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# First Web-Based Database on Total Phenolics and Oxygen Radical Absorbance Capacity (ORAC) of Fruits Produced and Consumed within the South Andes Region of South America

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**ABSTRACT:** This paper reports the first database on antioxidants contained in fruits produced and consumed within the south Andes region of South America. The database (www.portalantioxidantes.com) contains over 500 total phenolics (TP) and ORAC values for more than 120 species/varieties of fruits. All analyses were conducted by a single ISO/IEC 17025-certified laboratory. The characterization comprised native berries such as maqui (*Aristotelia chilensis*), murtilla (*Ugni molinae*), and calafate (*Barberis microphylla*), which largely outscored all other studied fruits. Major differences in TP and ORAC were observed as a function of the fruit variety in berries, avocado, cherries, and apples. In fruits such as pears, apples, apricots, and peaches, a significant part of the TP and ORAC was accounted for by the antioxidants present in the peel. These data should be useful to estimate the fruit-based intake of TP and, through the ORAC data, their antioxidant-related contribution to the diet of south Andes populations.

KEYWORDS: database, fruits, antioxidants, ORAC, phenolics, polyphenols

# INTRODUCTION

Considerable evidence has accumulated to substantiate the claim that a high consumption of fruits and vegetables is directly associated with major health-related benefits. At the epidemiological level, such benefits are expressed as a reduction in the relative risk of developing several nontransmissible chronic diseases, among which are included cardiovascular and tumoral diseases.<sup>1-5</sup> Although fruits and vegetables contain a large number of phytochemicals, most of the available evidence indicates that the health benefits associated with their high consumption could be largely attributed to the high content of molecules that feature antioxidant activity.<sup>6,7</sup> The claim that implies the involvement of such molecules as being primarily responsible for the health-promoting effects of fruits and vegetables is supported, largely, by the existence of experimentally proven hypotheses in which the occurrence of oxidative stress is key toward the initiation and/or progression of each of the above-mentioned diseases.<sup>8-10</sup> In addition, numerous pieces of evidence also exist whereby the prevention of such stress has been shown to be an effective manner to either ameliorate, retard, or prevent, in their corresponding animal models, the occurrence of cardiovascular or tumoral diseases.<sup>11–14</sup>

Within fruits and vegetables, molecules featuring antioxidant activity comprise (i) the so-called "antioxidant vitamins" (ascorbic acid and  $\alpha$ -tocopherol), (ii) the pro-vitamin A carotenoids ( $\alpha$ -carotene,  $\beta$ -carotene, and cryptoxanthine), (iii) other carotenoids (such as lutein, lycopene, and zeaxanthine), and (iv) a large number of phenolic compounds, which comprise mostly flavonoids and nonflavonoids. With few exceptions, phenolic compounds account for most of the antioxidant activity found in fruits and vegetables.<sup>15,16</sup> In view

of the latter, the total content of these compounds (total phenolics; TP) has been long assayed as a suitable form to estimate the antioxidant richness of plant-derived foods. In line with the abundance of phenolics in such foods and their recognized contribution to the whole antioxidant activity, correlations between total phenolics and ORAC values have often been reported.<sup>17</sup> As known, the oxygen radical absorbance capacity (ORAC) assay assesses the ability of phenolics, as well as that of all other nonphenolic molecules, to scavenge the (AAPH-derived) peroxyl radicals that characterize this method.<sup>18</sup> Although scavenging free radicals represents an important mode by which phenolic antioxidants are likely to act in vivo, their antioxidant activity is by no means limited to such a mechanism of action. In fact, some of these compounds are increasingly recognized for their potential to favorably modulate the activity of various antioxidant and pro-oxidant enzymes and/or to induce the expression of genes involved in the cell's antioxidant capacity.<sup>19-21</sup> No less important, besides displaying direct and indirect antioxidant activities, are the many specific phenolic compounds now being recognized for their potential to also exert anti-inflammatory, vasodilating, antimicrobial, and/or platelet aggregation inhibitory activities.<sup>21-24</sup> The latter has, reasonably, prompted many researchers to assess the concentration of individual phenolic compounds in foods.  $^{25-27}$  A major end point in such an

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endeavor has been the launching in 2009 of the Phenol-Explorer database,<sup>28</sup> which compiled over 37000 original data points collected from several hundred papers published in peerreviewed journals and offers data on each of the major known individual phenolics present in commonly consumed foods.<sup>29,30</sup>

Nevertheless, when the aim is to assess the total antioxidant capacity of a given food, the antioxidant activity is likely to result not only from the sum of the individual contributions of each phenolic compound but also from that provided by all other nonphenolic antioxidant molecules present in such food (vide supra). Certainly, assessing the total antioxidant activity of a given food by means of an in vitro assay does not imply that the total activity of its antioxidant components will become bioavailable to the organism. Yet, such type of assay could represent a practical form to assess the potential that a given food may have to contribute to the antioxidant status of the organism. When such assessment is done with the ORAC assay, it provides an index of the potential of such food to scavenge oxygen radicals.<sup>18</sup> In view of the latter, the existence of the USDA (U.S. Department of Agriculture) ORAC and TP database, launched in 2007, and updated as "release 2" in May 2010,<sup>31</sup> should also be considered a major contribution to the understanding of which foods have the greatest potential to provide free radical scavenging antioxidants.

