions. The common method of pectin amidation is ammonolysis of methyl ester groups of highly methoxylated (HM) pectins in heterogeneous reaction with ammonia in methanol (Anger & Dongowski, 1988; Reitsma, Thibault & Pilnik, 1986). Highly methoxylated pectins react with hydrazine and hydroxylamine in the same fashion, forming hydrazides and hydroxamic acids (Filippov, 1978,1992).

It is interesting to note that the reaction of pectin or pectic acid with phosphorus (III) amides was suggested as an alternative approach to pectin amidation (Yevdakov, Khorlina & Khelemskaya, 1972). This method can be used for direct conversion of free carboxyls into amides. Amidation with phosphorus (III) amides allows preparation of secondary and tertiary pectin amides. Nevertheless, classical ammonolysis is still attractive because a lot of natural pectins are highly methoxylated, reagents are cheap, and this reaction runs under mild conditions.

Introducing the primary aliphatic amines instead of ammonia in the reaction with HM pectins leads to partially amidated pectins with secondary amide groups. This method can be used to link various carbon radicals or functions to pectin macromolecules. It results in changes of physical and chemical properties of pectin that depend on the number of amide groups formed and the amine radical structure. In this context, the analysis of the degree of substitution, as the degree of amidation (DA) or (and) the remainder degree of methylation (DM), is very important for the characterisation of amidated pectins.

Infrared spectroscopy is an excellent method for structural and quantitative analysis of pectins. FTIR spectra of natural pectins and their derivatives have been recorded in potassium bromide tablets (Coimbra, Barros, Barros, Rutledge & Delgadillo, 1998; Kamnev, Colina, Rodriguez, Ptitchkina & Ignatov, 1998), emulsions with Nujol (Kamnev et al., 1998), films (Filippov, 1978,1992), powders (Engelsen & Nørgaard, 1996), D_2O-phosphate buffer solutions (Bociek & Welti, 1975), water solutions and gels (Wellner, Kačuráková, Malovíková, Wilson & Belton, 1998). Bociek and Welti (1975) analysed ester, amide and uronate contents by infrared spectroscopy of pectin

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Abbreviations: DA, Degree of amidation; DM, Degree of methylation (methoxylation, esterification); DRIFT, Diffuse reflectance infrared Fourier transform; FTIR, Fourier transform infrared; HM, Highly methoxylated; LM, Lowly methoxylated.

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solutions. FTIR methods for evaluation of the content of different groups, such as free carboxyls, carboxylate anions, methylesters, acetyl and amide groups, in pectin films have been presented (Filippov, 1984; Filippov & Kon, 1984; Filippov & Vaskan, 1987). Coimbra et al. (1998) studied uronic acid and neutral sugars in pectic samples using FTIR and multivariate analysis. Chatjidakis, Pappas, Proxenia, Kalantzi, Rodis and Polissiou (1998) estimated the degree of esterification of cell wall pectins by FTIR using a second derivative algorithm and peak decomposition allowed the elimination of spectral interferences from other cell wall components.

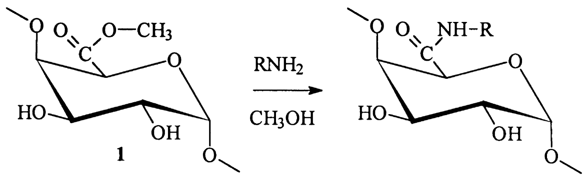
Diffuse reflectance technique of FTIR spectroscopy (DRIFT) has obvious advantages in the analysis of pectin derivatives in comparison to the other numerous techniques. This infrared technique can be successfully applied to record and analyse spectra of dried powder samples (Engelsen & Nørgaard, 1996). The last makes this method especially attractive since commercial pectins and their derivatives are slightly soluble or insoluble in common solvents. An attempt to use potassium bromide tablets of pectins for analytical purposes failed due to an ion exchange between free carboxylic groups and salt matrix (Filippov, 1992). Therefore, we decided to apply the DRIFT spectroscopy for amidated pectin structure elucidation.

In this paper we describe the preparation of partially amidated pectins by amidation with twelve primary aliphatic amines. The *N*-alkyl pectinamides obtained were characterised by elementary analysis, photometry and FTIR (DRIFT) spectroscopy.

2. Experimental

2.1. Preparation of amidated pectins

Highly methoxylated citrus pectin **1** (Genu pectin HM type B, Denmark) with a degree of methylation (DM) of 73% and galacturonic acid content of 89.7% was used for the preparation of amidated derivatives. Low methoxyl and amidated citrus pectins **2a–c** (Genu pectins LM, Denmark) with DM of 28–33% and DA of 15–20% were studied in comparison with prepared amidated derivatives of pectin **1**. The list of amines used is given below and the reaction conditions are shown in Table 1. The reaction was carried out in a heterogeneous system with methanol as the solvent:



R: H (**2a–c**) (commercial samples); Et (**3**); $CH(CH_3)_2$ (**4**); $CH_2CH(CH_3)_2$ (**5**); $CH_2(CH_2)_4CH_3$ (**6**); $CH_2(CH_2)_2OCH_3$ (**7**); $CH_2(CH_2)_6CH_3$ (**8**); Bzl (**9**); $CH_2CH=CH_2$ (**10**); CH_2CH_2OH (**11**); $CH_2CH(OH)$-CH_2OH (**12**); $CH_2(CH_2)_{16}CH_3$ (**13**); $CHPh_2$ (**14**).

