Pectic Substances in Fresh, Dried, Desiccated, and Oleaginous Spanish Fruits

Concepción Vidal-Valverde,* Inmaculada Blanco, and Enrique Rojas-Hidalgo

The pectic substance (PS) content [as anhydrogalacturonic acid (AGA)] in seventeen fresh fruits, some of them from different varieties and degrees of ripeness, five dried fruits, seven desiccated fruits, and five oleaginous fruits was investigated. For fresh fruits, the greater content of pectic substances in the edible portion corresponds to plantain (0.82%) and lemon and apricot (0.76%), followed by apple, cherimoya, and strawberry (0.55%). Botanical varieties did not significantly affect the pectic substance content of a fruit. The influence of the degree of ripeness was not very pronounced either. The pectic substance contents of dried, desiccated, and oleaginous fruits were higher than those for fresh fruits, due to the lower water content of the former. Chestnut and orgeat contained 7% of AGA, and the remainder of the fruits analyzed showed a PS content ranging between 4 and 2%.

Pectic substances (PS), a component of dietary fiber, are basically galacturonic acid polymers. Usually other sugar units, such as galactose, arabinose, or rhamnose, are present along with galacturonic acid as accompanying polysaccharide impurities or linked as side groups to the acid chain (Kerstez, 1951; Deuel and Stutz, 1958; Worth, 1967). The carboxylic groups can be partially methylated, and the C-2 and C-3 hydroxyl groups of the sugar ring can be acetylated.

Pectic substances have important physiological and nutritional consequences such as hypocholesterolemic effect, increased excretion of fecal sterols, and capacity for binding bile salts (Keys et al., 1961; Palmer and Dixon, 1966; Jenkins et al., 1975; Zilversmit, 1979; Ross and Leklem, 1981).

Koo and Stanton (1981) have demonstrated that pectin, when was administered in rats for 6 weeks, produced a significant decrease in the serum HDL cholesterol and increase in the cholesterol associated with LDL.

Due to the increased fecal transit time, pectic substances find application as antidiarrhoeics (Spiller et al., 1980).

Jenkins (1978), working with diabetic subjects, observed that PS slow down the absorption of soluble carbohydrates, causing a lesser increase of postprandial blood sugar. Recently, Tanton (1981) has shown that pectin supplementation in the diet improves glucose tolerance and also daily glycemia and glucosuria profiles, which were clearly connected with a decrease in endogenous immunoreactive insulin, as well as decrease of cholesterol and triglycerides. An adverse effect was registered, a decrease in the serum of two important cation (Fe^{2+} and Cu^{2+}). To these authors, a pectin-fortified diet could be considered as an important therapeutic tool in diabetes mellitus type II.

Labayle et al. (1980) and Leeds et al. (1981) observed that PS avoid or reduce the dumping syndrome of gastrectomized subjects.

The binding ability of polyvalent cations has found application as a detoxicant in the heavy metal industry (Kerstez, 1951; Surikova et al., 1977).

Pectic substance content of selected foods have been investigated with the aim of preparing diets effective in the correction of an ample human pathologic condition. The results are discussed in this report.

MATERIALS AND METHODS

Sample and Sample Preparations. Food samples used in this study were fresh fruits, dried fruits, nuts, and oleaginous fruits of acceptable quality and widely consumed by the Spanish population.

Fruits were weighed as purchased (total weight of the sample). When appropriate, the shell, peel, core, or stone was removed and weighed again (edible portion). This portion was homogenized in a Waring blendor until homogeneous consistency was achieved. Dry matter content was calculated from weight loss after heating in a vacuum oven at 35 °C until a constant weight.

Determination of Total Pectic Substances. Prior to the extraction of total PS, a selective removal of soluble carbohydrates was carried out. To this end, two aliquots (20 g each) of the total edible sample (≅600 g) were extracted by boiling under reflux with 80% aqueous ethanol, following the method of Krause and Bock (1973). If both replicates afforded a similar weight of nonsoluble material, the extraction of total PS was carried out. An aqueous solution (0.25%) of ammonium oxalate–oxalic acid was used for this purpose according to the method of Dekker and Richard (1972). Four replicated extractions were carried out with each fruit by using 10 mg of ethanol-insoluble material for each replicate extraction. Each one of the replicate extractions was subjected first to alkaline hydrolysis, according to McCready and McComb (1952) and Krause and Bock (1973), and then to enzymatic hydrolysis with 2–4 mg of polygalacturonase (Sigma, EC 3.2.1.15) following the method of Dekker and Richards (1972).

The concentrations of galacturonic acid obtained through these processes were adjusted separately by adding distilled water to reach 10–80 μg/mL anhydrogalacturonic acid (AGA).

