

Proanthocyanidins in Common Food Products of Plant Origin

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The contents of extractable and unextractable proanthocyanidins were determined in a large number of commercial food products of plant origin available in Finland. Proanthocyanidins were extracted with aqueous acetone–methanol and quantified by normal phase high-performance liquid chromatography (HPLC) according to their degree of polymerization. Unextractable proanthocyanidins were analyzed from the extraction residue by reversed phase HPLC after acid-catalyzed depolymerization as free flavan-3-ols (terminal units) and benzylthioethers (extension units). Proanthocyanidins were detected in 49 of 99 selected food items. The highest contents per fresh weight were determined in chokeberries, rose hips, and cocoa products. Berries and fruits were generally the best sources of proanthocyanidins, whereas most of the vegetables, roots, and cereals lacked them completely. Many of the samples contained a significant proportion of insoluble proanthocyanidins, which need to be quantified as well if total proanthocyanidins are studied. Considerable variation was observed in proanthocyanidin contents in berries, which requires further research.

KEYWORDS: Proanthocyanidins; condensed tannins; flavan-3-ols; database; food; HPLC

INTRODUCTION

Proanthocyanidins (condensed tannins) are plant secondary metabolites derived from the flavonoid pathway. They are widely present in the plant kingdom, for example, in fruits, berries, nuts, seeds, and bark of pine trees (1–4). Proanthocyanidins can be divided into several classes based on the hydroxylation of their constitutive units and the linkages between them. The most common constitutive units are (epi)catechins, (epi)gallocatechins, and, more rarely, (epi)afzelechins, leading to procyanidin, prodelphinidin, and propelargonidin structures, respectively (Figure 1). Heterogeneous proanthocyanidins composed of more than one type of flavan-3-ol unit are commonly found in plants. Flavan-3-ol units are most frequently linked via B-type bonds, that is, C₄ → C₈ or C₄ → C₆ linkages. Occasionally, an additional C₂ → O₇ or C₂ → O₅ linkage may exist, leading to doubly bonded A-type proanthocyanidins. Proanthocyanidins are powerful antioxidants, but they have also been reported to demonstrate antibacterial, antiviral, anticarcinogenic, anti-inflammatory, and vasodilatory activities (5–8). The physical, chemical, and biological features of proanthocyanidins depend largely on their structure and particularly on their degree of polymerization (9–11).

Despite the fact that proanthocyanidins have been associated with several health benefits, further studies are needed to fully understand their actions. It is essential to provide updated research data on their contents in foods and beverages to enable epidemiological analysis and to understand the possible

relationships between the intake of these compounds and the risk of developing various diseases. The existing quantitative information on the content of proanthocyanidins in plant products is rather limited, in large part because of a lack of appropriate analytical methodology. Nonetheless, the U.S. Department of Agriculture (USDA) has published a valuable database for proanthocyanidins in a wide range of foods (<http://www.nal.usda.gov/fnic/foodcomp/Data/PA>). The analytical data for the database were mainly generated from one, if extensive, study by Gu et al. (3), which is why more research is obviously needed to complete and confirm the previous research results. In the present study we used two HPLC methods, one with normal phase separation and another with reversed phase separation after thioacidolysis, to determine the extractable and unextractable proanthocyanidins in food products commonly consumed in Finland. To our knowledge, this is the first study to report the presence of both extractable and unextractable proanthocyanidins in such a wide range of plant foods. The results will be entered into the Finnish food composition database, Fineli, maintained by the National Institute of Health and Welfare in Finland.

MATERIALS AND METHODS

Chemicals. (–)-Epicatechin, (–)-epicatechin gallate, and (–)-epigallocatechin were purchased from Sigma-Aldrich Chemie Inc. (Steinheim, Germany), and (+)-catechin was purchased from Cayman Chemical (Ann Arbor, MI). Procyanidin dimers B1 (epicatechin-(4β→8)-catechin) and B2 (epicatechin-(4β→8)-epicatechin) were obtained from PlantChem Co. (Sandnes, Norway). Procyanidin oligomers—consisting of epicatechin units linked together via B-type bonds—with different degrees of polymerization (P1–P10 and a polymeric fraction PP with an average DP of 20)

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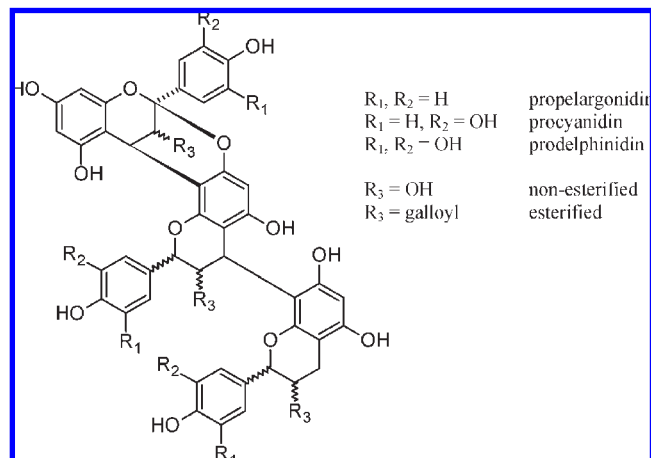


Figure 1. Structure of a trimeric proanthocyanidin with A- and B-type linkages.

were isolated from Saskatoon berry at MTT Agrifood Research Finland (12). Benzylmercaptan (α -toluolthiol) was provided by Fluka Sigma-Aldrich Chemie Inc. (Buchs, Switzerland). Twenty-five percent ammonium hydroxide, concentrated hydrochloric acid (37–38%), acetone, methanol, dichloromethane, acetic acid, and phosphoric acid (85%) were purchased from Mallinckrodt Baker Inc. (Utrecht, The Netherlands). Formic acid (99%) came from Acros Organics Fischer Scientific Inc. (Geel, Belgium), *N,N*-Dimethylformamide was from Rathburn Chemicals Ltd. (Walkerburn, Scotland) and sodium hydroxide from Merck, Sharp & Dohme GmbH (Haar, Germany). All chromatographic solvents were of HPLC grade.

Samples. A variety of food items and beverages commonly consumed in Finland were selected for the study (Tables 1 and 2). Sampling was performed as described before (13–16). All of the samples, except the berries, rhubarb, and red wine, were purchased from retail stores representing each of Finland's three main grocery chains in the Helsinki, Kuopio, and Forssa areas during 2003–2005. Berries and rhubarb, all domestic, were purchased from various parts of Finland during the summers of 2003–2007. Red wine samples of the 10 most popular brands in Finland were purchased in autumn 2004 from Alko Inc., which has a