So far, no database has been published on the antioxidant richness of plant foods grown and consumed within the south Andes region of South America. Constructing a database on the latter is important because, besides plant varieties, environmental factors and pre- and postharvesting agricultural practices can influence the composition of fruits and vegetables.<sup>32,33</sup> In addition, some species and varieties of fruits that are native to the region should also be considered because these are vastly consumed by its populations. In this paper, we report for the first time on a Web-based database on total phenolics and ORAC values of fruits produced and/or consumed within the south Andes region of America. The database is available online through a Web site specializing in antioxidants, www. portalantioxidantes.com, that was recently launched by the Nutrition and Food Technology Institute (INTA) of the University of Chile.

# MATERIALS AND METHODS

**Chemicals.** 2,2'-Azobis(2-amidinopropane) dihydrochloride (AAPH) was purchased from Wako Chemicals (Richmond, VA, USA). 6-Hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), fluorescein (sodium salt), Folin–Ciocalteu's phenol reagent, sodium carbonate, and gallic acid were all obtained from Sigma-Aldrich (St. Louis, MO, USA). All other reagents, including organic solvents, were of analytical grade.

Fruit Sampling. Fruits were sampled from supermarkets belonging to the two major food retail chains in Chile and located in 10 different important cities, from Antofagasta to Puerto Montt, located at latitudes of 23° and 41°, respectively. Fruits distributed by these retailers are supplied by nearby growers as well as growers located at some distance from such cities along the indicated latitudes. In addition, some fruits available at the above-mentioned sampling points originated from growers in Peru, Bolivia, and the Argentinian Patagonia region. Exceptionally, when the sampled fruits had their origin in places different from Chile or the other mentioned ones, the exact origin has been duly indicated. In each sampling, approximately 2.5 kg of each fruit (amount that secured a representative number of individual items) was randomly selected from bins located at the selling rooms of the retail outlet. Samples in their ready-to-be consumed fresh form were taken on, at least, three different occasions during two consecutive sampling years (from September 2009 to

November 2011). Immediately after sampling, the fruits were stored in iced coolers and transported to reach within 12–18 h the laboratory where the analyses were finally conducted. Upon arrival, samples were duly labeled and kept at 4  $^{\circ}$ C until analysis; the latter took place the same day or, at the latest, 24 h after arrival. An exception to the latter were those fruits that are consumed in their dry state; in view of their low water content, the latter fruits were kept at 4  $^{\circ}$ C and analyzed within 3 days from the arrival date. All analyses were conducted by the Laboratory of Analysis of Antioxidants in Foods (LAAF), located at the Nutrition and Food Technology Institute, University of Chile, Santiago, Chile. The LAAF has been granted the ISO/IEC 17025-certified laboratory condition to analyze antioxidant in foods.

Whereas most fruits were analyzed in their fresh condition (i.e., as they are regularly consumed), the drained pulps of others were analyzed following their cooking in boiling in water during 5–10 min, in the case of papaya, chestnuts, and pinon seed (or *Araucaria araucana*). For those fruits amenable to consumption without their peels, to compare the contribution of the peel to the ORAC and total phenolic contents, samples were subjected to analysis in the two forms, peeled and unpeeled (such as apples, pears, peaches, apricots, plums, nectarines, and sweet cucumber). In those fruits that are not amenable to consumption with their peels, samples were analyzed in the peeled form (such as watermelons, pomegranates, bananas, mangos, grapefruits, and oranges). Whenever possible, each of the varieties of fruits available to be sampled was subjected to separate analysis. The latter applied to fruits such as apples, peaches, pears, avocados, blueberries (highbush), nectarines, plums, cherries, melons, olives, and grapes.

Water content of all analyzed fruits was estimated by drying 10 g of each fruit (done in triplicate) during 6 h at 65 °C.