The AGA content of each replicate sample was measured colorimetrically by using a 0.15% carbazole reagent (in absolute ethanol) following the procedure of McCready and McComb (1952). The absorbance was determined at 530 nm (Zeiss PM2DL spectrophotometer).

Four replicates were measured with each one of the hydrolyzed products. Thus, a total of 16 replicate absorptions were measured for each edible fruit sample. For evaluation of the concentration of galacturonic acid, a standard curve was obtained with each run. The blank determination contained all the reagents except pectic substance extracts. So that interference from any components reacting with concentrated sulfuric acid could be avoided in every run several culture tubes were carried through the determination procedure, omitting the carbazole reagent. The optical density thus obtained was subtracted from the values observed for that particular run.

Nutrition Department, Clinica Puerta de Hierro, Centro Nacional de Investigaciones Mèdico-Quirùrgicas de la Seguridad Social, Universidad Autónoma, S. Martin de Porres 4, Madrid-35, Spain.

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Table I. Fruits Analyzed

fruits	date	ripening	edible matter, proportion of wt purchased	mean of fruit wt, g	% water of edible matter
apple (*Pyrus malus*, L.)					
var. Starking	Feb	ripe	0.75	205	87.0
var. Golden	June	ripe	0.75	117	86.1
apricot (Prunus armeniaca, L.)	June	ripe	0.94	80	91.3
cherimoya (Annona cherimolia, Mill.)	March	ripe	0.60	296	72.7
cherry (*Prunus avium*, L.)	June	ripe	0.79	6	83.2
early fig (*Ficus carica*, L.)	June	ripe	0.78	54	83.5
grape (*Vitis vinifera*, L.)					
var. Rosetti	Dec	unripe	0.96	8	81.6
	Dec	overripe	0.93	5	73.3
var. Villanueva	Dec	unripe	0.96	6	76.7
	Dec	overripe	0.98	6	75.8
grapefruit (*Citrus decumana*, L.)	June	ripe	0.65	347	86.9
lemon (*Citrus lemonis*, Osbeck)	June	ripe	0.72	137	90.3
mandarin orange (*Citrus deliciosa*, Ten)	March	ripe	0.71	60	85.0
melon (*Cucumis melo*, L.)	Sept	unripe	0.60	2000	91.3
	Sept	overripe	0.63	2010	91.6
orange (*Citrus sinensis*, L.)	June	ripe	0.62	251	86.7
peach (*Prunus persica*, Sieb and Zuce)	June	ripe	0.73	103	83.6
pear (*Pyrus communis*, L.)	March	unripe	0.76	103	84.4
	March	overripe	0.72	98	84.0
plantain (*Musa paradisiaca*, L.)	July	ripe	0.57	102	78.6
plum (*Prunus domestica*, L.)					
var. White	June	ripe	0.54	43	87.5
var. Red	June	ripe	0.52	50	87.0
strawberry (*Fragaria vesca*, L.)	June	ripe	0.96	8	90.0
watermelon (*Citrullus vulgaris*, Schered)	July	ripe	0.60	1705	92.6
almond (*Prunus amigdalus*, Stokes)			1.0	1.4	2.9
apricot, dried (*Prunus armeniaca*, L.)			1.0	8.1	16.3
coconut (*Cocos nucifera*, L.)			0.7	393.0	29.2
chestnut (*Castanea vesca*, G.)			1.0	3.5	6.6
date (*Phoenix dactylifera*, L.)			0.9	9.0	15.5
fig, dried (*Ficus carica*, L.)			1.0	9.3	35.3
hazelnut (*Corylus avellana*, L.)			0.4	2.2	1.9
olives var. Manzanilla (*Olea europea sativa* Hoffg, Link)		unripe	0.7	3.3	66.4
		ripe	0.7	2.9	46.8
orgeat (*Cyperus esculentus*, L.)			1.0	0.3	5.7
pistachio (*Pistacia vera*, L.)			0.5	0.8	1.9
peanut (*Arachis hipogea*, L.)			0.7	2.6	1.0
pine nut (*Pinus pinea*, L.)			0.2	0.8	2.8
prune (*Prunus domestica*, L.)			0.9	11.6	22.2
raisin, dried (*Vitis vinifera*, L.)			1.0	0.2	35.8
soybean (*Glycine max*)			1.0	0.15	6.2
sunflower, seed (*Helianthus annus*, L.)			0.7	0.1	7.0
walnut (*Juglans regia*, L.)			0.5	10.8	1.9

RESULTS AND DISCUSSION

The PS content (as anhydrogalacturonic acid) of a series of fruits (17 fresh fruits, 5 dried fruits—almonds, hazelnut pistachio, pine nuts, and walnuts—7 desiccated fruits—apricot, chestnut, prune, date, fig, raisin, and orgeat—and 5 oleaginnous fruits—olives, peanut, coconut, sunflower seeds, and soybean) was investigated.

