Controlling the Degree of Esterification of Citrus Pectin for Demanding Applications by Selection of the Source

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Supplementary Information

Table S1. Assignment of the DRIFT spectra of pectin from different sources, present work

Assignment	Orange outer skin	Lemon outer skin	Orange peel	Lemon peel	Grapefruit peel	Orange waste	Lemon waste
νO-H	$3483_{S,sh}$	3510_{VS}	3496_{VS}	3516_{VS}	$3479_{VS,sh}$	3465_{VS}	3467_{S}
νO-H	3303_{VS}	3271_{VS}	3253_{VS}	3290_{VS}	3290_{VS}	3373_{VS}	3270_{VS}
νCH		2943_{S}		2941_{S}			2941_{S}
νCH	2933_{S}		2929_{VS}		2931_{VS}	2935_{S}	
νCH	2914_{S}	2910_{S}		2910_{S}			2912_{S}
νCH	$2897_{S,sh}$				2895_{VS}	$2895_{S,sh}$	
ν(C=O)$_{carb.ac.}$	1724_{m}	1729_{m}	1724_{m}	1728_{VS}	1720_{m}	1726_{m}	1724_{VS}
		1670_{m}			1626_{m}		
ν_{as}(COO$^-$)	1603_{S}	1591_{m}	1601_{S}	1595_{S}	1603_{S}	1606_{S}	1597_{VS}
	1516_{w}		1514_{m}	1516_{w}	1518_{m}	1514_{w}	1512_{m}
					1500_{m}		1458_{S}
		1444_{m}			1442_{S}	$1443_{S,sh}$	1440_{VS}
δ_{as}(CH$_3$)$_{ester}$	1417_{S}	1427_{m}	1427_{S}		1421_{S}	1425_{S}	1419_{VS}
ν_{s}(COO$^-$)		1415_{m}	1414_{S}	1414_{m}	1412_{S}		1412_{VS}
δ_{s}(CH$_3$)$_{ester}$	1375_{m}	1369_{m}	1377_{m}	1371_{m}	1377_{S}	1372_{S}	1377_{S}
					1365_{S}		1365_{S}
					1296_{S}		
					1282_{S}		
ν(C-O-C)$_{ester}$		1265_{m}	1265_{m}	1261_{m}	1263_{S}	1261_{m}	1257_{S}
νC-O		1236_{m}		1232_{m}		$1232_{m,sh}$	1240_{S}
					1209_{m}		
					1176_{m}		
ν(C-O-C)$_{pyranose}$ + ν(C-OH) + ν(C-C)+…	$1146_{S,sh}$	1138_{m}	1132_{m}	$1144_{m,sh}$	1134_{S}	$1142_{S,sh}$	$1146_{S,sh}$
					1126_{S}		
	$1101_{VS,sh}$	1099_{m}	1101_{m}	$1097_{S,sh}$	1090_{S}	1099_{S}	$1101_{VS,sh}$
	$1072_{VS,sh}$	1078_{m}	1068_{m}	1070_{S}	1074_{S}	1078_{S}	1066_{VS}
	1046_{VS}				1043_{S}	$1039_{S,sh}$	1051_{VS}
	$1032_{VS,sh}$	$1034_{m,sh}$	$1032_{m,sh}$	$1033_{m,sh}$			1031_{VS}
γ_{op}(O-H)		$993_{w,sh}$	$990_{m,sh}$	$987_{m,sh}$		$995_{m,sh}$	$993_{S,sh}$
ρ(CH$_3$)$_{ester}$	920_{vw}	916_{vw}	924_{vw}	$920_{vw,sh}$	920_{vw}	921_{vw}	916_{vw}
				910_{vw}			
		900_{vw}		895_{vw}	895_{vw}		897_{vw}
	866 vw	864_{vw}	866_{vw}	866_{vw}	866_{vw}	868_{vw}	868_{vw}
	818 w	818_{vw}	820_{vw}	816_{w}	820_{w}	818_{vw}	818_{vw}
	777 m	777_{w}	777_{vw}	775_{m}	779_{w}	777_{w}	777_{w}

VS – very strong; S – strong; m- medium; w – weak; vw – vwey weak, sh – shoulder.