Sample Preparation. From a pool consisting of not less than 750 g of each of the fruits to be analyzed, three portions were independently weighted (10-30 g each), and then 150 mL of a solution consisting of acetone/water/acetic acid (70:29.5:0.5; AWA) was added. The mixtures were homogenized by means of an Ultraturrax homogenizer (IKA, Wilmington, NC, USA) during a 3-5 min period employing a controlled medium speed. The resulting homogenates were incubated at 30 °C during 40 min, with vortexing for 30 s every 10 min. The tubes were then centrifuged (2500g for 15 min at 4 °C) and the supernatants separated and kept at 4 °C. The pellets resulting from such centrifugation were subjected to a second extraction by adding 150 mL of AWA, homogenized, incubated, and centrifuged as described above. Each supernatant resulting from the second extraction was pooled with its corresponding supernatant obtained from the first extraction. The three resulting supernatant pools were independently subjected to the total phenolics and ORAC determinations.

**Measurement of Total Phenolic Content and ORAC Activity.** Phenolic compounds are believed to account for most of the antioxidant capacity or activity in plant foods.<sup>15,16</sup> Antioxidants, including all phenolics, can deactivate free radicals acting via the hydrogen atom transfer (HAT) or the single electron transfer (SET) mechanisms.<sup>18</sup> In the construction of the here-reported database, the antioxidant richness of the fruits was assessed using the ORAC and Folin–Ciocalteu (F–C) standardized methodologies, which could account independently for one such mechanism;<sup>18</sup> whereas in the ORAC assay, the ability of those molecules that (extracted from the fruit) could donate a hydrogen atom to the AAPH-derived peroxyl radicals is measured, in the F–C assay, the ability of those molecules that in a proton-coupled reaction can donate an electron is quantified. Although the F–C assay determines, besides polyphenols, some other reducing substances,<sup>34</sup> it remains as the single most used and systematically tested method to assay total phenolics in foods.

Total phenolic contents were assayed in the above-referred supernatant pools, using the F–C method,<sup>35</sup> as described by Wu et al.<sup>36</sup> Briefly, 15  $\mu$ L of the samples (diluted in AWA) or standards was mixed with 200  $\mu$ L of a solution containing the F–C reagent (previously diluted 1:10 v/v in distilled water), 40  $\mu$ L of sodium carbonate (20% w/v), and 45  $\mu$ L of distilled water. Following incubation of the resulting solution at 37 °C for 30 min, the OD at 765 nm was measured in a 96-well plate using a Multi-Mode Microplate

NDB	description	parameter	units	mean	N	SEM	min	max
СР	almond, with skin	ORAC	$\mu$ mol TE/100 g fw	3742	36	375	1209	6535
		ORAC	$\mu$ mol TE/100 g dw	3818	36	383	1234	6668
		TP	mg GAE/100 g fw	238	36	17	149	365
		TP	mg GAE/100 g dw	243	36	17	152	373
АСРО	organic almond, with skin	ORAC	$\mu$ mol TE/100 g fw	5314	14	457	4026	7694
		ORAC	$\mu$ mol TE/100 g dw	5503	14	473	4169	7967
		TP	mg GAE/100 g fw	301	14	28	206	430
		TP	mg GAE/100 g dw	312	14	29	213	445
ΑF	fresh blueberry	ORAC	$\mu$ mol TE/100 g fw	5481	22	414	3710	7617
		ORAC	$\mu$ mol TE/100 g dw	21080	22	1592	14270	292
		TP	mg GAE/100 g fw	262	22	23	133	432
		TP	mg GAE/100 g dw	1008	22	85	512	166
FA	fresh blueberry, Aurora	ORAC	$\mu$ mol TE/100 g fw	6883	3	583	6300	746
		ORAC	$\mu$ mol TE/100 g dw	26642	3	2257	24385	288
		TP	mg GAE/100 g fw	392	3	76	316	468
		TP	mg GAE/100 g dw	2140	3	294	1223	181
AFBC	fresh blueberry, Bluecrop	ORAC	$\mu$ mol TE/100 g fw	7127	4	1350	5192	972
		ORAC	$\mu$ mol TE/100 g dw	27412	4	5192	19970	374
		TP	mg GAE/100 g fw	393	4	26	354	441
		TP	mg GAE/100 g dw	1512	4	100	1362	169
FBG	fresh blueberry, Bluegold	ORAC	$\mu$ mol TE/100 g fw	8756	4	1119	6983	108
		ORAC	$\mu$ mol TE/100 g dw	33677	4	4304	26858	416
		TP	mg GAE/100 g fw	497	4	43	441	582
		TP	mg GAE/100 g dw	1912	4	165	1696	223
FBR	fresh blueberry, Brigitta	ORAC	$\mu$ mol TE/100 g fw	5539	6	762	3980	698
		ORAC	$\mu$ mol TE/100 g dw	21304	6	2931	15308	268
		TP	mg GAE/100 g fw	274	6	17	240	321
		TP	mg GAE/100 g dw	1054	6	65	923	123

Table 1. Typical Table from the Database on Antioxidants in Fruits

Reader (Synergy HT, Winooski, VT, USA). The analysis of each supernatant pool was done in triplicate. The results of TP were estimated on the basis of a standard curve of gallic acid and were expressed as milligrams of gallic acid equivalents (GAE) per 100 g of either fresh or dried sample weight (mg of GAE/100 g fw or dw). For the TP assay, the within-day repeatability ranged from 0.2 to 2%, the between-day repeatability was <2.5%, and variation between replicates was typically between 2 and 7.5 RSD%.