Table 1. Samples with No Detectable Proanthocyanidins

sample	Latin name	family
Fruits and Berries		
watermelon	<i>Citrullus lanatus</i>	Cucurbitaceae
grapefruit (orange and red varieties)	<i>Citrus paradisi</i>	Rutaceae
mandarin	<i>Citrus reticulata</i>	Rutaceae
orange (orange and red varieties)	<i>Citrus sinensis</i>	Rutaceae
Vegetables and Roots		
spinach/frozen	<i>Spinacia oleracea</i>	Amaranthaceae
celery root	<i>Apium graveolens</i> var. <i>rapaceum</i>	Apiaceae
carrot	<i>Daucus carota</i>	Apiaceae
parsnip	<i>Pastinaca sativa</i>	Apiaceae
Jerusalem artichoke	<i>Helianthus tuberosus</i>	Asteraceae
iceberg lettuce	<i>Lactuca sativa</i> var. <i>capitata</i>	Asteraceae
pot-grown lettuce (conventional and 'Lollo Rosso')	<i>Lactuca sativa</i> var. <i>crispa</i>	Asteraceae
rutabaga	<i>Brassica napus</i> var. <i>napobrassica</i>	Brassicaceae
cauliflower	<i>Brassica oleracea</i> var. <i>botrytis</i>	Brassicaceae
red cabbage	<i>Brassica oleracea</i> var. <i>capitata</i> f. <i>rubra</i>	Brassicaceae
white cabbage	<i>Brassica oleracea</i> var. <i>capitata</i> f. <i>alba</i>	Brassicaceae
broccoli	<i>Brassica oleracea</i> var. <i>italica</i>	Brassicaceae
Chinese cabbage	<i>Brassica pekinensis</i>	Brassicaceae
turnip	<i>Brassica rapa</i>	Brassicaceae
radish	<i>Raphanus sativus</i> var. <i>sativus</i>	Brassicaceae
red beet	<i>Beta vulgaris</i>	Chenopodiaceae
cucumber	<i>Cucumis sativus</i>	Cucurbitaceae
zucchini	<i>Cucurbita pepo</i>	Cucurbitaceae
onion (yellow and red varieties)	<i>Allium cepa</i>	Liliaceae
garlic	<i>Allium sativum</i>	Liliaceae
bell pepper (green, red and yellow varieties)	<i>Capsicum annuum</i>	Solanaceae
tomato	<i>Lycopersicon esculentum</i>	Solanaceae
eggplant	<i>Solanum melongena</i>	Solanaceae
potato (five cultivars: 'Timo', 'Siikli', 'Nicola', 'Van Gogh', 'Rosamunda')	<i>Solanum tuberosum</i>	Solanaceae
Cereal Products		
oat (flakes and brans)	<i>Avena sativa</i>	Poaceae
millet	<i>Panicum miliaceum</i>	Poaceae
rice	<i>Oryza sativa</i>	Poaceae
rye (flours and brans)	<i>Secale cereale</i>	Poaceae
wheat (flours and brans)	<i>Triticum</i> spp.	Poaceae
Others		
soybean	<i>Glycine max</i>	Fabaceae
pea	<i>Pisum sativum</i>	Fabaceae
broad bean	<i>Vicia faba</i>	Fabaceae
coffee beverage	<i>Coffea</i> spp.	Rubiaceae

Table 2. Proanthocyanidin Contents in Samples (Milligrams per 100 g of Fresh Weight, Mean \pm Standard Deviation, $n = 3$)^a