In addition, several side reactions leading to the formation of the alkylammonium salt can occur when traces of water are present in the reaction mixture, i.e.:

$$\text{R-NH}_2 + \text{H}_2\text{O} \rightarrow \text{R-NH}_3^+ + \text{OH}^-$$

$$\text{Pec-COOH} + \text{OH}^- \rightarrow \text{Pec-COO}^- + \text{H}_2\text{O}$$

$$\text{Pec-COOCH}_3 + \text{OH}^- \rightarrow \text{Pec-COO}^- + \text{CH}_3\text{OH}$$

$$\text{Pec-COO}^- + \text{R-NH}_3^+$$

$$\rightarrow \text{Pec-COO}^-\text{NH}_3^+\text{-R (alkylammonium pectinate)}$$

Amidated pectins were washed with chloroform to

Table 1
Reaction conditions of HM pectin amidation with primary amines (m_a and m_p are the masses of amine and pectin, respectively, V_r the volume of methanol, T the reaction temperature, and τ the reaction time)

Sample	m_p (g)	m_a (g)	V_r (ml)	T (°C)	τ (h)
3	0.25	8.2	11	5	12
4	0.10	2.1	2	5	12
5	0.10	5.2	3	5	12
6	0.10	4.3	3	5	12
7	0.25	7.0	10	5	12
8	0.10	6.9	3	5	12
9	0.25	4.0	2.5	5	12
10	0.10	4.0	3	5	12
11	0.10	2.2	3	5	12
12	0.10	2.3	8	5	12
13	4.00	9.0	40	45	144
14	0.10	6.9	4	25	24

Table 2
Characterisation of the samples, mass and molar yields of reaction by elemental analysis and photometry (M_N is the nitrogen content (%), M_C the carbon content (%), DA the degree of amidation (%), DM the degree of methylation (%), Y_m the mass yield of reaction (%), and Y_n the molar yield of reaction (%))

Sample	M_N (%)	M_C (%)	DA (%)	DM (%)	Y_m (%)	Y_n (%)
1	0.25	41.32	–	73	–	–
2a	1.13	35.84	18	35	–	–
2b	1.27	36.07	20	33	–	–
2c	1.44	36.11	23	29	–	–
3	3.38	39.24	51	20	10.8	70
4	0.62	35.92	10	56	2.6	14
5	1.10	39.76	16	55	5.7	23
6	1.62	41.97	24	36	11.7	33
7	2.77	39.79	44	27	14.9	60
8	0.98	40.09	15	44	9.1	21
9	1.83	41.38	28	42	14.0	39
10	2.48	41.92	36	38	10.8	49
11	2.17	38.31	33	31	8.8	46
12	3.12	39.68	48	24	16.3	66
13	2.14	54.18	32	28	41.2	43
14	0.42	41.02	6	58	5.5	9

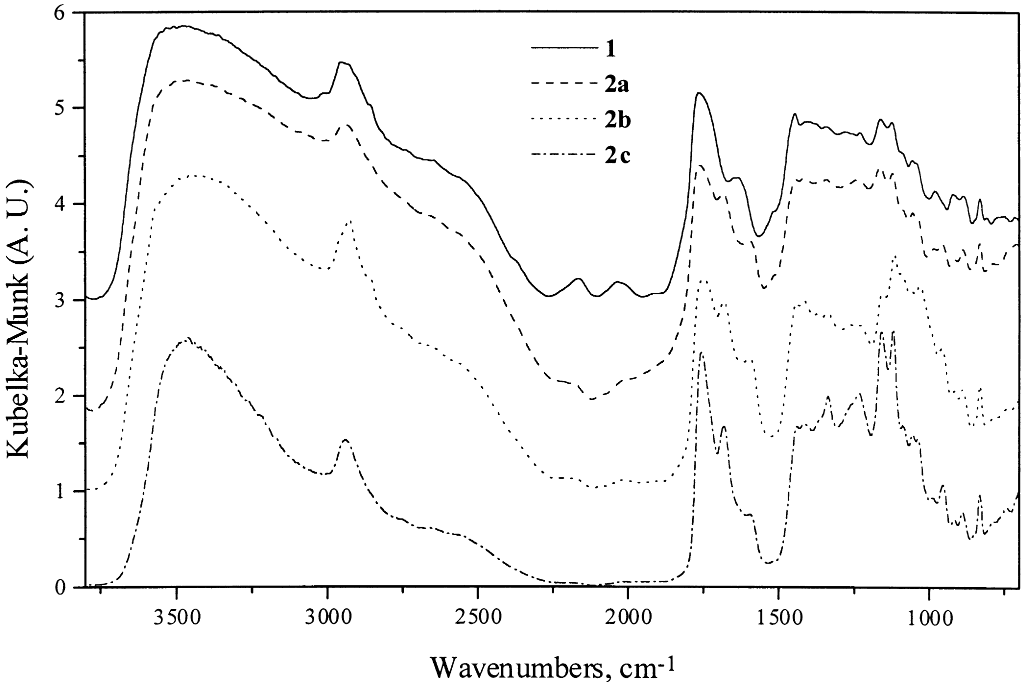


Fig. 1. FTIR spectra of HM pectin **1** and commercial amidated LM pectins **2a**–**c**.