The ORAC activity was assayed also in the above-referred supernatant pools, as described by Wu et al.,<sup>36</sup> using AAPH as a source of peroxyl radicals and fluorescein as oxidizable probe.<sup>37</sup> In brief, 45  $\mu$ L of the above-mentioned supernatant pools (diluted in AWA) was transferred to 96-well microplates containing each 50  $\mu$ L of AAPH (18 mM) and 175 µL of fluorescein (108 nM). The plates were placed in a Multi-Mode Microplate Reader (Synergy HT) and incubated for 60 min at 37 °C with shaking of the plates every 3 min. During the incubation, the fluorescence (485 nm Ex/520 nm Em) was monitored continuously every 3 min. The analysis of each pooled supernatant was done in triplicate. The results of ORAC activity were estimated on the basis of a standard curve of Trolox, using a quadratic regression equation obtained between the Trolox concentration and net area under the fluorescence decay curve. ORAC activity was expressed as micromoles of Trolox equivalents (TE) per 100 g of either fresh or dried sample weight ( $\mu$ mol of TE/100 g fw or dw). The within-day repeatability of the ORAC assay, measured as relative standard deviation (RSD) in standard solutions, ranged from 0.4 to 2.5%. The between-day repeatability was <3%. The variation in the

values for replicate food items obtained from the same source was typically between 2.5 and 8 RSD%.

In assessing the antioxidant activity of foods, some investigators distinguish between the contribution of the hydrophilic and that of the lipophilic extractable compounds to the ORAC activity.<sup>18,36</sup> The ORAC values informed in the here-reported database correspond to those arising from the hydrophilic acetone/water/acetic acid-extractable compounds.

**Statistics.** Descriptive statistical analysis was performed using Microsoft Excel and/or GraphPad Prism version 5.01 for Windows, GraphPad software (San Diego, CA, USA).

The data were expressed as mean and standard error of the mean (SEM) values for each food item.

Because the intent of the present study was to provide data on those fruits that are most commonly consumed by populations living around the south Andes region of South America, and not to evaluate the influence of factors that could affect the antioxidant capacity of fruits (such as environmental or postharvesting factors), results shown in the database represent, for a given fruit, a composite (mean and SEM) of the ORAC and TP values obtained upon the analyses of such fruit, independent of its geographic site of sampling or origin. Thus, the ORAC and TP values of a fruit correspond to those of a particular species and, in some cases, a particular variety of fruit.

# RESULTS

Table 1 shows a typical table-page from the Web-based database on antioxidants in fruits, obtained from www.

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portalantioxidantes.com and adapted to the present paper. Whereas the leftmost column of the table shows a code composed of at least two letters that identifies the fruit, the second column describes the common name of such fruit species and, in some cases, the variety and physical form under which the fruit was analyzed. The database provides the option to access further information by clicking the above-mentioned code. For instance, by doing so the user will find a picture of the fruit species, its corresponding scientific name, the number under which such fruit is identified by the USDA Nutrient Databank,<sup>31</sup> and a link which, through such number, allows access to the nutritional composition of the fruit species. The third column shows the two antioxidant parameters, ORAC and total phenolics, for which information is provided. Whereas the fourth column depicts the units of such parameters, expressing the data on both fresh and dry weight bases, the fifth and seventh columns show the mean and SEM values for each of the before-mentioned parameters. The last two columns provide the minimal and maximal values. The N column indicates the total number of samples analyzed. The database describes ORAC and TP values for a total of 120 fruits, considering all of the varieties analyzed.

A ranking of 27 species of fruits, commonly consumed by south Andes populations, was established according to their ORAC values. In each case, the variety that exhibited the higher ORAC value was selected. As shown in Figure 1, the antioxidant richness of these fruits spreads along a broad range of values. Differences of up to 80-fold in ORAC values were evident. Among the lowest ORAC exhibiting species (up to 5000  $\mu$ mol TE/100 g fw) were mangos, kiwis, bananas,

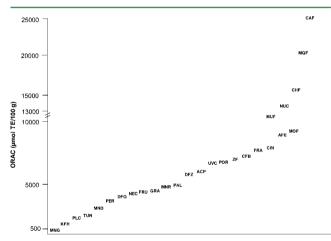
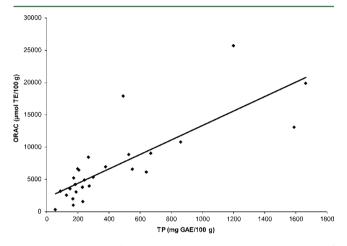