sample	Latin name	family	DM (%)	extractable proanthocyanidins							unextractable			total	type ^b
				P1	P2	P3	P4–P6	P7–P10	>P10	total	DP				
Fruits and Berries															
kiwi fruit	<i>Actinidia chinensis</i>	Actinidiaceae	17.6	0.56 \pm 0.06	0.87 \pm 0.07	0.42 \pm 0.05	0.66 \pm 0.06	tr	tr	24.0 \pm 2.2	2.51 \pm 0.24	9.7 \pm 0.7	12.2 \pm 1.3	12.3 \pm 1.0	PC
sea buckthorn	<i>Hippophae rhamnoides</i>	Elaeagnaceae	16.3	1.6 \pm 0.1	5.1 \pm 0.2	3.6 \pm 0.3	11.0 \pm 1.1	tr	tr	57.7 \pm 2.0	45.3 \pm 3.9	199 \pm 3	14.0 \pm 0.5	244 \pm 7	PC, PD
crowberry	<i>Empetrum nigrum</i>	Empetraceae	13.0	19.0 \pm 1.6	35.9 \pm 0.3	21.2 \pm 0.4	32.5 \pm 1.8	23.1 \pm 1.5	23.1 \pm 1.5	189 \pm 8	189 \pm 8	10.3 \pm 0.2	6.0 \pm 0.1	199 \pm 8	A, PC, PD
blueberry	<i>Vaccinium corymbosum</i>	Ericaceae	14.5	6.5 \pm 0.4	14.5 \pm 0.2	13.3 \pm 0.1	28.1 \pm 2.6	12.5 \pm 0.4	192 \pm 11	267 \pm 15	46.4 \pm 2.0	17.7 \pm 0.8	313 \pm 3	133 \pm 17	PC
bilberry 1	<i>Vaccinium myrtillus</i>	Ericaceae	14.8	1.2 \pm 0.1	5.2 \pm 0.2	8.5 \pm 0.1	8.7 \pm 0.6	0.7 \pm 0.1	48.7 \pm 1.5	73.0 \pm 2.6	60.0 \pm 0.3	8.8 \pm 0.4	133 \pm 3	133 \pm 3	A, PC, PD
bilberry 2	<i>Vaccinium myrtillus</i>	Ericaceae	12.6	6.5 \pm 0.2	8.1 \pm 0.7	14.2 \pm 1.2	25.4 \pm 1.6	11.3 \pm 1.1	85.3 \pm 7.2	151 \pm 12	40.5 \pm 1.8	11.0 \pm 0.7	192 \pm 14	192 \pm 14	A, PC, PD
bilberry 3	<i>Vaccinium myrtillus</i>	Ericaceae	13.9	4.2 \pm 0.2	5.9 \pm 0.3	6.4 \pm 0.5	11.4 \pm 0.8	7.4 \pm 0.3	44.2 \pm 0.4	79.5 \pm 2.5	67.2 \pm 6.2	11.8 \pm 0.8	147 \pm 9	147 \pm 9	A, PC, PD
bilberry 4	<i>Vaccinium myrtillus</i>	Ericaceae	14.8	4.6 \pm 0.3	6.7 \pm 0.5	9.2 \pm 0.8	15.8 \pm 1.2	9.0 \pm 0.7	51.9 \pm 2.7	97.2 \pm 6.2	66.4 \pm 4.0	13.8 \pm 0.8	164 \pm 10	164 \pm 10	A, PC, PD
bilberry 5	<i>Vaccinium myrtillus</i>	Ericaceae	11.3	4.1 \pm 0.1	5.9 \pm 0.4	6.8 \pm 0.6	13.9 \pm 1.1	7.7 \pm 0.8	56.8 \pm 0.9	95.2 \pm 3.9	58.2 \pm 3.6	13.6 \pm 0.3	153 \pm 8	153 \pm 8	A, PC, PD
bilberry 6	<i>Vaccinium myrtillus</i>	Ericaceae	13.6	3.7 \pm 0.1	5.6 \pm 0.2	8.3 \pm 0.3	13.6 \pm 0.4	7.9 \pm 0.5	32.6 \pm 1.4	71.7 \pm 2.8	30.5 \pm 2.9	8.7 \pm 0.4	102 \pm 6	102 \pm 6	A, PC, PD
bilberry (mean)	<i>Vaccinium myrtillus</i>	Ericaceae	13.5 \pm 1.4	4.1 \pm 1.7	6.2 \pm 1.0	8.9 \pm 2.8	14.8 \pm 5.7	7.3 \pm 3.5	59 \pm 18	95 \pm 30	54 \pm 15	11.3 \pm 2.2	148 \pm 45	148 \pm 45	A, PC, PD
bilberry soup (10% berry content)			11.0	0.29 \pm 0.01	0.55 \pm 0.05	0.51 \pm 0.03	0.58 \pm 0.06	0.15 \pm 0.03		2.1 \pm 0.1				2.1 \pm 0.1	A, PC, PD
European cranberry 1	<i>Vaccinium oxycoccos</i>	Ericaceae	12.9	5.6 \pm 0.5	8.8 \pm 0.6	8.1 \pm 0.2	22.0 \pm 2.1	7.7 \pm 0.2	17.4 \pm 4	226 \pm 8	186 \pm 8	23.0 \pm 0.9	412 \pm 16	412 \pm 16	A, PC, PD
European cranberry 2	<i>Vaccinium oxycoccos</i>	Ericaceae	13.1	6.2 \pm 0.5	11.1 \pm 0.9	11.9 \pm 0.8	31.2 \pm 2.7	15.7 \pm 1.7	148 \pm 5	224 \pm 12	175 \pm 12	23.8 \pm 2.2	399 \pm 24	399 \pm 24	A, PC, PD
European cranberry (mean)	<i>Vaccinium oxycoccos</i>	Ericaceae	13.0 \pm 0.1	5.9 \pm 0.4	10.0 \pm 1.6	10.0 \pm 2.7	26.6 \pm 6.5	11.7 \pm 5.7	161 \pm 18	225 \pm 2	181 \pm 8	23.4 \pm 0.6	406 \pm 9	406 \pm 9	A, PC, PD
bog whortleberry	<i>Vaccinium uliginosum</i>	Ericaceae	12.6	7.6 \pm 0.3	19.8 \pm 0.9	18.6 \pm 0.7	39.3 \pm 2.7	tr	0.92 \pm 0.09	80.2 \pm 4.7	24.4 \pm 2.1	9.3 \pm 0.5	105 \pm 7	105 \pm 7	A, PC
lingonberry 1	<i>Vaccinium vitis-idaea</i>	Ericaceae	14.7	25.9 \pm 1.2	55.6 \pm 3.2	48.8 \pm 2.7	59.7 \pm 2.3	16.5 \pm 1.5	146 \pm 8	353 \pm 19	27.9 \pm 0.7	7.0 \pm 0.1	381 \pm 20	381 \pm 20	A, PC
lingonberry 2	<i>Vaccinium vitis-idaea</i>	Ericaceae	14.5	25.3 \pm 0.7	52.6 \pm 0.2	44.5 \pm 1.2	57.3 \pm 2.8	13.3 \pm 1.4	87.5 \pm 2.1	281 \pm 9	27.4 \pm 2.7	7.0 \pm 0.1	308 \pm 12	308 \pm 12	A, PC
lingonberry 3	<i>Vaccinium vitis-idaea</i>	Ericaceae	15.8	32.3 \pm 1.8	74.1 \pm 5.5	67.7 \pm 6.0	95.5 \pm 6.8	42.6 \pm 1.2	184 \pm 7	496 \pm 28	51.8 \pm 0.2	6.1 \pm 0.5	548 \pm 28	548 \pm 28	A, PC
lingonberry 4	<i>Vaccinium vitis-idaea</i>	Ericaceae	15.0	24.6 \pm 1.9	46.3 \pm 2.9	43.0 \pm 2.9	73.5 \pm 4.0	34.0 \pm 2.9	50.6 \pm 0.5	272 \pm 13	25.7 \pm 1.9	7.4 \pm 0.3	298 \pm 15	298 \pm 15	A, PC
lingonberry 5	<i>Vaccinium vitis-idaea</i>	Ericaceae	14.9	41.0 \pm 0.4	76.1 \pm 0.5	76.0 \pm 1.3	140 \pm 8	69.3 \pm 6.0	106 \pm 10	508 \pm 26	30.9 \pm 0.1	5.7 \pm 0.6	509 \pm 26	509 \pm 26	A, PC