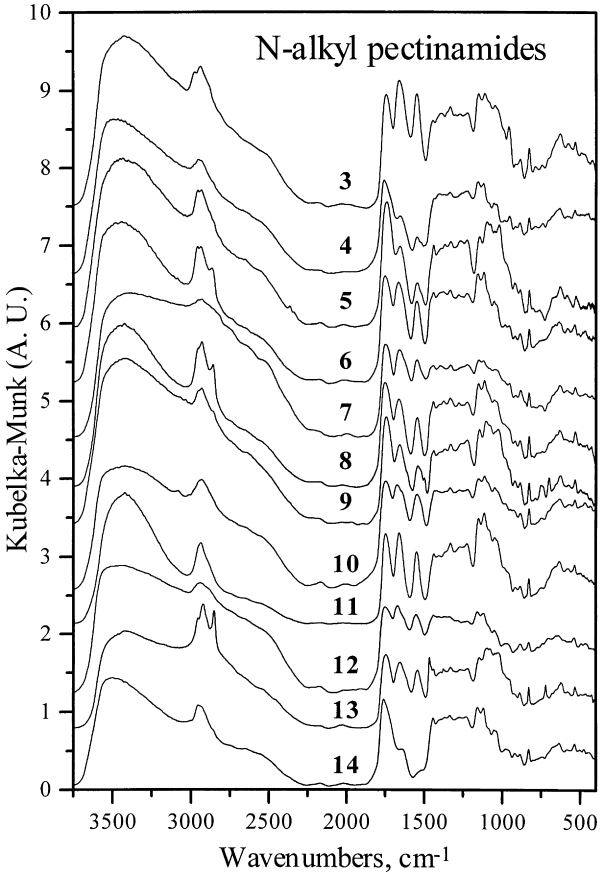


Fig. 2. FTIR spectra of partially amidated *N*-alkyl pectinamides **3**–**14**.

remove the excess amine. Samples were then treated with 0.1 M HCl in an ethanol–water mixture (1:1 (v/v)) to convert free carboxylic groups into the protonated form. In this case ion exchange between R-NH_3^+ and H^+ cations takes place on the pectin matrix and amine is removed as an alkylammonium chloride:

$$\text{Pec-COO}^-\text{NH}_3^+\text{-R} + \text{H}^+\text{Cl}^- \rightarrow \text{Pec-COOH} + \text{R-NH}_3^+\text{Cl}^-$$

Finally, the material was washed several times with 40% (v/v) ethanol until it showed a negative reaction to chloride, then treated with 80% (v/v) ethanol, filtered and dried at 60°C.

2.2. Analysis of pectin samples

The content of galacturonic acid in the original pectin **1** was measured photometrically with *m*-hydroxybiphenyl at 520 nm according to Blumenkrantz and Asboe-Hansen (1973). This value expresses the total content of uronic carboxylic groups as galacturonic units. The degree of methylation (DM) of pectin samples was determined by photometry with chromotropic acid at 570 nm according to Filippov and Kuzminov (1971). The degrees of amidation (DA), mass and molar yields of reaction (Y_m and Y_n, respectively) were calculated from the results of elemental analysis according to the formulas:

$$\mathrm{DA} = \frac{M_N}{M_C}\left[6 + \frac{73}{100} + (K-1)\frac{M_N}{14}\right]100$$

Table 3
Band positions (cm^{-1}) in the FTIR spectra of pectin samples

Samples																Assignment[a]
1	**2a**	**2b**	**2c**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	
3475	3458	3453	3458	3426	3464	3433	3424	3380	3426	3410	3421	3442	3421	3386	3480	ν(OH)
											3082				‘	$\nu_{as}(=CH_2)$
										3063						$\nu(C_{Ar}H)$
										3033						$\nu(C_{Ar}H)$
											3019					$\nu(=CH)$
										3008						$\nu(C_{Ar}H)$
											2984					$\nu_s(=CH_2)$
2951		2958			2953	2959	2960	2957	2960	2958	2951	2958	2955	2955	2953	$\nu_{as}(CH_3)$
							2915	2927	2928	2926	2927	2922	2913	2920		$\nu_{as}(CH_2)$
2905		2898		2901		2900	2895	2905	2904	2890	2894	2895	2891	2897		ν(CH)*ring*
				2870	2885	2876	2876	2884	2877			2881	2883	2877		$\nu_s(CH_3)$
2853		2854		2851	2855	2851	2855	2853	2854	2854	2858	2857	2854	2852		$\nu_s(CH_2)$
1763	1763	1747	1755	1746	1759	1741	1754	1751	1753	1744	1749	1753	1749	1747	1761	$\nu(C=O)$
	1682	1681	1681	1661	1655	1656	1667	1660	1663	1658	1676	1672	1661	1656	1645	Amide I
	1593	1596	1595	1549	1547	1546	1547	1547	1546	1548	1549	1553	1550	1544	1545	Amide II
										1500					1514	$\nu(C_{Ar}C_{Ar})$
				1469		1467	1468	1464	1466	1471	1458	1467	1462			$\delta(CH_2)$
										1457						$\nu(C_{Ar}C_{Ar})$
1444	1442	1441	1438	1447	1443	1441	1443	1442	1443	1439	1441	1446	1442	1440	1443	$\delta_{as}(CH_3)$
	1416	1415	1415	1420	1414	1415	1415	1412	1415	1415	1422	1426	1410	1412		Amide III
1395	1401	1400	1402	1401	1402	1394	1401	1397	1405	1403	1404	1407	1402	1396	1400	ν,δ(COH)*a*
1375	1362	1371	1370	1382	1373		1378	1376	1378	1367	1370	1372		1378	1368	$\delta_s(CH_3)$
1335	1337	1334	1334	1333	1335	1344	1334	1332	1334	1331	1335	1336	1332	1332	1336	δ(CH)*r*
1277	1273	1268	1271	1272	1276	1277	1282	1272	1280	1267	1278	1286	1273	1272	1274	ν(COC)*e*
1230	1220	1223		1220	1221	1223	1229	1226	1227	1218	1223	1224	1224	1222		ν(COC)*e*
1160	1164	1156	1159	1157	1160	1146	1157	1152	1157	1154	1156	1162	1159	1148	1159	ν(COC)
1123	1122	1116	1120	1112	1119	1098	1119	1122	1114	1109	1115	1120	1117	1098	1121	ν(CC)(CO)
1083	1086	1087	1087	1081	1085	1077	1094	1081	1084	1074	1088	1085	1081	1079	1085	ν,δ(COH)*ring*
1055	1056	1057	1054	1047	1055	1050	1053	1049	1052	1049	1050	1051	1050	1048	1053	ν(CC)(CO)
1043	1034	1031	1039	1028	1038	1021	1038	1032	1032	1028	1028	1036	1030	1027	1035	ν(CC)(CO)
981	985	988	988	989	987	980	984	990	985	976	976	989	986		979	γ(OH)
	957	959	954	959	955	955	957	955	952	951	947	962	953		955	γ(OH)
920	915	915	918	917	917	921	921	914	918	921	921	917	919	925	918	$\rho(CH_3)$
886	888	889	887	886	888	886	887	883	885	885	883	885	884	888	886	γ(OH)
833	830	831	831	829	830	829	830	830	829	829	829	831	830	830	831	γ(OH)
										737						$\gamma(C_{Ar}H)$
							727		724					721		$\rho(CH_2)$
										702						$\delta(C_{Ar}C_{Ar})$