Figure 1. Ranking of commonly consumed fruits based on their ORAC values. A ranking of ORAC values for 27 fruits, selected on the basis of their high frequency of consumption by populations from the south Andes region of South America, is shown. Fruits from lower to higher ORAC values are mangos (MNG), kiwis (KFH), bananas (PLC), prickly pears (TUN), Clementine tangerines (MND), Winter Nelly pears (PER), apricots (DFG), Platano nectarines (NEC), strawberries (FRU), pomegranates (GRA), Royal Deli apples (MNR), Hass avocados (PAL), Zee Lady peaches (DFZ), organic almonds (ACP), Chardonnay grapes (UVC), pink grapefruits (POR), Bing cherries (CFB), raspberries (FRA), red currants (ZF), black prunes (CIN), Elliot blueberries (AFE), blackberries (MOF), murtilla (Ugni molinae, MUF), walnuts (NUC), custard apples (CHF), maqui (Aristotelia chilensis, MQF), and calafate (Berberis microphylla, CAF). For those fruits of which more than one variety was analyzed, only the variety that exhibited the highest ORAC value is shown. ORAC values are expressed as  $\mu$ mol TE/100 g fw.

prickly pears, Clementine tangerines, Winter Nelly pears, apricots, Platano nectarines, strawberries, pomegranates, Royal Deli apples, and Hass avocados. Medium ORAC value fruits ( $5000-10000 \ \mu$ mol TE/100 g fw) included Zee Lady peaches, organic almonds, Chardonnay grapes, pink grapefruits, Bing cherries, raspberries, red currants, black plums, Elliot blueberries, and blackberries. The highest ORAC fruits ( $10000-25000 \ \mu$ mol TE/100 g fw) included walnuts, murtilla (*Ugni molinae*), custard apples, maqui (*Aristotelia chilensis*), and calafate (*Berberis microphylla*).



**Figure 2.** Correlation between total phenolics and ORAC values of commonly consumed fruits. The correlation between the TP and ORAC values for 27 fruits (shown in Figure 1), consumed by populations from the south Andes region of South America, is shown.

2121) the parameters ORAC and TP correlate with an  $r^2$  value of 0.651. Relative to most of the fruits included in the correlation, custard apple and calafate (two of the four fruits that show the highest ORAC values) show a greater separation from the correlation curve. Interestingly, these two fruits exhibit ORAC values that are notably higher than those expected from their actual TP contents. If custard apple and calafate are not considered in the correlation shown in Figure 2, the  $r^2$  value of the remaining 25 fruits increases to 0.805 (y = 9.11x + 2169; not shown).

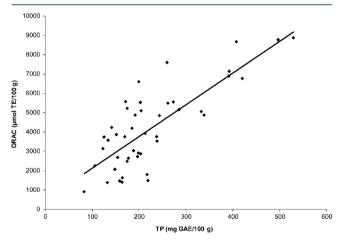
Whereas the ranking of ORAC values shown in Figure 1 was constructed on the basis of comparing, for each fruit, only the variety that presented the highest ORAC value, Table 2 depicts the differences in antioxidant activity that, for some fruits, could arise from comparing their different varieties. Toward that end, avocado and apples were taken as fruits belonging to the low ORAC range and cherries and blueberries as examples of fruits belonging to the medium ORAC range. In the case of avocado, a difference of >6-fold is evident between the Hass (highest ORAC value) and Edranol varieties. For apples, a 2-fold higher ORAC value was estimated when the Royal Deli and the Braeburn varieties were compared. In the case of cherries, the ORAC value of the Van variety is almost 1.8-fold higher than that of the Bing variety. An almost identical difference was found when the Elliot (highest ORAC value) and Duke varieties of blueberries were compared. Although not shown in Table 2, the online database also reveals a difference of 1.7-fold (higher) ORAC value for the Zee Lady variety compared to the

Table 2. ORAC Values for Different Varieties of Avocados, Apples, Cherries, and Blueberries<sup>*a*</sup>

Avoca	do	Apple	es	Che	rries	Bluebe	erries
Hass	4853	Royal Deli	4180	Bing	6608	Elliot	8869
Ester	1793	Red	3919	Brooks	5565	Bluegold	8756
Negra DLC	1607	Granny S.	3519	Rainier	4225	Bluecrop	7127
Fuerte	1390	Royal G.	2728	Granel	3918	Legacy	6771
Bacon	1387	Fuji	2679	Lapins	3847	Brigitta	5539
Edranol	779	Braeburn	2056	Van	3729	Duke	4864

<sup>*a*</sup>ORAC values are expressed as  $\mu$ mol TE/100 g fw.