lingonberry 6	<i>Vaccinium vitis-idaea</i>	Ericaceae	13.8	16.5 \pm 0.6	32.5 \pm 0.8	29.7 \pm 0.8	52.3 \pm 2.1	27.9 \pm 1.9	47.4 \pm 4.4	206 \pm 11	36.4 \pm 3.0	7.2 \pm 0.3	242 \pm 14	242 \pm 14	A, PC
lingonberry (mean)	<i>Vaccinium vitis-idaea</i>	Ericaceae	14.8 \pm 0.7	27.6 \pm 8.3	56 \pm 17	52 \pm 17	80 \pm 33	34 \pm 20	104 \pm 54	350 \pm 130	33.4 \pm 9.8	6.7 \pm 0.7	390 \pm 140	390 \pm 140	A, PC
black currant 1	<i>Ribes nigrum</i>	Grossulariaceae	17.2	2.6 \pm 0.2	3.4 \pm 0.2	2.1 \pm 0.1	7.3 \pm 0.6	1.1 \pm 0.1	227 \pm 19	244 \pm 20	224 \pm 20	37.7 \pm 2.6	468 \pm 27	468 \pm 27	PC, PD
black currant 2	<i>Ribes nigrum</i>	Grossulariaceae	18.9	1.3 \pm 0.1	2.2 \pm 0.2	1.2 \pm 0.1	3.3 \pm 0.2	tr	156 \pm 7	164 \pm 8	180 \pm 15	29.6 \pm 1.6	344 \pm 23	344 \pm 23	PC, PD
black currant 3	<i>Ribes nigrum</i>	Grossulariaceae	18.4	1.6 \pm 0.1	2.6 \pm 0.1	1.7 \pm 0.1	2.8 \pm 0.1	tr	185 \pm 3	194 \pm 4	201 \pm 16	36.1 \pm 1.4	395 \pm 20	395 \pm 20	PC, PD
black currant (mean)	<i>Ribes nigrum</i>	Grossulariaceae	18.2 \pm 0.9	1.8 \pm 0.7	2.7 \pm 0.6	1.7 \pm 0.5	4.5 \pm 2.5	0.4	189 \pm 36	200 \pm 40	202 \pm 23	35.1 \pm 5.1	400 \pm 60	400 \pm 60	PC, PD
black currant juice (80% berry content)				0.07 \pm 0.01	0.35 \pm 0.03	0.13 \pm 0.01	0.38 \pm 0.02	tr	3.5 \pm 0.1	4.4 \pm 0.2			4.4 \pm 0.2	4.4 \pm 0.2	PC, PD
red currant	<i>Ribes rubrum</i>	Grossulariaceae	14.4	2.4 \pm 0.1	2.9 \pm 0.2	2.3 \pm 0.2	4.2 \pm 0.2	tr	24.0 \pm 0.5	35.8 \pm 1.2	86.8 \pm 3.9	39.2 \pm 3.6	123 \pm 5	123 \pm 5	PC, PD
gooseberry, red	<i>Ribes uva-crispa</i>	Grossulariaceae	11.3	2.7 \pm 0.2	2.5 \pm 0.1	3.7 \pm 0.1	6.2 \pm 0.3	1.3 \pm 0.1	36.4 \pm 2.8	52.8 \pm 3.6	7.7 \pm 0.7	10.2 \pm 0.2	60.5 \pm 4.3	60.5 \pm 4.3	PC, PD
gooseberry, yellow	<i>Ribes uva-crispa</i>	Grossulariaceae	12.1	0.64 \pm 0.07	1.5 \pm 0.1	0.89 \pm 0.08	1.3 \pm 0.2	tr	115 \pm 6	119 \pm 7	27 \pm 1.8	12.6 \pm 1.0	146 \pm 9	146 \pm 9	PC, PD
gooseberry (mean)	<i>Ribes uva-crispa</i>	Grossulariaceae	11.7 \pm 0.6	1.7 \pm 1.5	2.0 \pm 0.7	2.3 \pm 2.0	3.8 \pm 3.5	0.7	80 \pm 60	90 \pm 50	17 \pm 14	11.4 \pm 1.7	100 \pm 60	100 \pm 60	PC, PD
avocado	<i>Persea americana</i>	Lauraceae	25.1	2.2 \pm 0.2	2.4 \pm 0.2	2.6 \pm 0.2	4.8 \pm 0.3	1.1 \pm 0.1		13.1 \pm 1.0	4.7 \pm 0.1	6.0 \pm 0.5	17.8 \pm 1.1	17.8 \pm 1.1	PC
banana	<i>Musa sapientum</i>	Musaceae	25.4								64.3 \pm 6.2	102 \pm 10	64.3 \pm 6.2	64.3 \pm 6.2	PC, PD
Saskatoon berry	<i>Amelanchier alnifolia</i>	Rosaceae	12.8	21.4 \pm 0.4	20.2 \pm 0.7	21.7 \pm 1.3	46.1 \pm 3.7	21.0 \pm 1.9	44.6 \pm 4.1	175 \pm 12	101 \pm 9	8.2 \pm 0.1	276 \pm 21	276 \pm 21	PC
chokeberry 1	<i>Aronia mitschurinii</i>	Rosaceae	21.9	4.1 \pm 0.2	3.9 \pm 0.2	3.7 \pm 0.3	11.5 \pm 1.0	7.1 \pm 0.7	1930 \pm 150	1960 \pm 150	215 \pm 14	22.5 \pm 2.2	2170 \pm 170	2170 \pm 170	PC
chokeberry 2	<i>Aronia mitschurinii</i>	Rosaceae	22.3	1.9 \pm 0.1	3.2 \pm 0.1	2.6 \pm 0.1	3.9 \pm 0.3	1.3 \pm 0.1	1920 \pm 60	1930 \pm 60	187 \pm 2	23.3 \pm 0.2	2120 \pm 60	2120 \pm 60	PC
chokeberry 3	<i>Aronia mitschurinii</i>	Rosaceae	20.1	2.7 \pm 0.1	5.1 \pm 0.3	5.2 \pm 0.4	14.4 \pm 1.2	12.4 \pm 1.2	1300 \pm 80	1340 \pm 80	157 \pm 18	15.2 \pm 0.4	1500 \pm 100	1500 \pm 100	PC
chokeberry 4	<i>Aronia mitschurinii</i>	Rosaceae	18.5	3.0 \pm 0.2	3.7 \pm 0.2	3.5 \pm 0.3	10.5 \pm 0.8	13.7 \pm 1.1	1360 \pm 90	1400 \pm 90	346 \pm 24	50.4 \pm 3.3	1740 \pm 120	1740 \pm 120	PC
chokeberry 5	<i>Aronia mitschurinii</i>	Rosaceae	18.7	5.1 \pm 0.5	9.2 \pm 0.8	8.1 \pm 0.5	22.9 \pm 1.9	18.8 \pm 1.8	1990 \pm 100	2050 \pm 100	117 \pm 5	20.6 \pm 2.3	2170 \pm 110	2170 \pm 110	PC
chokeberry (mean)	<i>Aronia mitschurinii</i>	Rosaceae	20.3 \pm 1.8	3.4 \pm 1.3	5.0 \pm 2.4	4.6 \pm 2.2	12.6 \pm 6.9	10.7 \pm 6.7	1700 \pm 340	1730 \pm 340	150 \pm 57	19.4 \pm 3.9	1880 \pm 370	1880 \pm 370	PC
sweet rowanberry	<i>Crataegus mitschurinii</i>	Rosaceae	20.4	1.0 \pm 0.1	1.5 \pm 0.1	1.4 \pm 0.1	3.8 \pm 0.2	2.5 \pm 0.2	31.4 \pm 1.9	318 \pm 20	167 \pm 2	18.8 \pm 1.7	485 \pm 22	485 \pm 22	PC
strawberry 'Honeye'	<i>Fragaria ananassa</i>	Rosaceae	10.0	3.6 \pm 0.2	4.7 \pm 0.7	8.9 \pm 0.3	13.4 \pm 0.5	0.55 \pm 0.06	9.9 \pm 0.7	45.1 \pm 2.5	4.1 \pm 0.5	9.4 \pm 0.2	49.2 \pm 3.0	49.2 \pm 3.0	PP, PC
strawberry 'Jonsoke'	<i>Fragaria ananassa</i>	Rosaceae	8.3	3.4 \pm 0.2	8.9 \pm 0.2	6.8 \pm 0.2	12.9 \pm 0.5	0.88 \pm 0.09							