[a] ν—stretching, δ—in-plan bending, γ—out-off-plan bending, ρ—rocking, $_{as}$—antysymmetric, $_s$—symmetric, *a*—carboxylic acid, *e*—methylester, *ring*—pyranoic ring.

$$Y_m = \frac{M_N}{14} M_A$$

$$Y_n = \frac{DA}{73} 100$$

where DA is the degree of amidation (%), Y_m the mass yield of reaction, i.e. the relative mass of bonded amine (%) in reaction product, Y_n the molar yield of reaction, i.e. the relative content of ester groups substituted by amine (%), M_N the nitrogen content (%), M_C the carbon content (%), M_A the molar mass of amine (g mol^{-1}), 12 the carbon atomic mass (g mol^{-1}), 14 the nitrogen atomic mass (g mol^{-1}), 6 the sum of carbons in galacturonic unit, K the sum of carbons in the amine molecule and 73 the methylation degree (DM) of original pectin (%).

2.3. FTIR (DRIFT) spectroscopy

Diffusion reflectance infrared (DRIFT) spectra of samples were measured on a Nicolet 740 with DCT 680 (Nicolet Analytical Instruments, Madison, WI, USA) spectrometer. The Fourier deconvolution of some spectra was applied to resolve the overlapping bands. The spectra of samples have been analysed by the normalised least-squares curve-fitting procedure (Origin 3.75 software) using multiple Gaussian curves. The Fourier deconvolution algorithm assisted the curve-fitting procedure. The relative content of ester, amide, protonated (acid) and anionic (salt) forms of uronic carboxyl was calculated on the basis of the areas of separated peaks.

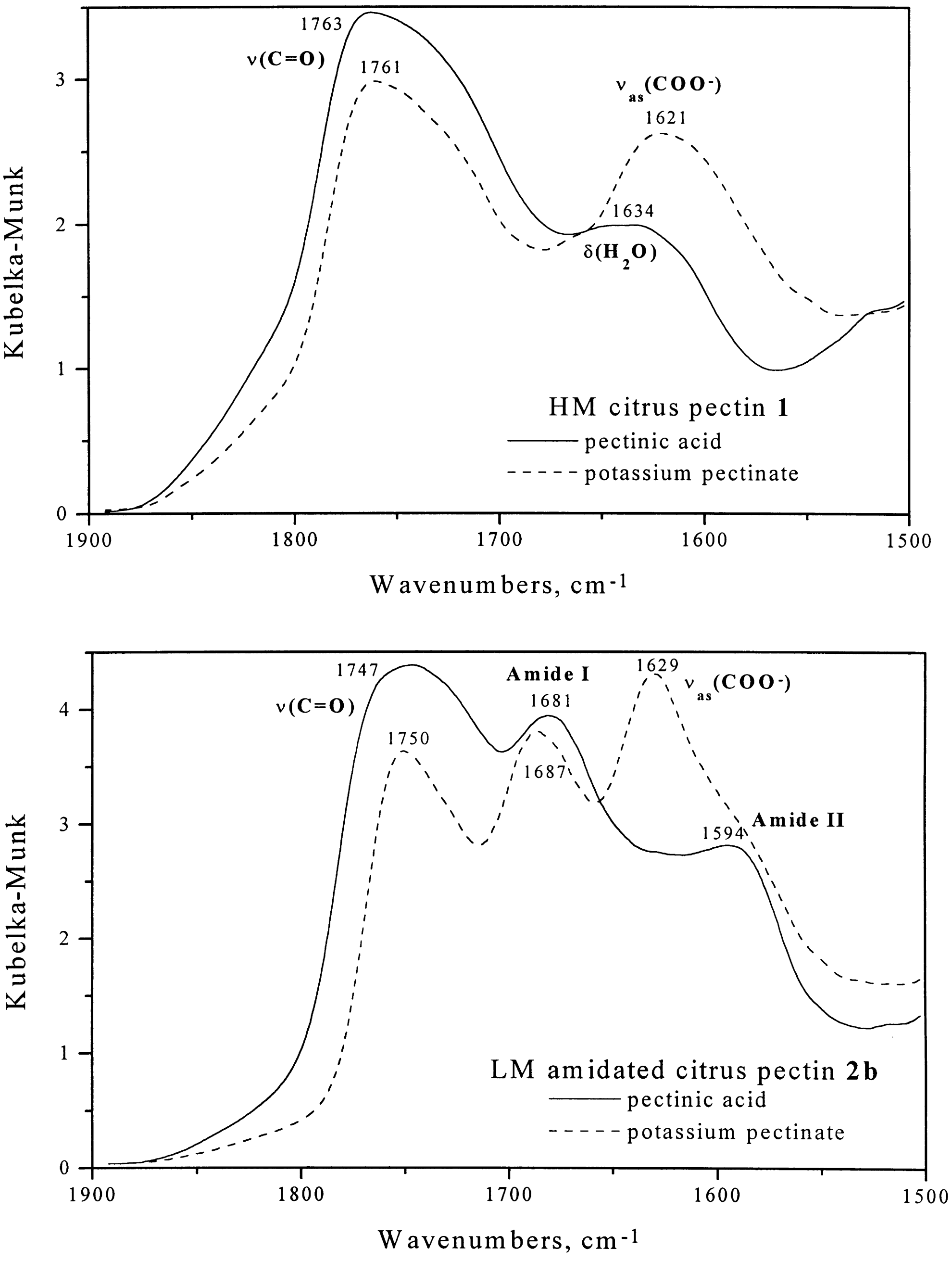


Fig. 3. FTIR spectra of HM pectin **1** and amidated LM pectin **2b** in pectinic acid and potassium pectinate forms in the region of 1900–1500 cm^{-1}.