Elegant lady variety of peaches. Slightly smaller but still significant differences (of near 1.5-fold) were found for plums, between the black and the Blackamber varieties, and for pears, between the Winter Nelly and Asian varieties. Figure 3 depicts the results from correlating the ORAC values for the 8 varieties of avocado, 8 apples, 6 cherries, 11 blueberries, and 4 each of peaches, plums and pears with their corresponding TP contents (data extracted from the database). The curve obtained from plotting the ORAC/TP data from these 45 varieties (y = 16.40x + 500) gives an  $r^2$  value of 0.631.



**Figure 3.** Correlation between total phenolics and ORAC values of different varieties of avocados, apples, cherries, blueberries, peaches, plums, and pears. The correlation between the TP and ORAC values for the 8 varieties of avocado, 8 varieties of apples, 6 varieties of cherries, 11 varieties of blueberries, and 4 varieties each of peaches, plums, and pears, is shown.

Because the peel can be an important source of antioxidants, and taking into consideration the widespread habit of some south Andes communities of consuming certain fruits without peel, ORAC and TP values in peeled and unpeeled fruits were included in the Web-based database. Such values could allow estimating the contribution of the peel to the whole antioxidant activity. Table 3, which depicts the ORAC values of eight analyzed fruits, shows the existence of particularly high differences in the case of the Asian pears, for which the ORAC value increases by 163% when these fruits are analyzed with peel. Smaller but significant differences (in favor of the Table 3. ORAC Values for Eight Different Fruits Analyzed in Their Unpeeled and Peeled Forms  $^a$ 

	X						Y
Asian pe	ear	Zee Lady	peach	B. Bosc	pear	Bulk apr	ricots
Unpeeled	2254	Unpeeled	5213	Unpeeled	2896	Unpeeled	3158
Peeled	857	Peeled	2542	Peeled	1577	Peeled	1837
	J.	Bar 10 1		0			V
E. Ladype	each	Blackam	. plum	Bulk red	apples	Quin	ce
	each	Blackam Unpeeled	. plum 4856	Bulk red Unpeeled	apples 3909	Quin Unpeeled	Ce 6009

<sup>a</sup>ORAC values are expressed as  $\mu$ mol TE/100 g fw.

unpeeled fruits) are also evident in Blackamber plums (54%), bulk red apples (48%), and quinces (40%).

From the ORAC ranking of fruits shown in Figure 1, the fruits belonging to the berry species arise among the highest ones. Such fruits include berries that have been traditionally grown in the northern hemisphere and others that grow wild and/or are increasingly grown in the south Andes region of South America. Figure 4 depicts the ORAC values of the South American native murtilla, calafate, and maqui berry species and those corresponding to the raspberry, blueberry, and blackberry species (in the case of blueberries, the value corresponds to that of the variety that exhibits the highest ORAC). The three species of native berries were found to individually outscore any of the here-studied traditionally grown berries. Thus, the ORAC value of murtilla (lowest among the three native berries) is still higher than that of blackberries (highest ORAC among the three traditionally grown berries). On the other hand, the ORAC value of calafate (highest among the three native berries) is 2.8-fold higher than that of blackberries. It should be noted, however, that native berries show an up to 2.4-fold difference in ORAC values between themselves (calafate versus murtilla). Large differences between native and traditionally grown berry species are also evident when the comparison is made on the basis of their TP contents. TP for murtilla, calafate, and maqui were  $863 \pm 30$ ,  $1201 \pm 104$ , and  $1664 \pm 83$  mg GAE/100 g fw, respectively. Raspberry, blueberry, and blackberry exhibit TP of  $380 \pm 32$ ,  $529 \pm 5$ , and  $671 \pm 21$  GAE/100 g fw, respectively. Upon correlation of the ORAC versus TP values for the six above-mentioned berry species, the curve obtained (y = 13.03x + 1989) showed an  $r^2 =$ 0.687 (not shown). If in the latter correlation calafate is not considered, an  $r^2$  value of 0.986 (y = 10.03x + 2850) is obtained for the remaining berry fruits.

