1. Introduction

1.1 Protected geographical indication (PGI) products

Europe is known for the diversity of its agricultural products, both fresh and processed. Some of these products have strong associations with their regions of origin. The distinctive characteristics of an agricultural product result from area factors such as climate, soil conditions, know-how and local breeds (European Commission, 2010). Because of their uniqueness, these products are sold using their origin names as commercial names, which consumers then remember. To avoid the misuse of well-known names on imitation products, the European Union (EU) developed a policy to protect geographical indications using two different designations, namely Protected Geographical Indication (PGI) and Protected Designation of Origin (PDO). While the PDO requires every step of the registrant's production to take place in the region of origin, only one step of the production is required by the PGI.

Germany is applying the policy of Geographical Indication (GI). Based on the distribution data of the registered PGI/PDO products in EU countries up to June 2010, 87 German products accounted for 25% of the overall value of the total 906 registered products in the EU. The production volumes, values and the percentages of several kinds of PGI/PDO products in Germany during the years of 2007 and 2008 are shown in Table 1.1. The EU estimated the value of PGI/PDO products at the retail level in 2008 to be worth €3.6 billion (Table 1.1). About 88% of the products are traded on the national market, while the rest of them are traded on internal and external EU markets (Figure 1.1a). Furthermore, between 2007 and 2011, there was an increase in the number of PGI products in Germany (Figure 1.1b).

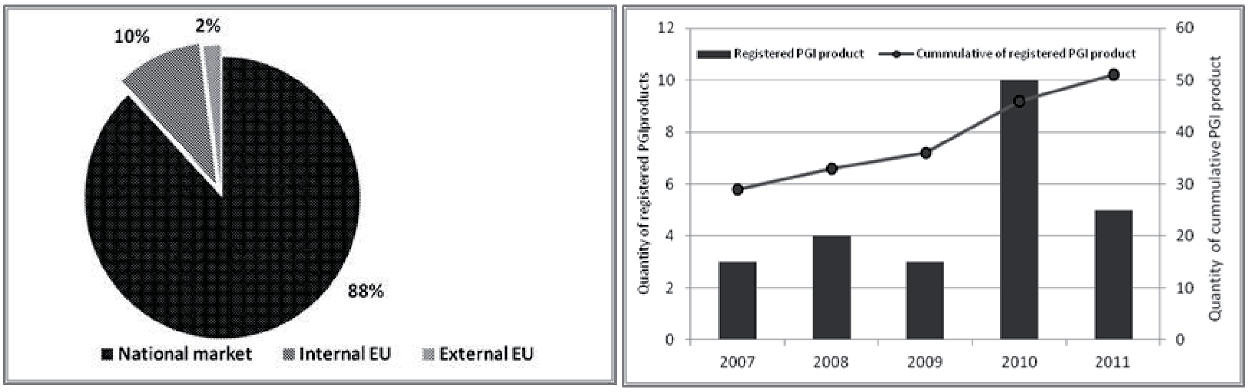
Table 1.1 Production volume and value of PGI/PDO products in Germany in 2007 and 2008 (European Commission, 2011)

Kind of products	Volume (t)		% to total production [a]		Value (1,000 €)	
	2007	2008	2007	2008	2007	2008
Meat products	82,987	89,863	1.18	1.12	439,951	465,893
Cheeses	5,200	5,200	0.26	0.26	44,100	45,590
Fruits, vegetables and cereals	12,964	13,464	0.03	0.03	33,200	37,200
Fisheries	1,501	1,525	0.06	0.054	7,412	8,050
Bread, pastry, confectionary	131,612	131,612	n.a	n.a	627,014	627,014
Beers	2,394,415	2,381,588	24.76	24.637	2,282,734	2,284,918
Mineral and spring waters	442,332	441,025	n.a	n.a	136,375	137,045

[a] Percentage of PGI/PDO product to total production of specific kind of food and agricultural products. Data of total production were taken from FAO (2012). n.a: not available

At the end of 2011, Germany had a total number of 51 PGI products (Figure 1.1b). One of the PGI products is the Lüneburger Heide potato (in German: Lüneburger Heidekartoffel). Lüneburger Heide potatoes are the brand of early table potatoes grown in the Lüneburger Heide area of Germany. In August 2010, the potatoes were accorded PGI status (European Commission, n.d.). Excessive land use in the past has caused the Lüneburger Heide area to have low humus sandy soil with low nitrogen content (European Union, 2009), allowing the area to typically produce pale-skinned potatoes.