Table 2. Continued

sample	Latin name	family	DM (%)	extractable proanthocyanidins							unextractable			total	type ^b
				P1	P2	P3	P4–P6	P7–P10	>P10	total	DP				
strawberry (mean)	<i>Fragaria ananassa</i>	Rosaceae	9.7 ± 1.1	3.5 ± 0.6	6.4 ± 1.6	7.8 ± 1.7	13.7 ± 3.1	2.8 ± 2.8	11.0 ± 6.8	45.2 ± 9.2	2.6 ± 1.1	6.6 ± 2.7	47.8 ± 9.7	PP, PC	
strawberry jam (35% berry content)			53.3	0.62 ± 0.03	1.3 ± 0.1	0.48 ± 0.05	tr	tr	tr	2.4 ± 0.2	9.8 ± 0.2	12.3 ± 0.4	12.1 ± 0.4	PP, PC	
apple 'Lobo'	<i>Malus domestica</i>	Rosaceae	12.2	6.7 ± 0.3	5.5 ± 0.3	5.1 ± 0.3	11.6 ± 1.1	4.3 ± 0.4	5.2 ± 0.5	38.4 ± 2.9	4.9 ± 0.2	9.1 ± 0.1	43.3 ± 3.1	PC	
apple 'Valkeakuijas'	<i>Malus domestica</i>	Rosaceae	10.5	7.6 ± 0.4	10.5 ± 0.9	9.4 ± 0.7	18.8 ± 1.3	7.1 ± 0.5	37.7 ± 3.3	91.1 ± 7.1	4.1 ± 0.1	10.4 ± 0.1	95.2 ± 7.2	PC	
apple 'Red Delicious'	<i>Malus domestica</i>	Rosaceae	13.7	19.5 ± 1.0	25.5 ± 1.3	23.2 ± 1.2	49.5 ± 4.6	15.1 ± 1.3	21.6 ± 0.8	154 ± 10	7.4 ± 0.4	6.0 ± 0.3	162 ± 10	PC	
apple 'Granny Smith'	<i>Malus domestica</i>	Rosaceae	14.5	7.6 ± 0.3	13.3 ± 0.5	11.1 ± 0.3	22.3 ± 0.5	9.1 ± 0.5	8.6 ± 0.4	72.0 ± 2.5	7.0 ± 0.7	9.6 ± 0.3	79.0 ± 3.2	PC	
apple (mean)	<i>Malus domestica</i>	Rosaceae	12.7 ± 1.8	10.4 ± 6.1	13.7 ± 8.5	12.2 ± 7.8	26 ± 17	8.9 ± 4.6	18 ± 15	90 ± 50	5.9 ± 1.6	8.8 ± 1.9	79.0 ± 32	PC	
apple juice				0.15 ± 0.01						0.15 ± 0.01			0.15 ± 0.01	PC	
apple cider, domestic				0.13 ± 0.01						0.13 ± 0.01			0.13 ± 0.01	PC	
apple cider, imported 1				0.83 ± 0.02	0.66 ± 0.06					1.49 ± 0.08			1.49 ± 0.08	PC	
apple cider, imported 2				1.25 ± 0.05	1.06 ± 0.04	0.65 ± 0.01	0.58 ± 0.06			3.54 ± 0.16			3.54 ± 0.16	PC	
cherry	<i>Prunus avium</i>	Rosaceae	17.4	6.1 ± 0.4	4.8 ± 0.2	4.9 ± 0.1	7.2 ± 0.7	1.6 ± 0.2		24.6 ± 1.6	2.2 ± 0.1	5.9 ± 0.4	26.8 ± 1.7	PC	
plum	<i>Prunus domestica</i>	Rosaceae	10.7	2.0 ± 0.1	2.7 ± 0.1	3.0 ± 0.1	5.8 ± 0.2	2.1 ± 0.2	86.4 ± 8.2	102 ± 9	3.3 ± 0.4	12.9 ± 0.7	105 ± 10	A, PC	
peach	<i>Prunus persica</i>	Rosaceae	10.9	2.2 ± 0.1	3.1 ± 0.1	2.9 ± 0.1	7.3 ± 0.3	3.1 ± 0.3	13.5 ± 1.0	32.1 ± 1.9	5.6 ± 0.5	11.0 ± 0.9	37.7 ± 2.4	PC	
nectarine	<i>Prunus persica</i> , var. <i>nectarine</i>	Rosaceae	11.9	1.3 ± 0.1	1.9 ± 0.2	2.0 ± 0.2	3.2 ± 0.3	1.1 ± 0.2	9.3 ± 0.8	18.8 ± 1.8	2.8 ± 0.2	10.7 ± 0.9	21.6 ± 2.0	PC	
peach/nectarine (mean)	<i>Prunus persica</i>	Rosaceae	11.4 ± 0.7	1.8 ± 0.6	2.5 ± 0.8	2.5 ± 0.6	5.3 ± 2.9	2.1 ± 1.4	11.4 ± 3.0	25.5 ± 9.4	4.2 ± 2.0	10.9 ± 0.2	29.7 ± 11.4	PC	
pear	<i>Pyrus communis</i>	Rosaceae	17.4	2.9 ± 0.2	1.9 ± 0.1	1.8 ± 0.1	3.7 ± 0.3	0.58 ± 0.06		10.9 ± 0.8	9.8 ± 0.2	10.8 ± 1.1	20.7 ± 1.0	PC	
rose hip	<i>Rosa rugosa</i>	Rosaceae	21.2	6.6 ± 0.7	24.2 ± 2.2	9.2 ± 1.0	77.7 ± 6.8	12.9 ± 1.1	404 ± 15	535 ± 27	166 ± 6	14.0 ± 0.7	701 ± 21	PC, Glycos	
cloudberry	<i>Rubus chamaemorus</i>	Rosaceae	14.3	2.2 ± 0.2	11.4 ± 1.1	6.0 ± 0.6	7.3 ± 0.6			26.9 ± 2.5	5.0 ± 0.5	3.7 ± 0.4	31.9 ± 3.0	PP, PC	
raspberry 1	<i>Rubus idaeus</i>	Rosaceae	13.7	11.2 ± 0.7	34.5 ± 2.3	9.8 ± 0.5	12.9 ± 0.4	2.4 ± 0.1		70.8 ± 4.0	6.1 ± 0.3	3.0 ± 0.2	76.9 ± 4.3	PP, PC	
raspberry 2	<i>Rubus idaeus</i>	Rosaceae	14.3	12.5 ± 0.7	40.6 ± 2.0	10.5 ± 0.9	12.9 ± 0.6	1.2 ± 0.1		77.6 ± 4.3	3.0 ± 0.2	2.7 ± 0.1	80.6 ± 4.7	PP, PC	
raspberry (mean)	<i>Rubus idaeus</i>	Rosaceae	14.0 ± 0.4	11.9 ± 0.9	37.6 ± 4.3	10.2 ± 0.5	12.9 ± 0.1	1.8 ± 0.8		74.2 ± 4.8	4.6 ± 0.2	2.9 ± 0.2	78.8 ± 7.0	PP, PC	
raspberry jam (35% berry content)			51.2	1.3 ± 0.1	1.9 ± 0.2	1.0 ± 0.1	0.47 ± 0.05			4.7 ± 0.5	2.2 ± 0.1	2.5 ± 0.1	6.9 ± 0.6	PP, PC	
rowanberry	<i>Sorbus aucuparia</i>	Rosaceae	21.0	5.4 ± 0.4	4.1 ± 0.1	3.9 ± 0.3	7.7 ± 0.3	3.8 ± 0.2	248 ± 11	273 ± 12	158 ± 10	20.8 ± 1.6	431 ± 32	PC	
grape, green	<i>Vitis vinifera</i>	Vitaceae	14.8	2.6 ± 0.1	2.9 ± 0.1	2.1 ± 0.1	3.6 ± 0.3	tr	19.3 ± 1.4	30.5 ± 2.0	23.5 ± 1.8	12.3 ± 0.8	54.0 ± 4.2	PC, PD, Gall	
grape, red	<i>Vitis vinifera</i>	Vitaceae	14.7	1.8 ± 0.1	2.3 ± 0.1	1.6 ± 0.1	2.7 ± 0.2	tr	3.8 ± 0.2	12.2 ± 0.8	20.4 ± 0.9	19.4 ± 1.1	32.6 ± 1.7	PC, PD, Gall	
grape (mean)	<i>Vitis vinifera</i>	Vitaceae	14.8 ± 0.1	2.2 ± 0.6	2.6 ± 0.4	1.9 ± 0.4	3.2 ± 0.6	tr	11.6 ± 1.0	21.4 ± 1.9	22.0 ± 2.2	15.9 ± 5.0	43 ± 15	PC, PD, Gall	
red wine				5.7 ± 0.1	9.3 ± 0.3	5.7 ± 0.1	8.6 ± 0.4	1.3 ± 0.1	3.8 ± 0.3	34.4 ± 1.3			34.4 ± 1.3	PC, PD, Gall	
Vegetables and Roots															
rhubarb	<i>Rheum rhabarbaricum</i>	Polygonaceae	6.4	4.6 ± 0.2	1.7 ± 0.1	1.8 ± 0.1	3.4 ± 0.2	1.9 ± 0.2	79.0 ± 1.3	92.4 ± 2.1	27.4 ± 0.6	7.1 ± 0.3	120 ± 3	PC, PD	
Cereal Products															
barley flour	<i>Hordeum vulgare</i>	Poaceae	90.3	1.3 ± 0.1	4.7 ± 0.4	5.5 ± 0.4	5.3 ± 0.5			16.8 ± 1.4	8.7 ± 0.3	5.2 ± 0.2	25.5 ± 1.7	PC, PD	
barley beer				0.27 ± 0.01	0.58 ± 0.01	0.18 ± 0.01	0.21 ± 0.02			1.24 ± 0.05			1.24 ± 0.05	PC, PD	
buckwheat grits	<i>Fagopyrum esculentum</i>	Polygonaceae	90.9	13.2 ± 0.7	33.9 ± 2.9	14.2 ± 0.6	26.5 ± 1.5	7.6 ± 0.8		95.4 ± 6.5	22.2 ± 2.0	4.3 ± 0.1	118 ± 7	PP, PC	
Others															
peanut	<i>Arachis hypogaea</i>	Fabaceae	94.4	2.9 ± 0.1	33.2 ± 1.1	48.8 ± 1.0	48.1 ± 2.2	tr		133 ± 5	53.0 ± 3.8	3.4 ± 0.4	186 ± 9	A, PC	
cocoa powder	<i>Theobroma cacao</i>	Sterculiaceae	94.4	129 ± 5	109 ± 3	86.8 ± 6.6	94.8 ± 7.6	33.2 ± 3.2	404 ± 23	857 ± 48	602 ± 13	3.9 ± 0.1	1460 ± 60	PC	
dark chocolate (46% cocoa)			99.2	47.7 ± 3.5	35.7 ± 3.3	36.1 ± 3.2	63.0 ± 5.0	19.1 ± 1.6	12.5 ± 1.3	214 ± 18	42.5 ± 4.1	3.9 ± 0.1	257 ± 22	PC	
milk chocolate (30% cocoa)			98.8	30.5 ± 2.2	20.4 ± 1.8	22.4 ± 2.2	39.0 ± 2.6	8.6 ± 0.8	tr	121 ± 10	36.4 ± 1.8	4.0 ± 0.2	157 ± 12	PC	
tea beverage, black	<i>Camellia siniensis</i>	Theaceae		1.9 ± 0.1	0.70 ± 0.05	0.34 ± 0.03	0.35 ± 0.03			3.3 ± 0.2			3.3 ± 0.2	PC, PD, Gall	
tea beverage, green	<i>Camellia siniensis</i>	Theaceae		6.3 ± 0.1	3.8 ± 0.1	1.2 ± 0.1	0.95 ± 0.08			12.2 ± 0.4			12.2 ± 0.4	PC, PD, Gall	