Brief analysis

The 3800-2200 cm^{-1} region is dominated by broad bands related to the stretching vibrations of hydroxyl and CH_x groups (νO-H and νC-H). The νO-H band, with maximum at 3200-3300 cm^{-1}, is associated with hydroxyl groups of the pyranose rings and adsorbed water, interacting in different intra- and intermolecular hydrogen bonds; the fraction of OH groups with weaker hydrogen-bond interactions is responsible for the high wavenumber shoulder (at ~3500 cm^{-1}). The maximum at 2930-2940 cm^{-1} is assigned to νCH and $\nu_{as}CH_3$ modes of the pectin backbone, and to $\nu_{as}CH_2$ modes of galactose and arabinose rings of the "hairy" regions. The shoulder at 2860-2890 cm^{-1} correlates with the ν_sCH_3 modes of the backbone and also with different νCH modes of the pyranose rings, both in HG and RG regions. Two shoulders located near 2700 and 2500 cm^{-1} are frequently assigned as satellite ν(CO)O-H bands of carboxylic acid dimers. The two strong bands in the 1800-1500 cm^{-1} region, with maxima at ~1730 and ~1610 cm^{-1}, are assigned to the stretching modes of carbonyl groups (mostly from esterified galacturonic acid, ν(C=O)ester) and of carboxylate groups ($\nu_{as}COO^-$), respectively. The weaker band at 1670 cm^{-1} may correlate with nonesterified hydrogenated acidic carbonyl groups, ν(C=O) acid. The main CH_x and C-O-H deformation modes appear partially overlapped, in the 1500-1200 cm^{-1} region. The band at 1230 cm^{-1}, visible in all the spectra, and the one at 1330 cm^{-1}, only detected in the orange derived samples, are assigned to in-plane deformation modes of alcohol hydroxyl groups in the pyranose rings of the pectin chain, δ(C-O-H)pyranose. The band at 1370 cm^{-1} is assigned to the symmetric methyl deformation mode, $\delta_s(CH_3)$, of ester methyl groups in the galacturonic rings and of rhamnose rings of the pectin backbone. The corresponding antisymmetric mode is hardly identified as a shoulder, at ~1440 cm^{-1}. The other ester-related band in this region is the C-O-C stretching mode, ν(C-O-C) ester, which appears at 1265 cm^{-1}, partially overlapped with the 1230 cm^{-1} band. The band at 1410 cm^{-1} is assigned to the symmetric stretch of carboxylate groups, νsCOO-, present in all the samples. The group of five intense and partially overlapped bands observed in the 1200-950 cm^{-1} region is typical of pectin. These are assigned to the skeletal and C-O-C stretching modes of the pyranose ring, ν(C-C) pyranose and ν(C-O-C) pyranose, to C-O-C stretching vibrations of the glycosidic bond, ν(C-O-C)glycoside, and to a combination of the νC-OH and νC-C modes from the pyranose rings. The 950-700 cm^{-1} region contains the bands related to the external deformation vibrations of methyl, methylene and methyne groups. The band at 919 cm^{-1} is assigned to the rocking mode of the ester methyl group, $\rho(CH_3)$ ester.

Table S2. Summary of the results obtained by deconvolution of the DRIFT spectra in the 1850 to 1500 and 1150 to 950 cm^{-1} regions: $\tilde{\nu}$ - wavenumber (cm^{-1}); FWHM - full width at half maximum; A - integrated area.

Orange outer skin			Orange peel			Orange waste			Grapefruit peel			Assignment
$\tilde{\nu}$	FWHM	A	$\tilde{\nu}$	FWHM	A	$\tilde{\nu}$	FWHM	A	$\tilde{\nu}$	FWHM	A	
1720	89	41.70	1731	73	41.10	1736	61	28.03	1720	85	47.29	$\nu(C=O)_{ester}$
1658	42	6.27	1666	66	24.37	1672	89	31.38	1648	49	18.83	$\nu(C=O)_{acid}$
1601	86	58.67	1596	91	69.47	1599	86	54.98	1596	90	74.95	$\nu_{as}COO^-$
1140	59	27.88	1141	64	31.96	1153	39	16.14	1140	52	23.08	$\nu(C\text{-}O\text{-}C)_{pyranose}$
1106	21	1.91	1100	43	13.15	1116	60	35.71	1089	69	49,63	$\nu(C\text{-}O\text{-}C)_{pyranose}$
1069	81	82.86	1069	46	15.20	1063	71	51.30	1036	56	30.92	$\nu(C\text{-}O\text{-}C)_{glycoside}$
1015	54	28.34	1023	73	37.36	1014	51	23.27	1001	39	12.16	$\nu(C\text{-}OH)_{pyranose} + \nu(C\text{-}C)_{pyranose}$

Lemon outer skin			Lemon peel			Lemon waste			Assignment
$\tilde{\nu}$	FWHM	A	$\tilde{\nu}$	FWHM	A	$\tilde{\nu}$	FWHM	A	
1738	56	22.14	1733	60	32.27	1728	73	77.38	$\nu(C=O)_{ester}$
1675	62	19.08	1683	79	26.08	1668	64	29.33	$\nu(C=O)_{acid}$
1599	92	49.53	1596	78	36.18	1594	93	88.34	$\nu_{as}COO^-$
1148	32	5.55	1147	25	3.66	1149	27	3.64	$\nu(C\text{-}O\text{-}C)_{pyranose}$
1109	32	3.17	1096	80	62.03	1096	90	76.57	$\nu(C\text{-}O\text{-}C)_{pyranose}$
1082	110	104.10	1051	54	30.34	1050	52	26.30	$\nu(C\text{-}O\text{-}C)_{glycoside}$
1018	67	38.73	1014	50	33.68	1012	49	34.14	$\nu(C\text{-}OH)_{pyranose} + \nu(C\text{-}C)_{pyranose}$

Table S3. Summary of the results obtained by deconvolution of the DRIFT spectra of commercial citrus pectins in the 1850 to 1500 and 1150 to 950 cm^{-1} regions: $\tilde{\nu}$ - wavenumber (cm^{-1}); FWHM - full width at half maximum; A - integrated area.