PGI/PDO products may have an economic advantage in the market and could have the risk of being imitated by other producers. Therefore, one of the important issues related to the PGI/PDO policy is the authentication of the products (Gonzalves et al., 2009). In recent years, analytical techniques have been developed to authenticate the geographical origin of foodstuffs and agricultural products such as wine (González et al., 2009), rice (Kelly et al., 2002), durum wheat (Brescia et al., 2002) and potatoes (Anderson et al., 1999).



A B

Figure 1.1 a) Percentage of German PGI/PDO products value in the national market and internal and external EU market (European Commission, 2011); (b) Number of registered PGI products and cumulative amount of registered PGI products in Germany from 2007 to 2011 (European Commission, n.d.)

The determination of the geographical origin of foodstuffs and agricultural products should consider several factors that may influence the chemical compositions of the commodity. Several factors, such as varietal differences, age, seasonality, and sampling techniques, influence the chemical compositions of the agricultural products (Lewis & Hird, 2007).

1.2 Discriminate parameters for characterizing the geographical origin of plant products

Discriminate parameters, which can be used to determine the geographical origin of an agricultural product, must have enough discriminatory power to distinguish the 'true product' from its imitation. In this context, discriminatory power can be defined as the ability of the parameters to distinguish a unique product from an ordinary one. Gonzalves et al. (2009) summarized that there are several parameters used to characterize the geographical origin of foodstuffs and agricultural products, and mentioned that the two most used are stable isotope ratios and minerals.

1.2.1 Stable isotope ratio (SIR)

Isotopes are the atoms of an element whose nuclei contains the same number of protons but a different number of neutrons. Isotopes can be divided into two fundamental kinds, stable and unstable. One important rule used to characterize the stability of nuclides is the symmetry rule, which states that in a stable nuclide with a low atomic number, the number of protons is approximately equal to the number of neutrons (Hoefs, 2009). SIRs are defined as the ratio of the abundance of isotopes with the number of heavy isotope to the abundance of isotopes with the number of light isotopes (Equation 1.1), such as $^{18}O/^{16}O$, $^{2}H/^{1}H$ and $^{13}C/^{12}C$.

Instead of being reported as absolute numbers, isotope ratios are generally reported as a deviation (δ) of the isotope ratio of a sample relative to that of a reference sample or standard (Equation 1.2). The main reasons for this are mentioned by Mook (2000) as follows: (1) the type of mass spectrometer is basically not suitable for measuring reliable absolute ratios; (2) the necessity of an international comparison requires the use of references to which the samples have to be related; (3) the use of isotope ratios would lead to reporting results as numbers consisting of a large number of digits; and (4) absolute ratios are in principal less relevant than the changes in ratios occuring during transitions between phases or molecules. The Vienna-Standard Mean Ocean Water (V-SMOW) is used as the international standard for oxygen and hydrogen isotopes, while the Vienna-Pee Dee Belemnite (V-PDB) is used for carbon isotope (Table 1.2).

$$R=\frac{number\ of\ heavy\ isotope}{number\ of\ light\ isotope} \qquad (1.1)$$

$$\delta\ (‰) = \frac{Rs - R\ std}{R\ std} x\ 1000 = \frac{Rs}{Rstd} - 1\ x1000 \qquad (1.2)$$

R = Stable isotope ratios
Rs = Ratio between 'heavy' and 'light' isotopes of the samples
Rstd = Isotopes ratio of international standard sample
δ = Deviation of isotope ratio of a sample relative to that of reference sample or standard