3. Results and discussion

The carbon and nitrogen contents, the calculated values of methylation and amidation degrees and reaction yields are shown in Table 2. The highest molar yield, 70% of substituted ester groups, was found in the case of reaction with ethylamine (**3**), whereas the highest relative amount of bound amine, 41.2% (m/m), was found in *N*-octadecyl pectinamide **13**. Amines with a branched chain (**4**, **5** and **14**) gave low molar yields because of steric effects. The presence of hydroxyl groups, double carbon–carbon bonds or aromatic rings in the amines **9–12** did not lead to a significant decrease in the molar yield.

FTIR (DRIFT) spectra of original HM pectin **1**, commercial amidated LM pectins **2a–c** and products of HM pectin amidation with primary amines (**3–14**) are shown in Figs. 1 and 2. Vibration frequencies are presented in Table 3. All samples were prepared in the acid form. The carboxyl vibration region of 1900–1500 cm^{-1} is the most important for our analysis. FTIR spectra of original HM pectin **1** and commercial LM amidated pectin **2b** (the acid and the salt forms) in this region are shown in Fig. 3. HM pectin **1** in the

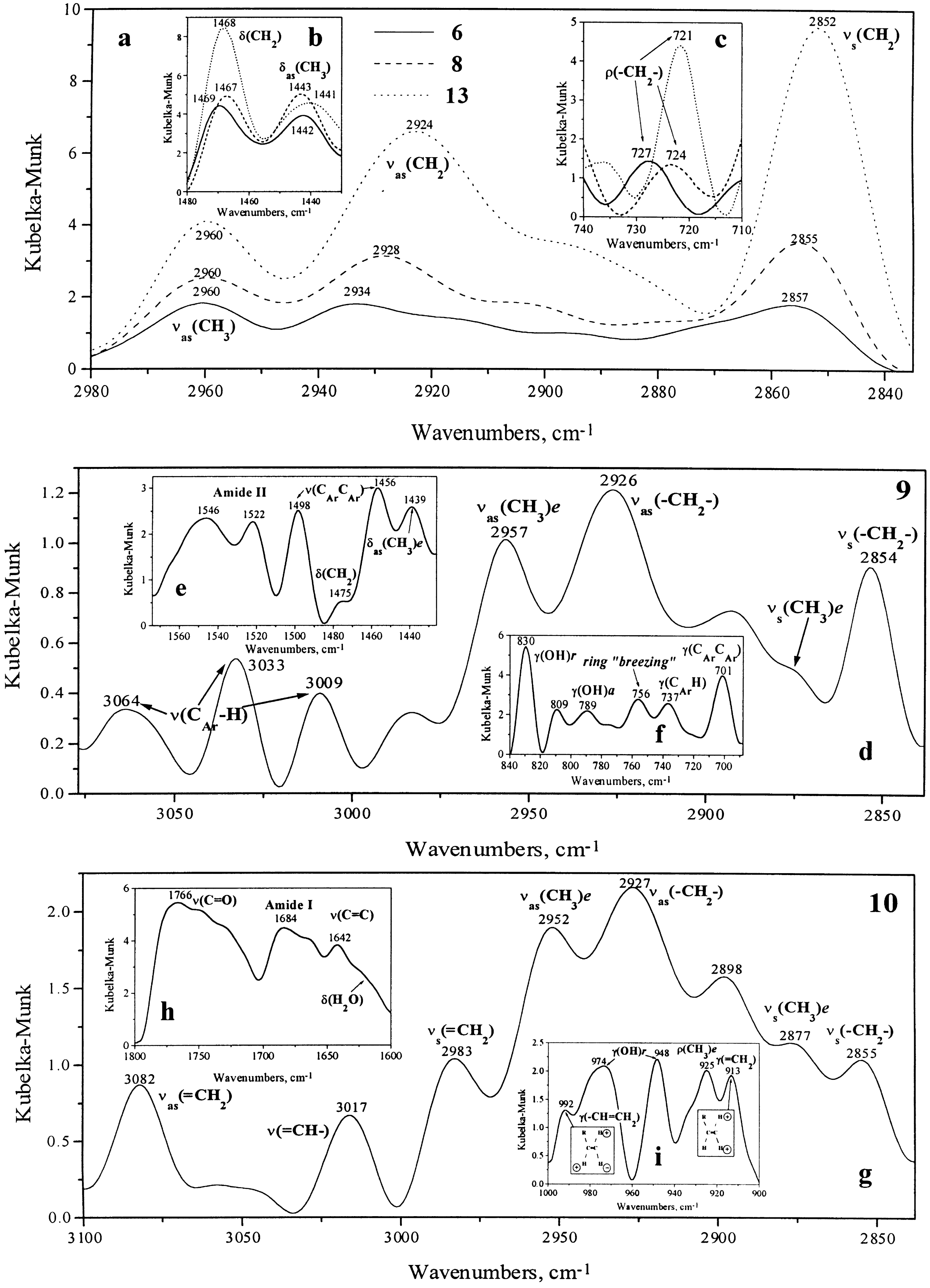


Fig. 4. Fourier-transformed deconvoluted FTIR spectra of samples **6**, **8**, **13** (*N*-alkyl pectinamides where alkyl is *n*-hexyl, *n*-octyl and *n*-octadecyl, respectively; (**a**–**c**)), *N*-benzyl pectinamide **9** (**d**–**e**) and *N*-allyl pectinamide **10** (**g**–**i**).