Table I shows the edible matter proportion of weight purchased, the mean weight of fruit analyzed, and the water content of edible matter.

Table II shows the PS content (expressed as anhydrogalacturonic acid, AGA) of 34 fruits analyzed. Percentages of AGA were indicated on a fresh and dry matter basis of the edible portion. Several parameters, such as botanical variety, ripeness, and date of analyses, were considered in the case of fresh fruits, since the AGA content can be affected by them (Pilnik and Voragen, 1970). The purchasing date gives some indication of the time elapsed between harvest time and the time of analyses.

The method employed for the determination of the PS content uses soluble carbohydrate-free material since those carbohydrates can interfere with the carbazole determination of AGA (Krause and Bock, 1973). The presence of methyl ester groups in the PS sample gives rise to lowered AGA values (McCready and McComb, 1952), and hence the chemical hydrolysis was performed as a step previous to the enzymic hydrolysis. The latter was carried out with polygalacturonase (EC 3.2.1.15) to ensure that there was no simultaneous break apart of other polymeric materials such as proteins, xylans, modified cellulose, etc., which could create possible interferences with the carbazole reaction (Williams and Bevenue, 1954).

For fresh fruits, the greater content of pectic substances in the edible portion corresponds to plantain (0.82%) and lemon and apricot (0.76%), followed by apple, cherimoya, and strawberry (0.55%). Botanical varieties did not significantly affect the PS content of a fruit. The influence of the degree of ripeness was not very pronounced either. Generally, there was a slight increase in the PS content with increased ripeness, which was more marked in the case of grapes (Villanueva variety), and a slight decrease for the Rosetti variety of the same fruit.

The PS contents of dried, desiccated, and oleaginous fruits were higher than those for fresh fruits. Chestnut and orgeat contained 7% of AGA and the rest of these

Table II. Pectic Substances in Spanish Fruits (Means ± SD)

fruits	% AGA, fresh matter of edible portion	% AGA, dry matter of edible portion
apple, without skin and core		
var. Starking	0.56 ± 0.01	4.31 ± 0.08
var. Golden	0.50 ± 0.02	3.60 ± 0.14
apricot, with skin and without stone	0.76 ± 0.01	8.73 ± 0.11
cherimoya, without skin and stone	0.54 ± 0.06	1.98 ± 0.22
cherry, with skin and without stone	0.37 ± 0.01	2.20 ± 0.06
early fig, without skin	0.35 ± 0.03	2.12 ± 0.18
grape, with skin and without pips		
var. Rosetti: unripe	0.42 ± 0.03	2.28 ± 0.16
ripe	0.37 ± 0.01	1.39 ± 0.04
var. Villanueva: unripe	0.41 ± 0.02	1.76 ± 0.08
ripe	0.68 ± 0.05	2.80 ± 0.21
grapefruit, without skin and pips	0.51 ± 0.01	3.89 ± 0.08
lemon, without skin and pips	0.75 ± 0.10	7.73 ± 0.10
mandarin orange, without skin and pips	0.41 ± 0.01	2.73 ± 0.07
melon, without skin and pips		
unripe	0.15 ± 0.00	1.72 ± 0.00
ripe	0.19 ± 0.01	2.26 ± 0.12
orange, without skin and pips	0.42 ± 0.01	3.16 ± 0.07
peach, without skin and stone	0.45 ± 0.01	2.74 ± 0.06
pear, without skin and core		
unripe	0.28 ± 0.01	1.79 ± 0.06
ripe	0.39 ± 0.01	2.43 ± 0.06
plantain, without skin	0.82 ± 0.10	3.84 ± 0.05
plum, without skin and stone		
var. White	0.47 ± 0.05	3.76 ± 0.40
var. Red	0.37 ± 0.01	2.85 ± 0.08
strawberry, with skin	0.56 ± 0.01	5.60 ± 0.10
watermelon, without skin and pips	0.22 ± 0.01	2.97 ± 0.13
almond, without skin	2.16 ± 0.03	2.22 ± 0.03
apricot, dried, with skin and without stone	2.58 ± 0.18	3.08 ± 0.21
coconut, without shell, with skin	0.51 ± 0.12	0.72 ± 0.17
chestnut, dried, without skin	7.38 ± 0.13	7.90 ± 0.14
date, with skin and without stone	1.61 ± 0.14	1.90 ± 0.17
figs, dried, with skin	2.42 ± 0.11	3.74 ± 0.17
hazelnut, without skin	2.97 ± 0.12	3.03 ± 0.12
olives, with skin and without stone, var. Manzanilla		
unripe	0.94 ± 0.11	2.80 ± 0.33
ripe	1.97 ± 0.21	3.70 ± 0.39
orgeat, with skin	7.05 ± 0.22	7.48 ± 0.23
pistachio, with skin and without shell	2.66 ± 0.03	2.72 ± 0.03
peanut, with skin and without shell	2.61 ± 0.12	2.64 ± 0.12
pine nut, without skin	1.33 ± 0.16	1.37 ± 0.16
prune, with skin, without stone	2.50 ± 0.16	3.21 ± 0.21
raisin, dried, with skin and pips	0.99 ± 0.05	1.54 ± 0.08
soybean, with skin	3.45 ± 0.17	3.68 ± 0.18
sunflower, without shell	3.17 ± 0.64	3.41 ± 0.69
walnut, with skin	1.96 ± 0.19	2.00 ± 0.19