SIRs have been recognized as parameters for characterizing several agricultural products. Kelly et al. (2005) mentioned the potential use of oxygen, hydrogen and strontium isotope for characterizing the geographical origin of agricultural products. Water, which is composed of hydrogen and oxygen, is the primary hydrogen source of all organic compounds in the biosphere (Keppler & Hamilton, 2008) and the major source of oxygen atoms for terrestrial plants (Brescia et al., 2002). During various evaporation-condensation processes in the water cycle, isotopic fractionation occurs (Brescia et al., 2002), causing spatial variations in the stable isotope composition of precipitation (de Oliveira & Lima, 2009), which can be measured as changes in the ratio of 'heavy' to 'light' isotopes of a given element (Kelly et al., 2005).

Table 1.2 International standards of stable isotopes (Mook, 2000)

Elements	Reported as	International standards	Ratios	Absolute isotope ratios
Hydrogen	$\delta^{2}D$	Vienna Standard Mean Ocean Water (V-SMOW)	$^{2}H/^{1}H$	0.00015575
Oxygen	$\delta^{18}O$	Vienna Standard Mean Ocean Water (V-SMOW)	$^{18}O/^{16}O$	0.00200520
Carbon	$\delta^{13}C$	Vienna Pee Dee Belemnite (V-PDB)	$^{13}C/^{12}C$	0.01123720

Besides oxygen and hydrogen isotopes, the SIR of $^{13}C/^{12}C$ is also used to discriminate the geographical origin of plant materials like wheat (Brescia et al., 2002), rice (Kelly, et al., 2002) and potatoes (Longobardi et al., 2011). Physical and biochemical processes, such as temperature changes and photosynthetic fixation, can result in significant fractionation of heavy to light stable isotopes in biological materials (Perez et al., 2006). Kelly et al. (2002) noted two principal fractionating processes, namely (1) the diffusion of CO_2, through the leaf stomata to the site of assimilation and (2) the carboxylation reaction to fix CO_2 in the leaves, which discriminate the heavier isotope ^{13}C and are dependent on environmental factors such as light intensity and relative humidity. In addition, Brescia et al. (2002) also mentioned that climatic factors that include light intensity and relative humidity within the plant's growing area, which can affect the exchanges of water and CO_2 between the plant and the environment, influence the $^{13}C/^{12}C$ ratio of the plant material. Perez et al. (2006) mentioned the possibility of value differences of $^{13}C/^{12}C$ ratios in plants depending on geography, latitude, location, and climate.

1.2.2 Mineral composition

The mineral composition of fruits and vegetables might provide useful information pertaining to the discrimination of the geographical origin of plant products because it reflects to some extent the mineral composition of the soil and the environment in which the plants grows (Anderson et al., 1999). Unlike organic compounds, which are altered during storage (Anderson et al., 1999), the mineral composition of fresh commodities is stable and not influenced by storage conditions (Padin et al., 2001).

Among other plant products, potatoes are important sources of different minerals for humans (Navarre et al., 2009). Most of the minerals present in potato tubers originate from the main roots, being delivered first to the shoot via the xylem, and then loaded into the phloem for translocation to the tuber (Kärenlampi & White, 2009). The mineral composition of potato tubers is determined to some extent by the phytoavailability of minerals in the soil (Kärenlampi & White, 2009), which depend upon the local geology (True et al., 1978) and fertilization rates (Kärenlampi & White, 2009). In addition to the local geology, variations in tuber mineral concentration have also been observed among potato cultivars (Rivero et al., 2003; Di Giacomo et al., 2007). Although the composition and concentration of minerals are influenced simultaneously by the mentioned factors, they have been shown to be one of the most effective parameters used for determining the geographical origin of fresh commodities (Di Giacomo et al., 2007).