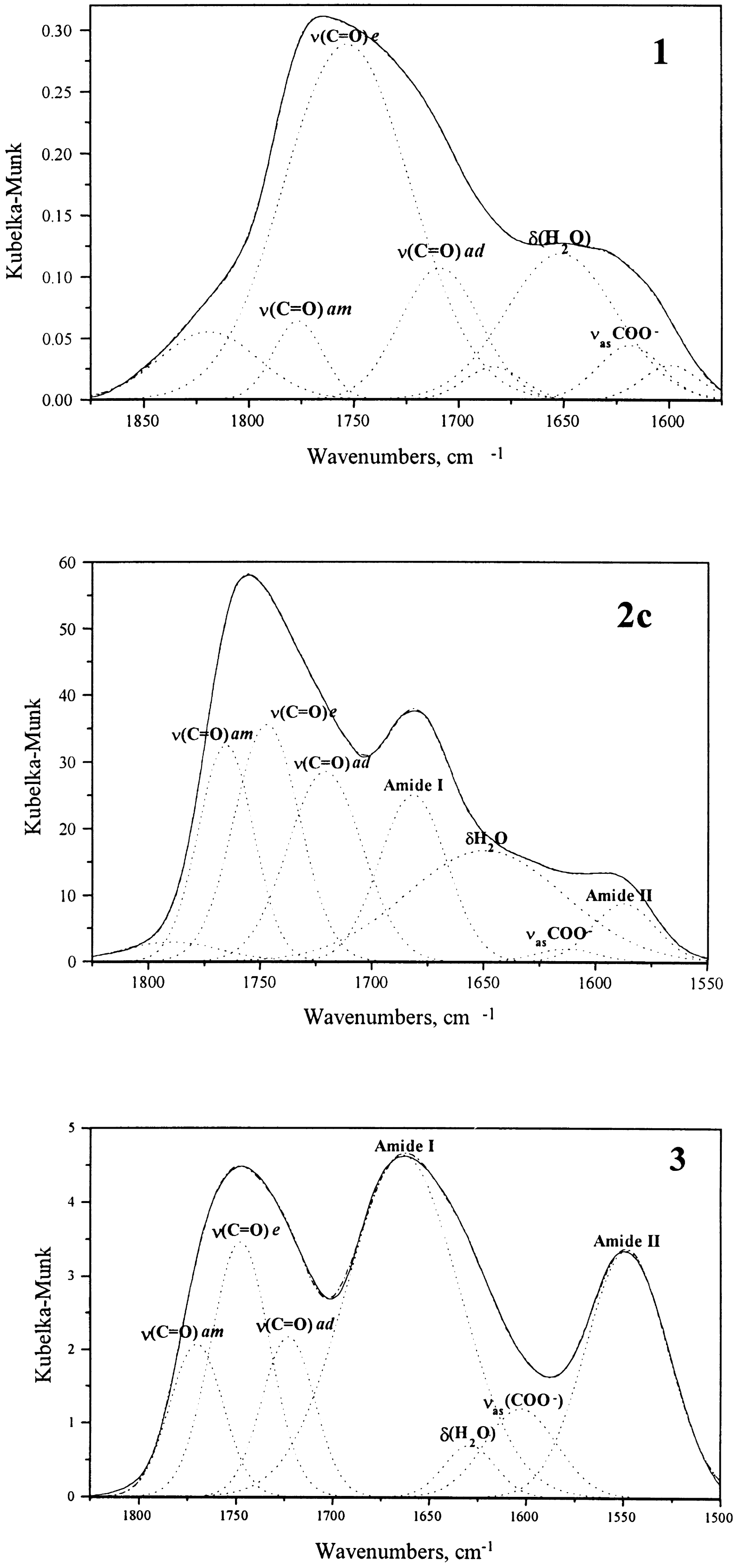


Fig. 5. FTIR spectra decomposition of HM pectin **1**, commercial amidated pectin **2c** and *N*-ethyl pectinamide **3** in the region of 1850–1500 cm^{-1} (*am*-carboxylic acid monomers, *e*-methylesters, *ad*-carboxylic acid dimers).

Table 4
Degrees of amidation (DA) and methylation (DM) obtained by decomposition of FTIR spectra (1840–1500 cm^{-1}) (A_{amide} is the area of amide I Gaussian component, A_{ester} the area of ν(C=O)*e* Gaussian component, A_{tot} the sum of areas of all Gaussian components assigned to carboxylic, amide and ester groups: ν(C=O), amide I and $\nu_{\mathrm{as}}(\mathrm{COO}^-)$, DA (%) = ($A_{\mathrm{amide}}/A_{\mathrm{tot}}$) × 100, and DM (%) = ($A_{\mathrm{ester}}/A_{\mathrm{tot}}$) × 100)

Sample	A_{amide}	A_{ester}	A_{tot}	DA (%)	DM (%)
1	–	219	305	–	72
2a	153	354	998	15	35
2b	78	138	412	19	33
2c	95	131	452	21	29
3	342	131	675	51	19
4	76	379	712	11	53
5	20	74	135	15	55
6	138	203	566	24	36
7	116	81	312	37	26
8	45	114	278	16	41
9	55	92	218	25	42
10	151	175	453	33	39
11	70	71	228	31	31
12	73	38	155	47	25
13	83	74	241	34	31
14	38	390	714	5	55

acid form has a single band in the carboxyl vibration region at 1763 cm^{-1} that belongs to C=O vibration of methyl ester and free carboxyl groups. The acid form of amidated pectin **2b** has three bands: at 1765 cm^{-1} (C=O vibration), 1681 cm^{-1} (amide I) and at 1594 cm^{-1} (amide II). The conversion into the salt form lowers the carbonyl frequency and brings about the strong absorption band around 1618 cm^{-1} belonging to the antisymmetric stretching vibration of COO$^-$. The remaining band near 1750 cm^{-1} belongs to the C=O vibration of methyl ester groups. The intense antisymmetric carboxylate band overlaps with both amide bands, which greatly complicates the analysis. Therefore, we have prepared acid forms of amidated pectins for IR spectroscopy in order to circumvent this complication.