# DISCUSSION

The recognition that populations showing a higher consumption of plant-based foods have a lower relative risk of developing oxidative stress-related cardiovascular and tumoral diseases has prompted a number of studies aimed at assessing



**Figure 4.** ORAC values for three native berry species and three traditionally grown berry species. The ORAC values for the native berry species murtilla, maqui, and calafate and those for the traditionally grown berry species raspberry, blueberry, and blackberry are shown. In the case of blueberry the value shown corresponds to the Elliot variety (the one exhibiting the highest ORAC). ORAC values are expressed as  $\mu$ mol TE/100 g fw, and their corresponding SEM are shown in parentheses.

the antioxidant richness of fruits and vegetables and led to the development of databases compiling the results of such studies.<sup>38</sup> Examples of the latter include the database on ORAC and total phenolics<sup>31</sup> and that on specific flavonoids<sup>39</sup> in fruits and vegetables developed by the USDA, the EuroFIReBASIS database on bioactives that includes the content of various polyphenols in plant based foods,<sup>40</sup> a database on ferric reducing antioxidant power (FRAP) values for a large number of typical foods, herbs, spices, and dietary supplements,<sup>41</sup> and the Phenol-Explorer database,<sup>28</sup> which comprises the largest number of known specific phenols (including their contents as glycoside and ester forms) in a vast number of food categories. Some of the main differences between the USDA and the Phenol-Explorer databases have been recently addressed.<sup>38</sup> The information contained in all referred databases represents major contributions to the field of food chemistry. It should be noted, however, that data provided by these databases arise from the analysis of foods largely grown and consumed in the northwestern hemisphere countries.

The present study reports, for the first time, the existence of a Web-based database on total phenolics and ORAC values of fruits produced and consumed within the south Andes region of South America. These fruits include, besides a large number of species that are also regularly grown and consumed beyond the mentioned region, various species and varieties of fruits that are native to it, among which the Chilean varieties of papaya (Carica papaya), sweet cucumber (Solanum muricatum), and custard apple (Annona reticulata) and the small edible berries, endemic to the Chilean-Argentinian patagonia region, murtilla (a red fruit also called "mutilla or Chilean cranberry"), maqui (a purple-black fruit also called "clon, queldron, or koelon"), and calafate (a dark blue fruit also called "michay or mulun") are included. Interestingly, among the 27 fruit species ranked by their ORAC activity, as shown in Figure 1, the three latter berry species emerge, along with custard apple, as the fruits exhibiting the highest antioxidant values. The antioxidant richness of these three berries largely outscores that of the traditionally worldwide consumed and broadly regarded as high-ORAC

fruits raspberries, blueberries, and blackberries (shown in Figure 4). A similar conclusion can be reached when the native and traditionally consumed berries are compared on the basis of their total phenolics. When the ORAC and TP for these six berry species were correlated, a reasonable correlation coefficient ( $r^2 = 0.687$ ) was obtained. Such a parameter, however, was substantially increased (to  $r^2 = 0.986$ ) when calafate was excluded from the correlation. The reason for the latter is not clear because the phenolic composition of calafate, accounted for mainly by the presence of anthocyanins, does not differ significantly from that recently reported for maqui.<sup>42</sup> Although the total anthocyanin content of calafate and magui is substantially higher than that of murtilla, the flavonol content of the latter fruit is comparatively higher.<sup>42</sup> Because the ORAC value shown by calafate is far above the curve obtained when the 27 fruit species were correlated (Figure 2), it would seem that besides its high content of phenolics, the calafate fruit would contain other nonphenolic molecules that actively sum to its overall capacity to scavenge peroxyl radicals. Like calafate, the custard apple fruit also exhibits a much higher ORAC value than that expected from its TP contents (Figure 2). The differences observed between the two correlations (with and without calafate and custard apple) are likely to reflect differences in the phenolic profiles of the two latter fruits. Thus, addressing the exact chemical nature and phenolic profile of the molecules responsible for the relatively higher ORAC activity of calafate and custard apple appears to be warranted.

Relative to the still very limited information on the calafate and murtilla fruits, increasing attention has been paid to the phytochemical profile and bioactivity of the maqui fruit.43 Studies on the phytochemical composition of Aristotelia chilensis indicate the presence of phenolic acids, proanthocya-nidins, and mostly anthocyanins.<sup>42,44,45</sup> With regard to the bioactivity of maqui, aqueous extracts from this fruit were previously described to be antioxidant, to prevent copperinduced LDL oxidation, and to protect human endothelial cell cultures against hydrogen peroxide-induced oxidative stress.<sup>46</sup> More recently, maqui extracts have been shown, also in vitro, to inhibit adipogenesis and inflammation<sup>47</sup> and to protect in vivo rat hearts against acute ischemia/reperfusion-induced damage.45 The antiatherogenic and anti-inflammatory potential shown for the maqui extract is in line with the emerging impact that other berries have in the promotion of cardiovascular health.48