1.3 Relevance of potatoes production and consumption

Potatoes (*Solanum tuberosum L.*) have become important food commodities in the world. They are the world's number one non-grain food commodity (FAO, 2008), with a total world production quantity of more than 324 million metric tons in 2010 (FAO, 2011). In addition to their high production number, potatoes are also spread throughout most of the world's continents, mostly in temperate regions and highland areas (Lisinska & Leszczynski, 1989), because of their ability to be cultivated under a wide range of altitudes, latitudes, (Horton & Anderson, 1992) soils and climatic conditions (Jadhav & Kadam, 1998). In terms of consumption, in the year 2007, more than 208 million metric tons of potatoes were consumed as food (Table 1.3). Asia has the world's highest potato production, followed by Europe (Table 1.3). Europe, however, consumed more potatoes than any other region, showing the importance of this commodity in Europe. The four largest potato producers in Europe are the Russia, Ukraine, Germany and Poland (Table 1.3).

Table 1.3 Potatoes production and consumption by region (FAO, 2012)

	Harvested area (ha)[a]	Production (t)[a]	Yield (t ha^{-1})[a]	Population (1000)[b]	Consumption as food (t)[b]	Consumption per capita (kg)[b]
World	18,653,007	324,420,782	17.39	6,661,633	209,251,734	31.4
Africa	1,830,402	22,333,333	12.20	954,153	13,229,184	13.9
Asia	9,078,332	152,498,393	16.79	4,033,235	95,139,875	23.6
South America	942,423	14,475,788	15.36	380,155	11,024,076	29.0
North America	547,868	22,760,270	41.54	335,390	19,471,168	58.1
Oceania	49,459	1,811,688	36.63	34,720	1,459,864	42.0
Europe	6,110,058	108,120,149	17.69	733,694	66,323,459	90.4
Russia	2,109,100	21,140,500	10.02	143,295	19,522,830	136.2
Ukraine	1,411,900	18,705,000	13.24	46,282	6,066,702	131.1
Germany	255,200	10,201,900	39.97	82,516	5,397,847	65.4
Poland	490,853	8,765,960	17.85	38,190	4,618,956	120.9

[a] data obtained in 2010, [b] data obtained in 2007

Potatoes are the most important non-grain crop in Germany, in terms of economical value, having been worth more than €1.1 billion in 2010 (FAO, 2012). Nevertheless, the production number of over 10 million metric tons (Table 1.3) is still lower than wheat, sugar beet and barley (FAO, 2012). Potatoes are cultivated in several regions in Germany, but most of them are produced in Niedersachsen (47.1%), Bayern (16.5%) and Nordrhein-Westfalen (12.1%) (Statistische Ämter des Bundes und der Länder, 2010). The distribution of potato production in Germany is shown in Table 1.4.

Table 1.4 Distribution of potato production in Germany in 2009 (Statistische Ämter des Bundes und der Länder, 2010)

Federal state	Production (1,000 t)	Percentage of total production (%)
Baden-Württemberg	219	1.87
Bayern	1,933	16.55
Berlin	-	-
Brandenburg	341	2.92
Bremen	-	-
Hamburg	-	-
Hessen	189	1.62
Mecklenburg-Vorpommern	564	4.83
Niedersachsen	5,507	47.14
Nordrhein-Westfalen	1,422	12.17
Rhineland-Pfalz	303	2.59
Saarland	6	0.05
Sachsen	306	2.62
Sachsen-Anhalt	578	4.95
Schleswig-Holstein	222	1.90
Thüringen	92	0.79
Germany	11,683	100.00

Potatoes are either consumed fresh, or as processed food. Approximately 60% of the total potato-growing area in Germany is dedicated to industrial or processing potatoes, while the rest are table potatoes (UNIKA e.V., 2012). In Germany in 2007, the consumption per capita was about 65.4 kg, higher than the world's average consumption (Table 1.3).

Potatoes have become important as more than just a staple food. Along with the development of food and non-food industries based on the potato, potatoes with better quality than was accepted in the past are increasingly required as raw materials; thereby making quality of key importance (Sulaiman, 2005). In order to improve the quality of potatoes as raw materials for food, many experiments were conducted to investigate the effects of fertilizers (Pardede, 2005; Sulaiman, 2005; Wang-Pruski et al., 2007; Khan et al., 2012), water supply (Zhang et al., 1997; Sulaiman, 2000) and post-harvest treatment (Wulkow, 2009; Montouto-Graña et al., 2012) on selected quality parameters of several cultivars that were cultivated in several locations.