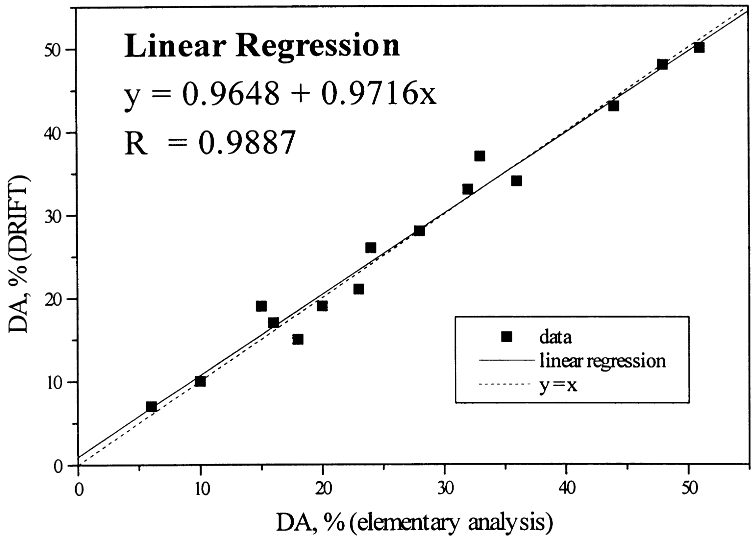
As shown in Fig. 2 and Table 3, the FTIR spectra of pectin amidated with primary amines also show two peaks in the same region. Amide I and amide II bands of the samples **3**–**14** (secondary amides) are shifted to lower wave numbers in comparison to the corresponding bands of commercial amidated pectins (primary amides). The presence of these two bands and the absence of intense carboxylate stretching bands indicates that the substituent is bound to the pectin chain by a covalent amide bond, although we do not exclude the possibility that small amounts of the amine salt might be found in the samples.

Amidation of pectin with primary amines causes the appearance of bands from *N*-substituents in FTIR spectra (Table 3). The samples **6**, **8** and **13** showed more intensive C–H absorption in the region of 2970–2930 cm^{-1} than the original pectin (Fig. 2). It can be explained by an increased C–H bond content after amidation by aliphatic amines with long chains. The Fourier deconvolution of this spectral region allows different C–H modes to be resolved (Fig. 4). The largest change in the spectrum was observed in the case of sample **13** that contains *n*-octadecyl groups. It had two very intense bands at 2920 and 2852 cm^{-1} that were assigned as antisymmetric and symmetric C–H vibrations of methylene groups. Intense bands near 1468 (scissoring of CH$_2$) and 720 cm^{-1} (rocking of CH$_2$) also indicate methylene units of *n*-alkyl groups (Fig. 4(b) and (c)). In the shorter *n*-alkyl residue the rocking band of CH$_2$ appears at somewhat higher frequencies (Silverstain, Bassler & Morrill, 1997). A similar shift of this band took place in the case of the *n*-alkylamides studied (**6**, **8** and **13** (Fig. 4(c))).

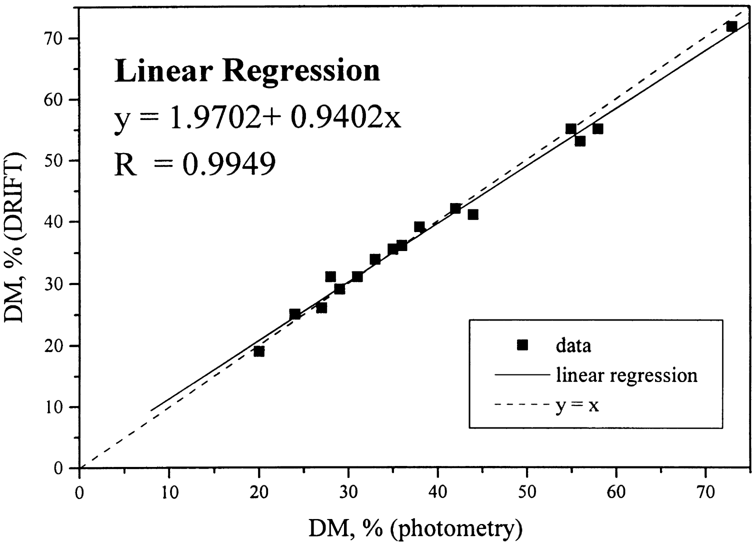
The Fourier-deconvoluted FTIR spectra of **9** and **10** in the region of 3100–2800 cm^{-1} contained some C–H stretching bands belonging to benzyl and allyl groups in these samples (Fig. 4(d) and (g)). The *N*-benzyl pectinamine **9** had two skeletal stretching bands of aromatic ring at 1498 and 1456 cm^{-1} overlapped with methylene scissoring about 1475 cm^{-1} (Fig. 4(e)). This sample also showed two bands at 737 (out-off-plan aromatic C–H bend) and 701 cm^{-1} (out-off-plan ring bending), the second one is very intense (Fig. 4(f)). *N*-allyl pectinamide **10** had a C=C stretching band at 1642 cm^{-1}, interfering with the amide I and water bending bands (Fig. 4(h)). Sample **10** also showed two out-off-plan C–H bending bands of vinyl at 992 and 913 cm^{-1} (Fig. 4(i)). These bands overlap with pectin bands at 974 (out-off-plan O–H bend of pyranoid ring) and 925 cm^{-1} (methyl rocking). All the bands were separated by Fourier deconvolution in the region of 1000–900 cm^{-1}.