Citrus Pectin A			Citrus Pectin B			Citrus Pectin C[a]			Citrus Pectin D[b]			Assignment
$\tilde{\nu}$	FWHM	A	$\tilde{\nu}$	FWHM	A	$\tilde{\nu}$	FWHM	A	$\tilde{\nu}$	FWHM	A	
1758	49	2.55	1760	29	1.94	1756	31	0.33	1764	26	0.46	$\nu(C=O)_{ester}$
1722	47	2.14	1735	57	10.84	1731	48	0.79	1734	83	5.78	$\nu(C=O)_{ester}$
1670	55	1.60	1671	77	4.32	1680	43	0.15	1666	42	0.69	$\nu(C=O)_{acid}$
-	-	-	1628	90	6.69	1627	84	1.24	1631	50	1.76	$\delta H\text{-}O\text{-}H$ (H_2O)
1600	43	0.60	1598	49	3.64	1595	55	0.40	1594	41	0.34	$\nu_{as}COO^-$
1149	18	5.94	1149	47	6.43	1146	45	0.77	1152	52	2.90	$\nu(C\text{-}O\text{-}C)_{pyranose}$
1110	26	10.02	1100	46	8.62	1103	38	0.80	1106	48	1.80	$\nu(C\text{-}O\text{-}C)_{pyranose}$
1052	17	6.03	1051	23	1.82	1049	19	0.09	1052	93	6.46	$\nu(C\text{-}O\text{-}C)_{glycoside}$
1025	21	11.15	1022	50	10.05	1021	54	1.37	1009	42	1.25	$\nu(C\text{-}OH)_{pyranose} + \nu(C\text{-}C)_{pyranose}$

[a] esterified potassium salt
[b] esterified

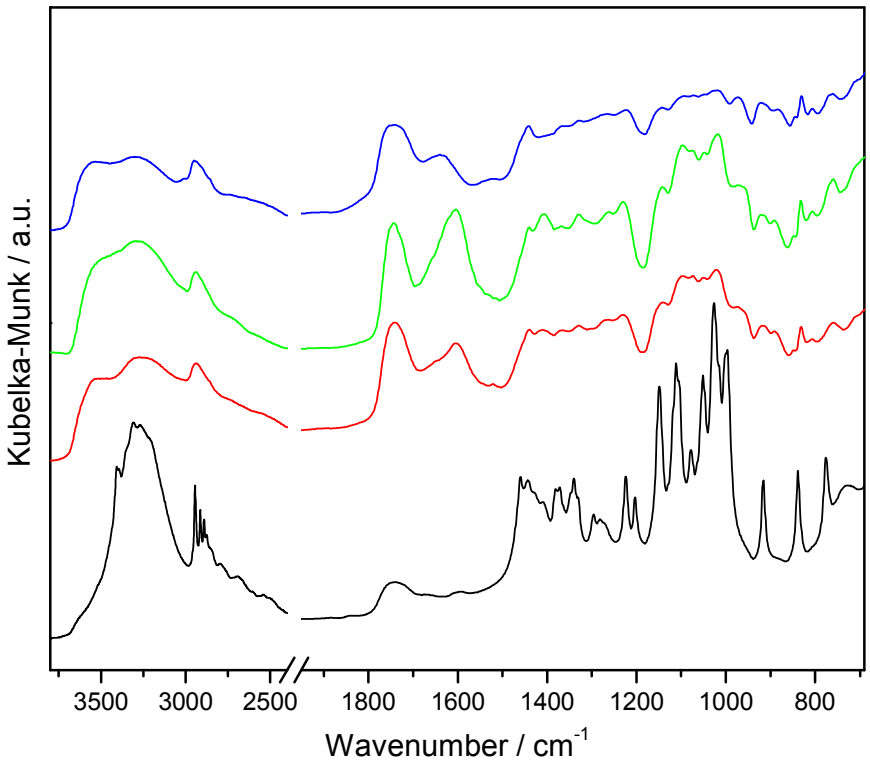

Figure S1. DRIFT spectra of commercial pectins: black – citrus pectin A; red – citrus pectin B; green – citrus pectin C; blue – citrus pectin D.