1.4 Quality parameters of table potatoes

Table potatoes are consumed worldwide, although their acceptance as food differs as a result of regional habits (Wulkow, 2009). Potatoes for table use need to be cooked because of the indigestibility of their ungelatinized starch (Burton, 1989); this is frequently done through baking, boiling, steaming, roasting, deep-fat frying or microwave cooking (Bradshaw & Ramsay, 2009). Good appearance, texture and flavor are three factors important to the consumer and the subject of many research activities (Taylor et al., 2007).

1.4.1 After-cooking darkening (ACD)

One important quality parameter of cooked potatoes is ACD, which is one of the most widespread undesirable characteristics of cultivated potatoes (Wang-Pruski & Nowak, 2004). After cooking, the non-periderm color may range from the normal white of unaffected potatoes to grey when exposed to the air as the result of a non-enzymatic oxidation reaction of the ferrous-chlorogenic acid complex (Wang-Pruski & Nowak, 2004). The intensity of the darkening is largely affected by organic acids, especially citric acid that competes with chlorogenic acid in binding iron (Lisinska & Leszczynski, 1989). Therefore, ACD is a complex quality parameter because it involves chemical parameters, the most important of which are organic acids and minerals.

1.4.2 Chemical parameters affecting ACD

Chlorogenic acid is one of the chemical parameters that influence the darkening intensity after cooking. The acid is the most abundant phenolic compound in the tuber with a percentage of more than 90% on dry matter basis (Navarre et al., 2009). Chlorogenic acid is concentrated more in the cortex than in the parenchyma (Lewis et al., 1998; Wang-Pruski & Nowak, 2004), and is related to the defense mechanism of the tuber against diseases (Jonasson & Olsson, 1994). During cooking, cell modification allows chlorogenic acid and iron ions to leave the cell and form a colorless ferrous-chlorogenic acid complex, which is then oxidized into ferri-dichlorogenic acid, the dark pigment progressively seen in potatoes after they have been cooked and exposed to the air (Wang-Pruski & Nowak, 2004). Chlorogenic acid content in tubers is genetically controlled and influenced by environmental conditions (Wang-Pruski & Nowak, 2004). For example, Delgado et al. (2001) reported that potato tubers harvested from drought-stressed plants have higher concentrations of chlorogenic acid than in well-watered plants.

Citric acid, a major organic acid in potato tubers, can compete with chlorogenic acid in binding iron ions to prevent the formation of the ferrous-chlorogenic acid complex, because it can bind iron more efficiently than chlorogenic acid (Mulder, 1949), and its quantity is higher than that of other organic acids (Wang-Pruski & Nowak, 2004). Therefore, citric acid is an important quality parameter related to the ACD.

Besides citric acid, ascorbic acid can also compete with chlorogenic acid in binding iron (Wang-Pruski & Nowak, 2004). Nevertheless, the resulting compound shows a light purple color (Shekhar et al., 1978; Muneta & Kaisaki, 1985) and the complex has been shown to be unstable at low pH values (Muneta & Kaisaki, 1985) and in the presence of strong chelating agents such as citric acid, EDTA and sodium hydrogen phyrophosphate (Muneta & Kaisaki, 1985; Friedman, 1997).

Mineral content may influence the intensity of ACD in potato tubers. A study conducted by Hughes and Swain (1962) suggested that Fe, P and Ca may be linked to the occurrence and severity of ACD. The distribution of minerals varies within the tuber between the stem end and the bud end (Kärenlampi & White, 2009). Furthermore, Etienne et al. (2009), after investigating mineral distribution in tubers, reported the relationship between ACD and some minerals, namely P, Mg, Ca, S, and Cu.

1.5 Aims of the research

Considering the demand for GI products and the increasing number of agricultural products applying for GI status, characterizing the geographical origin of these products is useful supplementary information for both the consumer and the producer. Potatoes, one of the several kinds of GI products in Germany, are cultivated mostly in the northern, western and southern parts of the country. These three main potato-producing regions are characterized by