^a DM, dry matter (%); P_n, proanthocyanidins with n degree of polymerization; DP, average degree of polymerization; DP⁺, average degree of polymerization; DP⁻, average degree of polymerization; Glycos, glycosidic structures; Gall, 3-O-gallate.

national monopoly over retail sales of beverages containing over 4.7% of alcohol by volume.

One pooled sample was prepared representing 9–12 subsamples of each food item, except for berries and grain products, for which the number of subsamples was 2–10. The subsamples were peeled and diced when necessary, and identical amounts (usually 100 g) of each were added to the pool. Only edible parts of the samples were included in the analyses. Grape pool included both seedless and seeded cultivars from which the seeds were removed before analyses. Apples and pears were analyzed unpeeled. Potatoes were boiled before analysis: summer potatoes for 18 min and winter potatoes for 23 min. Winter potatoes were peeled after boiling, whereas summer potatoes were analyzed without peeling. The coffee beverage sample was prepared by combining identical amounts (100 mL) of two outputs brewed separately with a conventional coffee maker by percolating 35 g of fine-grind coffee powder (pool of 10 brands) with 700 mL of water. The tea sample was obtained by brewing one tea bag from all 10 different tea sample packets separately in 200 mL of water for 3 min at 95 °C, after which the bags were picked up without squeezing and 100 mL of each of these brews were combined. Nuts and grain products (except flours) were ground in a flour mill, and berries, fruits, and vegetables were freeze-dried before analysis. All samples were stored at –20 °C until analyzed.

Proanthocyanidin Analyses. Extractable and unextractable proanthocyanidins were analyzed according to the methods described by Hellström and Mattila (17). Briefly, samples were extracted with acetone/methanol/water (2:2:1) and the extracts purified with Supelco Discovery DPA-6S (Sigma-Aldrich Chemie Inc.) polyamide SPE columns. Samples with considerably high fat content, that is, peanut, cocoa powder, and chocolate, were first defatted with hexane (1:15 w/v), after which proanthocyanidins were extracted as described above. The extractable proanthocyanidins were determined by normal phase HPLC. Proanthocyanidins were separated on a 250 × 4.6 mm i.d., 5 μm, Silica Luna column (Phenomenex Inc., Darmstadt, Germany) according to their degrees of polymerization using a gradient elution developed by Gu et al. (18). An external standard consisting of procyanidin oligomers isolated from Saskatoon berry along with commercially available monomeric and dimeric procyanidins was used for the quantification of extractable proanthocyanidins by fluorescence detection ($\lambda_{\text{ex}} = 280$ nm, $\lambda_{\text{em}} = 323$ nm). The unextractable proanthocyanidins in the extraction residue were analyzed by reversed phase HPLC with a 150 × 4.0 mm i.d., 3 μm, Inertsil ODS-3 column (GL Sciences Inc., Torrance, CA) after thiolytic degradation under conditions originally introduced by Guyot et al. (19). Acid-catalyzed cleavage of proanthocyanidin interflavan linkages was performed in the presence of benzylmercaptan; the terminal units were detected as free flavan-3-ols and extension units as their benzylthioether adducts. The mobile phase consisted of (A) 50 mM phosphoric acid (aqueous), pH 2.5, adjusted by NaOH and (B) acetonitrile. Elution was started isocratically with a constant flow of 5% B in A, 5 min, followed by 5–27.5% B in A, 5–30 min; 27.5–50% B in A, 30–32 min; and 50% B in A, 32–38 min. Separation was monitored by diode array detection (DAD; $\lambda_1 = 270$ nm, $\lambda_2 = 280$ nm). External standards derived from authentic compounds were used for the quantification of terminal units ($\lambda = 280$ nm; catechin, epicatechin, epicatechin gallate; $\lambda = 270$ nm, epigallocatechin.). The standard curve for epicatechin benzylthioether ($\lambda = 280$ nm) was obtained by thioacidolysis of procyanidin B2. Other extension units were quantified against epicatechin benzylthioether using the response factor ratios reported by Vivas et al. (20). The HPLC analyses were carried out with an Agilent 1100 liquid chromatograph (Agilent Technologies, Santa Clara, CA) equipped with diode array and fluorescence detectors.