Phenolics can be found in most fruits within the pulp and the peel. In some fruits, however, these compounds can concentrate preferentially within the peel.<sup>49-51</sup> Although the latter has been often reported in the specialized scientific literature, such information has not extended into the antioxidants-in-food databases. In line with such consideration, and on the basis of results contained in the here-presented database, the Asian pear, the Zee Lady peach, and the bulk apricot cases illustrate the major contribution that the peel (163, 105, and 72%, respectively) can make to the antioxidant capacity. The ORAC-incrementing effect of the peel can, however, also depend on the fruit variety. In fact, in the Beurre Bosc pear and in the Elegant Lady peach, the peel increments the ORAC value by 84 and 61%, respectively. From both cases, however, it is clear that to maximize the intake of phenolic compounds, fruits should be consumed preferentially in the unpeeled form. Strengthening further the latter consideration is the recognition that besides containing phenolics, the peel can be often a good source of fiber, microminerals, and vitamins,

which are likely to also contribute to the benefits associated with fruit consumption.<sup>49,51</sup> Nonetheless, given the widespread habit of peeling fruits that prevails among some populations within the south Andes region of South America, promoting the consumption of whole fruits may prove to be challenging.

Besides the large differences in ORAC and TP that can arise from the fruit species condition (evidenced in Figure 1), the present study shows that large differences can also emerge among varieties within a given species. Examples featuring the latter are the >6-fold differences in ORAC values seen between the Hass and Edranol varieties of avocado and the 2-fold differences that exist between the higher and lower ORACcarrying varieties of apples, cherries, and blueberries (as evidenced in Table 2). The latter differences would need to be considered in all databases because, in some cases varietyrelated differences in ORAC and TP can be comparable to those that have been typically associated with the fruit species; in addition, it highlights the need to point out the specific variety of fruit whenever a ranking of antioxidant richness is made or when a given species of fruit is to be considered for the development and/or preparation of a nutraceutical.<sup>43</sup>

Although scientific journals and textbooks concentrate most of the scientific data and represent an excellent and dynamic peer-review form of communicating research advancements, the need to condense information pertaining to the phytochemical composition of foods has recently prompted its compilation under the form of Web-based databases.<sup>38</sup> Indeed, the latter could represent an easy, public, and rapid online way of accessing amounts of information that otherwise would largely exceed the capacity of a single publication in a scientific journal. A major aim in building the database on antioxidants in fruits reported in the present study has been that of reporting for first time data on the ORAC and TP of fruits produced and consumed within the south Andes region of South America. On the basis of their ORAC and TP values, the ranking of the herecompared fruits is, in general terms, similar to that inferred from most other comparable databases.<sup>31,41</sup> Thus, walnuts, berries, plums, cherries, grapefruits, and almonds are among the highest ORAC-containing fruits. Yet, as already mentioned, the present database also includes information on several native species, some being endemic to the Chilean-Argentinean Patagonia, which now emerge as examples of high ORAC fruits. A particular aspect that distinguishes this database is that its construction was made using data originated from analyses conducted by a single (ISO/IEC 17025-certified) laboratory (at the Nutrition and Food Technology Institute), rather than by a contract analytical laboratory, and using standardized ORAC and TP methodologies.<sup>18</sup> Another important feature of the present database is the fact that all data have been generated from the analysis of samples that were obtained through a twoyear systematic fruit-sampling program, which comprised fruits grown or consumed between the  $23^{\circ}$  and  $41^{\circ}$  southeast latitudes of the south Andes region of South America (namely, along a 2377 km length region). Thus, the results shown in the database arise from fruits sampled during, at least, two sequential harvesting seasons and constitute, through the mean, SEM, and maximal and minimal ORAC and TP values, an expression of the homogeneity or variability that each analyzed fruit has within the areas where these fruits either grow or are consumed. Additionally, it should be noted that to allow comparisons with other databases, especially between fruits that primarily differ in their water content, in the tables of the present database all ORAC and TP values have been expressed in terms of fresh and dried fruit weight bases.

The here-presented database, first to describe data on TP and ORAC of fruits produced and consumed within the south Andes region of South America, is expected to be useful to estimate the intake of total phenolics and, through the ORAC data, the antioxidant-related contribution of fruits in populations from the mentioned region. As with other databases, the usefulness of the present one should include the establishment of associations between such intake and the prevalence of those diseases having etiologies that appear to be primarily linked to the existence of oxidative stress. Finally, the fact that the present database makes now broadly available information on certain fruits, such as maqui, calafate, murtilla, and custard apple, that stand out for their particularly high TP and ORAC values could encourage food and nutrition scientists to explore further the potential health benefits of such types of fruits. Prompted by its potential usefulness, our laboratory has plans to release in the future an updated database version that will not only extend the number of fruits but also include other types of locally grown foods.

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# ABBREVIATIONS USED

AAPH, 2,2'-azobis(2-amidinopropane) dihydrochloride; F–C, Folin–Ciocalteu; GAE, gallic acid equivalents; ORAC, oxygen radical absorbance capacity; TE, Trolox equivalents; TP, total phenolics.

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