Table III. Pectic Substances in Fruits according to Different Authors (Grams per 100 Grams Fresh Matter of Edible Portion)

fruits	Belo and Lumen (1981)	Campbell and Palmer (1978)[a]	Hardinge et al. (1965)[a]	Krause and Bock (1973)[a]	Money and Christian (1950)	Southgate (1976)[a]	our results
apple	1.81[b]	0.71-0.84	0.60	0.45-0.44	0.55-0.53	0.38	0.50-0.56
apricot		0.71-1.32	1.00	0.70	0.99[d]	0.46	0.76
cherry		0.24-0.54	0.30	0.40	0.32	0.09	0.37
grape		0.09-0.28		0.20	0.22[d]		0.37-0.68
grapefruit		3.30-4.50					0.51
lemon		2.80-2.99	3.00		1.14	0.51	0.75
melon			0.30				0.15-0.19
orange	7.72[c]	2.34-2.38	1.30		0.59	0.46	0.42
peach			0.70	0.64	0.78[d]	0.40	0.45
pear	1.31[b]		0.60-0.70	0.46	0.46		0.28-0.39
plum			0.90-1.00	0.59-0.61	0.79-0.90[d]	0.70	0.37-0.47
raisin		0.82-1.04	1.00				0.99
strawberry				0.50	0.54	0.33	0.56
watermelon			0.10				0.22

[a] Not specified which edible parts are dealth with. [b] With skin and core. [c] From the albedo. [d] With skin.

fruits analyzed showed a PS content ranging between 4 and 2%. These values were comparable with those obtained for fresh fruits when they were referred to edible portion on a dry matter basis. Thus, the higher PS content obtained for dried fruits was only a reflection of the low water content of these fruits (5–10%) when compared with

the water content of fresh fruits (75–90%) (see Table I).

It is obvious from the data obtained that most of these foods may have a considerable role in the design of pectin-rich diets if required for medical reasons.

Table III shows the PS content of fruits according to published literature. In general, there is good agreement between our results and published data. Slight variations can be ascribed to the fact that the data of the literature were obtained for fruits with skin while our data were obtained with peeled fruits. In the case of citrus fruit, most of the published data refer to whole fruit or albedo only. Since this portion of the citrus fruit is very rich in PS, the values collected in Table III are clearly higher than those reported in Table II. No information has been found on the PS content of dried, desiccated, or oleaginous fruits.

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Seasonal and Regional Variation in the Quantitative Composition of Cold-Pressed Lemon Oil from California and Arizona

James A. Staroscik* and Alicia A. Wilson

Cold-pressed peel oils from California and Arizona lemons were analyzed by glass capillary gas chromatography. Thirty-eight components were determined in early-, mid-, and late-season desert and coastal fruit by using the internal standard method. Several of these, including β-pinene, limonene, neral, geranial, nonanal, linalool, and geranyl acetate, showed large variations in concentration as a function of either maturity or geographic origin of the fruit. Climatic differences between the two growing regions are presumed to be most responsible for the compositional differences observed.

About one-fourth of the world's lemon crop is now produced in the United States ("Citrus Fruit Industry Statistical Bulletin", 1981). Virtually all of this production is confined to the citrus growing regions of California and Arizona. Currently, 40–50 million, 38-lb cartons of lemons per year are harvested in these regions. On average, about half of this crop is not suitable for the fresh fruit market, being either incorrectly sized or cosmetically defective, and is diverted to the processing plant. Cold-pressed lemon oil is the most valuable commodity derived from this "products fruit".

Products Research and Development Division, Sunkist Growers, Inc., Ontario, California 91761.

Although Argentina and Brazil are steadily increasing their processing capacity, lemon oil from California and Arizona still represents about 40% of world production. Because of cooperative marketing agreements, most of this oil is blended prior to sale, usually to meet the specifications of the Food Chemicals Codex or other user specifications. Large-scale bulking and blending eliminates or minimizes yearly variation in physicochemical and organoleptic properties.

Recently, we applied the technique of glass capillary gas chromatography to the quantitative analysis of a typical, blended, cold-pressed lemon oil derived from California and Arizona fruit (Staroscik and Wilson, 1982). The concentrations of 37 components were determined and the results compared to those obtained earlier by packed-

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