Characterization of the native proanthocyanidins (type of flavan-3-ol constituent units, presence of A-type linkages, and the degree of polymerization) and the thiolytic degradation products (monomeric as well as A-type dimeric terminal flavan-3-ols together with corresponding extensional flavan-3-ol benzylthioethers) was performed by HPLC-MS as described before (12, 17). A Thermo Finnigan Surveyor HPLC with DAD was connected to a Finnigan MAT ion trap mass spectrometer (Thermo Electron Corp., Waltham, MA). An ESI interface in negative ionization mode was used under full-scan conditions (m/z 200–2000). The spray voltage was set at 4.50 kV and the capillary temperature at 270 °C.

RESULTS AND DISCUSSION

Among the 99 different analyzed food items, 50 did not contain detectable amounts of proanthocyanidins (Table 1). The analyzed concentrations and structural features (types of flavan-3-ol subunits, types of interflavan linkages, and size distributions) are presented in Table 2. Extractable proanthocyanidins were quantified as nonconjugated procyanidins; that is, the mass of sugars and acids possibly attached to the molecule were not included in the results. To the best of our knowledge, a proanthocyanidin database including both extractable and unextractable forms was created for the first time in the present study. Furthermore, for many food items this was also the first time that their proanthocyanidins were characterized and quantified by HPLC. Regarding the same food items, our results on extractable proanthocyanidins are generally in the order reported earlier in the USDA database (<http://www.nal.usda.gov/fnic/foodcomp/Data/PA>).

An interesting finding in botanical terms is that with regard to the edible parts (fruits, seeds, leaves, etc.) of different plant species there seem to exist proanthocyanidin-positive and proanthocyanidin-negative genera—a characteristic that may be related even to families to some extent, because only two families (Poaceae and Fabaceae) among the plants in our study were found to include both proanthocyanidin-positive and -negative species.

Fruits and Berries. Most of the analyzed fruits and berries contained proanthocyanidins. *Citrus* fruits were an exception, as no proanthocyanidins were detected in this genus. Chokeberries had by far the highest content of total proanthocyanidins in all of the samples in this study. The proanthocyanidins in chokeberries were essentially highly polymerized procyanidins with B-type linkages. This result is in accordance with previous studies (3, 21–23), although the concentrations reported here are generally somewhat higher. It should be noted, however, that the common chokeberry in Finland is *Aronia mitchurinii*, whereas earlier studies have been mainly concerned with *Aronia melanocarpa* species.

Rose hip also had a remarkably high content of proanthocyanidins. Proanthocyanidins are not usually covalently attached to sugars, but the HPLC-MS of the rose hip extracts gave peaks with molecular ions at $m/z [289 + 288(n - 1) + 162h]^-$ ($n =$ degree of polymerization, $h =$ number of hexosides), indicating the presence of glycosidic structures. This was further confirmed by thioacidolysis of the unextractable proanthocyanidins, which, when analyzed by HPLC-MS, gave catechin (m/z 289), (epi)catechin hexoside (m/z 451), and epicatechin benzylthioether (m/z 411) as minor products and (epi)catechin benzylthioether hexosides (m/z 573, two compounds) as major products. Previously, glycosylated proanthocyanidins have been detected in rose hip of another *Rosa* species, *Rosa canina* (24).

In addition to chokeberry and rose hip, high proanthocyanidin contents were determined in sweet rowanberry, rowanberry, black currant, Saskatoon berry, sea buckthorn, and basically in all *Vaccinium* species, notably in European cranberry, lingonberry, and blueberry (Table 2). Also, apple and raspberry were moderately good sources of proanthocyanidins. Certain divergence of proanthocyanidin contents between our results and the USDA database can be seen on some berries, such as raspberry and strawberry. According to USDA (<http://www.nal.usda.gov/fnic/foodcomp/Data/PA>) raspberry has considerably lower (25 mg/100 g) and strawberry considerably higher (142 mg/100 g) proanthocyanidin contents than determined in this study (77–81 and 34–57 mg/100 g for raspberries and strawberries, respectively). This kind of disparity between the results can arise, for instance, from analytical differences but also from natural

variability (e.g., differences in berry cultivars and in growing and harvesting conditions). The processed products (bilberry soup, black currant, apple juices, apple cider, and strawberry and raspberry jams) had on average much lower proanthocyanidin contents than the corresponding fruits and berries (**Table 2**). Although the proanthocyanidin concentration level in red wine was comparable with the amounts measured in grapes, it should be noted that the grape cultivars usually preferred in winemaking are different from those used as table grapes, in which high tannin contents are undesirable. Furthermore, a large part of wine proanthocyanidins may originate from grape seeds, whereas the table grapes were analyzed without seeds in this study.

There was wide variation in the size distribution of the proanthocyanidins in the fruits and berries. The smallest oligomers, that is, from monomers to trimers, were predominant in the proanthocyanidin extracts of raspberry, kiwi fruit, cloudberry, cherry, pear, bog whortleberry, and avocado, whereas highly polymerized proanthocyanidin forms (DP > 10) dominated in the extracts of sweet rowanberry, chokeberry, black currant, rowanberry, plum, rose hip, blueberry, cranberry, red currant, bilberry, and sea buckthorn (**Table 2**). The degree of polymerization may have a great influence on the bioavailability and bioactivity of flavan-3-ols (9, 10, 25) and, hence, not only the total content but also the size distribution of proanthocyanidins should be considered when the potential health effects of proanthocyanidin-rich foods are evaluated.

The proportion of unextractable forms in the total proanthocyanidins varied considerably in different fruits and berries (**Table 2**). All of the determinable proanthocyanidins in banana were characterized as unextractable, whereas plum proanthocyanidins were almost entirely extractable into the current extraction solvent. It should be noted that some alternative extraction solvents would most probably give different extractable/unextractable ratios. However, the extraction solvent selected for this study was found to be efficient for proanthocyanidins in our previous survey (17). In addition to banana, the proportion of unextractable proanthocyanidins was remarkably high in several samples, such as sea buckthorn, kiwi fruit, red currant, black currant, pear, cranberry, and grapes. These results indicate that it is important to analyze also the unextractable proanthocyanidins when total proanthocyanidin content is studied. In two of the processed products, strawberry jam and raspberry jam, the proportion of unextractable proanthocyanidins was higher than in the unprocessed berries. The heat treatments in jam-making can induce oxidative polymerization of proanthocyanidins and produce some new covalent linkages between proanthocyanidins and matrix components, thereby decreasing the extractability of proanthocyanidins (26–28). The average degree of polymerization for unextractable proanthocyanidins showed considerable variation between samples, being lowest (2.5) in raspberry jam and highest (102) in banana fruit.