The curve-fitting decomposition of FTIR spectra in the region of 1850–1500 cm^{-1} distinguished several component peaks assigned as C=O vibrations of different functional groups in amidated pectins. An example of peak separation for samples **1**, **2c** and **3** is shown in Fig. 5. The mixed peak of ester and carboxylic C=O vibrations decomposed into three Gaussian component bands appearing at 1770–1760 cm^{-1} (carboxylic monomer), 1755–1735 cm^{-1} (ester) and 1720–1710 cm^{-1} (carboxylic dimer). The assignment of component bands in the amide I region is more complicated in some cases, but one or more peaks at 1685–1665 cm^{-1} were indicative of C=O bond vibration of the amide group. The Gaussian component near 1650 cm^{-1} was assigned as the rotation mode of water presented in the samples. The small component at 1630–1605 cm^{-1} belongs to the antisymmetric vibration of carboxylate anion. The component near 1550 cm^{-1} characterised amide II vibrations.

The ν(C=O) ester and amide I components were used to determine DM and degree of amidation (DA), respectively. These values were calculated as the ratio of the corresponding component area to the sum of the areas of all the components assigned to carboxylic, ester and amide groups (Table 4). The degrees of amidation (DA) calculated on the basis of FTIR spectra decomposition correlated with DA values obtained from elemental analysis (Fig. 6(a)). In no case did the reaction lead to total demethylation. The methylation degrees (DM) of samples were in the range of



a



b

Fig. 6. (a) Correlation between DA values of the samples **2**–**14** obtained by elemental analysis and decomposition of FTIR spectra; (b) correlation between DM values of the samples **1**–**14** obtained by photometry and decomposition of FTIR spectra.

10–50%. These values were in good agreement with the results of photometry (Fig. 6(b)).

4. Conclusions

In this work partially amidated *N*-alkyl pectinamides have been prepared by amino-de-alkoxylation (aminolysis) of HM pectin with twelve selected primary amines. The molar yield of reaction ranged from 6 to 70% depending on the amine structure and reaction conditions. The structural changes in pectin derivatives have been investigated using FTIR spectroscopy. Vibration bands of amide bonds (amide I and amide II) and *N*-alkyl groups have been observed in FTIR spectra of amidated pectins and assigned. The data obtained by means of FTIR spectroscopy were in good agreement with other analytical methods (elemental analysis and photometry).

The amidation with primary amines permits various functional groups to be attached to a pectin macromolecule, which influences the physical and chemical properties of pectin derivatives and their possible application. For instance, *N*-alkyl pectinamides with aliphatic or aromatic groups are more hydrophobic than the original pectin, whereas amidated pectins with an amine radical containing polar or charged groups can still have hydrophylic properties. If the amine radical carries cationic groups like in the case of diamines, the resulting derivatives will have properties of polyampholytes. Moreover, introduction of such amine radical groups as double carbon–carbon bonds or aromatic rings may lead to new pectin derivatives following electrophilic addition or substitution. Cross-linking between pectin macromolecules can occur when another part of the amine radical carries such active groups as chlorine, oxyrane rings or other amino groups. Finally, such bioactive molecules as proteins, peptides, enzymes or drugs can be immobilized on the pectin surface via amidation.

We think the *N*-alkyl pectinamides chemistry could be of interest in the design of new materials that could be useful in different applications.

References

Anger, H., & Dongowski, G. (1988). *Food Hydrocolloids*, *2*, 371–379.

Blumenkrantz, N., & Asboe-Hansen, G. (1973). *Analytical Biochemistry*, *54*, 484–489.

Bociek, S. M., & Welti, D. (1975). *Carbohydrate Research*, *42*, 217–226.

Chatjidakis, A. K., Pappas, C., Proxenia, N., Kalantzi, O., Rodis, D., & Polissiou, M. (1998). *Carbohydrate Polymers*, *37*, 395–408.

Coimbra, M. A., Barros, A., Barros, M., Rutledge, D. N., & Delgadillo, I. (1998). *Carbohydrate Polymers*, *37*, 241–248.

Engelsen, S. B., & Nørgaard, L. (1996). *Carbohydrate Polymers*, *30*, 9–24.

Filippov, M. P. (1978). *Infrared spectra of pectic compounds*, (p. 75). Kishinev: Shtiintsa.

Filippov, M. P. (1984). *Zhurnal Analiticheskoj Khimii*, *39*, 92–94.

Filippov, M. P. (1992). *Food Hydrocolloids*, *6*, 115–142.

Filippov, M. P., & Kon, R. (1984). *Zhurnal Analiticheskoj Khimii*, *41*, 1890–1894.

Filippov, M. P., & Kuzminov, V. I. (1971). *Zhurnal Analiticheskoj Khimii*, *26*, 143–146.

Filippov, M. P., & Vaskan, R. N. (1987). *Zhurnal Analiticheskoj Khimii*, *42*, 1700–1703.

Kamnev, A. A., Colina, M., Rodriguez, J., Ptitchkina, N. M., & Ignatov, V. V. (1998). *Food Hydrocolloids*, *12*, 263–271.

Reitsma, J. C. E., Thibault, J.-F., & Pilnik, W. (1986). *Food Hydrocolloids*, *1*, 121–127.

Silverstain, R. M., Basssler, G. C., & Morrill, T. C. (1997). *Spectrometric identification of organic compounds* (p. 104). (5). New York: Wiley.

Wellner, N., Kačuráková, M., Malovíková, A., Wilson, R. H., & Belton, R. (1998). *Carbohydrate Research*, *308*, 123–131.

Yevdakov, V. P., Khorlina, I. M., & Khelemskaya, H. M. (1972). *Zhurnal Organicheskoj Khimii*, *43*, 388–393.