A-type linkages between flavan-3-ol units were frequently detected in the berries, especially in the genus *Vaccinium* (**Table 2**). However, B-type linkages were highly dominant in most of the samples, with the exception of crowberry and lingonberry, in which the proportions of proanthocyanidins with A-type linkages were remarkably high. In both berries, the terminal units were more often connected by A-type linkages than the extension units. A-type proanthocyanidins have previously been identified in Nordic *Vaccinium* species (29).

(Epi)gallocatechins (i.e., prodelphinidins) were predominant constituent units in sea buckthorn, black and red currant, gooseberry, and banana, whereas in European cranberry and crowberry they contributed to roughly half of the proanthocyanidins determined. In other fruits and berries they were either

detected as minor units or not detected at all (**Table 2**). (Epi)afzelechin units (i.e., propelargonidins) were found only in the proanthocyanidins of cloudberry, strawberry, and raspberry. The results confirm that (epi)catechin (i.e., procyanidin structure) is by far the most common constituent unit of proanthocyanidins; it was always present when proanthocyanidins were detected. Among the fruits and fruit products analyzed, gallolyated proanthocyanidins were detected only in grapes and red wine.

None of the samples could be assumed to carry all three common types of proanthocyanidins: procyanidins, prodelphinidins, and propelargonidins. Mass spectral data do not allow, for example, (epi)afzelechin–(epi)gallocatechin (propelargonidin–prodelphinidin structure) from (epi)catechin–(epi)catechin (procyanidin structure), to be distinguished, but considering that no procyanidin–prodelphinidin structures were detected along with propelargonidin–procyanidin structures, it is reasonable to suppose that propelargonidins did not occur together with prodelphinidins in the samples analyzed. This was further confirmed by thioacidolysis of the unextractable proanthocyanidins, in which no (epi)gallocatechin thioethers were detected with (epi)afzelechin thioethers. Interestingly, a parallel observation has been made earlier among the anthocyanidins delphinidin and pelargonidin, which are normally never detected together in berries and fruits (13).

To monitor the variation in proanthocyanidin content among samples, we analyzed several individual sample pools of bilberry, European cranberry, lingonberry, black currant, chokeberry, and strawberry ‘Polka’ (**Table 2**). Proanthocyanidin contents were observed to vary, especially in the bilberry and lingonberry samples, in which the total amounts varied between 133 and 192 mg/100 g (mean = 148 mg/100 g, CV 30%, $n = 6$) and between 298 and 548 mg/100 g (mean = 390 mg/100 g, CV 36%, $n = 6$), respectively. Proanthocyanidin contents can be strongly influenced by factors such as climate, soil type, seasonal differences, and the berry’s state of maturity, as well as harvesting conditions (30, 31), so that differences in the results between samples were to be expected.

Vegetables and Roots. In general, vegetables and roots did not contain proanthocyanidins, rhubarb being the only exception, with a fairly high proanthocyanidin content (**Table 2**). Rhubarb contained both procyanidin and prodelphinidin structures, and almost one-fourth of the total proanthocyanidins remained unextractable. Gallolyated and glycosylated proanthocyanidins have been previously identified in rhubarb (32–35), but these were not detected in the present study. However, the samples in the earlier studies were mainly of Asian *Rheum* species, and *Rheum rhaponticum*, the rhubarb of the current study, was not included in them.

Grain Products. Buckwheat grits, barley flour, and beer were the only grain products in which proanthocyanidins were detectable. In buckwheat grits, most of the proanthocyanidins were extractable small oligomers with a high proportion of (epi)afzelechin subunits; that is, propelargonidins dominated over procyanidins. Barley flour had a much lower concentration of proanthocyanidins than buckwheat grits (**Table 2**). (Epi)gallocatechin subunits (i.e., prodelphinidins) were abundant, and one-third of the proanthocyanidins in barley flour were unextractable. Beer contained only low levels of small oligomers, in good agreement with the recent results of Callemien et al. (36). It is already known that a majority of the barley proanthocyanidins is lost during brewing and beer clarification (37, 38).

Other Food Products. Among the four members of the Fabaceae family analyzed in this study (**Tables 1 and 2**), only peanut contained detectable amounts of proanthocyanidins. A fairly high content of (epi)catechin polymers (i.e., procyanidins) was

determined, with a high abundance of A-type linkages. This is in accordance with previous studies (39–41). A fourth of the peanut proanthocyanidins were measured as unextractable with a rather low average degree of polymerization, and the extractable proanthocyanidins similarly consisted mainly of small oligomers (Table 2). In this study proanthocyanidins were not detected in broad beans, although they have been identified previously in hulls and seed coats of *Vicia faba* (42, 43), and in several cases their concentration has been considerable in beans (44, 45). However, proanthocyanidin content in broad bean is strongly dependent on genotype (44, 46), and tannin-free varieties, which are common in Europe (47), are probably favored for cultivation in Finland. Cocoa powder had a high content of proanthocyanidins, as much as 40% of which were quantified in the unextractable fraction. In the USDA database (<http://www.nal.usda.gov/fnic/foodcomp/Data/PA>) the content of extractable proanthocyanidins in cocoa powder is somewhat higher but with a huge standard deviation (1370 ± 2080 mg/100 g). Substantial variability in proanthocyanidin contents can be largely explained by different processing conditions. The commonly used alkali treatment, also known as Dutching, reduces significantly the amount of flavan-3-ols (48). In Finland the cocoa powders available for domestic use are predominantly Dutched, and the proanthocyanidin contents determined in this study are in good agreement with the results reported for Dutched powders (48, 49). Fairly high amounts of proanthocyanidins were also determined in the chocolate samples, although the concentrations were much lower than in cocoa powder. Only B-type procyanidins were detected in cocoa powder and chocolate, as in previous studies (48, 49). Low concentrations of proanthocyanidins were found in the brewed tea beverages, with green tea having a higher content than black tea, although the overall amounts were rather low compared with the published data (50, 51). This discrepancy in results may be ascribed to the detection method used in our study. Tea is known to contain high amounts of gallolyated prodelphinidins, which do not fluoresce strongly, and thus quantification by fluorescence detection against a procyanidin standard curve may underestimate their contents.

To summarize, in this study we determined both extractable and unextractable proanthocyanidins in a large number of food items commonly consumed in Finland. A large proportion of proanthocyanidins could remain insoluble during the extraction procedure and had to be hydrolyzed before HPLC analyses. The majority of the detected proanthocyanidins in several fruits and berries, including banana fruit, sea buckthorn, kiwi fruit, table grape, and red and black currant, were in unextractable form. Most berries were excellent sources of proanthocyanidin, whereas vegetables and cereal products were generally poor. There was some variation in proanthocyanidin contents between different sampling times, suggesting that further research is needed to study these variations in more detail.

ACKNOWLEDGMENT

We are grateful to Tarja Vikman for skillful technical assistance in HPLC analysis, and we thank Jani Koponen and Anu Ryyänen for purchasing and handling part of the samples for this study.

LITERATURE CITED

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Received April 30, 2009. Revised manuscript received July 14, 2009.
Accepted July 27, 2009.