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# Coffee berry and green bean chemistry – Opportunities for improving cup quality and crop circularity

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ABSTRACT

Coffee cup quality is primarily determined by the type and variety of green beans chosen and the roasting regime used. Furthermore, green coffee beans are not only the starting point for the production of all coffee beverages but also are a major source of revenue for many sub-tropical countries. Green bean quality is directly related to its biochemical composition which is influenced by genetic and environmental factors. Post-harvest, on-farm processing methods are now particularly recognised as being influential to bean chemistry and final cup quality. However, research on green coffee has been limited and results are fragmented. Despite this, there are already indications that multiple factors play a role in determining green coffee chemistry – including plant cultivation/fruit ripening issues and ending with farmer practices and post-harvest storage conditions. Here, we provide the first overview of the knowledge determined so far specifically for pre-factory, green coffee composition. In addition, the potential of coffee waste biomass in a biobased economy context for the delivery of useful bioactives is described as this is becoming a topic of growing relevance within the coffee industry. We draw attention to a general lack of consistency in experimentation and reporting and call for a more intensive and united effort to build up our knowledge both of green bean composition and also how perturbations in genetic and environmental factors impact bean chemistry, crop sustainability and ultimately, cup quality.

## 1. Introduction

Although coffee is not a nutritional staple crop, for many people across the world its products are considered a daily necessity. It is now widely cultivated in more than 80 countries mainly located in the (sub) tropical regions of Africa, America and Asia (Davis, Govaerts, Bridson, & Stoffelen, 2006). Furthermore, for many of these countries, coffee represents a (*the*) major source of national revenue (Kanitnuntakul, Meeasa, & Borompichaichartkul, 2017). Brazil, having more than one third of global production and exportation, is the biggest coffee producer and exporter followed by Vietnam, Indonesia and Colombia (Esteves Vieira et al., 2006). The term coffee refers to the products of trees and bushes from the genus *Coffea*. However, while this genus comprises 103 – 124 species – depending on the broadness of taxonomic classification (Davis, Tosh, Ruch, & Fay, 2011; Souard et al., 2018) – only 2 are responsible for almost the entire global coffee production. *Coffea arabica*, often referred to as 'Arabica', accounts for ca. 70% of the market, while *Coffea canephora,* ('Robusta'), provides the remaining ca. 30% (Geromel et al., 2006). While *C. arabica* is tetraploid (2n = 4x = 44), all other *Coffea spp*., including *C. canephora* are diploid (2n = 2x = 22). Studies also indicate a close genetic relationship between the two commercial species as *C. arabica* is considered to be an amphidiploid hybrid between *C. canephora* and *C. eugenoides* (Herrera, Combes, Cortina, Alvarado, & Lashermes, 2002).

Arabica coffee is thought to have higher bean quality and therefore delivers a better tasting, 'more rounded', coffee beverage as compared to Robusta which is considered to be more bitter and 'earthy'. However, it must be borne in mind that local/national/cultural taste preferences differ enormously (Seninde & Chambers, 2020). How we define quality is a never-ending discussion but it is clear that for determining market value, quality, however defined, is always a driving factor (Pizarro, Esteban-Díez, & González-Sáiz, 2007). Therefore, defining quality in an objective and reliable way is still a difficult topic to address. Many studies have been published focusing on the chemical properties of coffee beans and how these might relate to final coffee flavour - the so-called, 'cup quality' (Barbosa, Scholz, Kitzberger, & Benassi, 2019). The literature also contains many articles on roasting chemistry and coffee cup quality (see Bicho, Lidon, & Ramalho, 2013; Seninde & Chambers,

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2020) and in relation to green bean chemistry (Celli and de Camargo 2019; Bayle and Adamu 2019). Attention given to the factors determining the chemistry of the initial green bean has been sporadic and our knowledge is clearly fragmented in comparison to that for roasted coffee beans. This is surprising as these green beans (often referred to in the industry as 'green coffee') are the starting point for every coffee product. As will become evident below, green bean chemistry is the result of a dynamic interaction between genetics, environment and seasonality. Furthermore these dynamics relate not only to the bean itself but also and equally importantly, to the surrounding fruit tissues.

Green coffee chemistry is also receiving growing attention within the coffee industry as there are increasing demands from both consumer and producer alike to create a more sustainable industry. To achieve this, two key aspects are of greatest importance – firstly, reduction in the loss of product (quality) at pre-, during and post-harvest stages. This requires a better understanding of those factors having greatest environmental and chemical impact. Secondly, the introduction of better crop circularity with the early stages of the industry. Much coffee berry waste is still unused/underexploited despite both its magnitude and it being a potentially huge and valuable source of bioactive chemicals. This review shall bring together the information available on coffee berry development and chemistry in a comprehensive overview of our current knowledge. Gaps in our knowledge are exposed and proposals are made as to how we should progress in this field in order to design strategies for a more sustainable coffee production with effective and efficient use of all (waste) materials and which delivers high quality green beans with the best chemical composition. All this is aimed to meet the growing demands of the ever-expanding, coffee-drinking public for sustainability as well as quality.

### 1.1. Origins

To introduce all the relevant components in coffee processing we need to consider all the important pre- and post-harvest steps and determine and understand how each of these has potential chemical impact. These aspects give the structure to this review. As with all plant tissues, the biochemistry of a green bean is primarily the product of genetics × environment and differences in the chemistry of the harvested materials has major impact on the chemistry of the coffee brew. Ripening stage is also important because as seen with diverse berry species such as tomato and melon (Moing et al., 2011; Quinet et al., 2019), during ripening, fruits and seeds undergo a paradigm shift in metabolism. Coffee berries are climacteric fruits and the moment of increased ethylene production and its associated increased respiration and metabolic changes in *e.g.* sugar metabolism, deglycosylation and depolymerisation as discussed by Pereira, Galvão, Kobayashi, Cacao, & Vieira (2005) is of great chemical importance. Consequently, the precise moment of harvest is crucial. All treatments applied post-harvest – both on-farm and in the factory, represent the second main phase of influence. Proper on-farm treatment of the berries - needed to enable the farmer to isolate and dry the seeds (beans) - has already been identified as essential for a high-grade quality coffee brew (Selmar & Bytof, 2007). Regardless of the type of treatment, the final products are the exposed, dried green beans which are the commercial starting point for roasted coffee production. In this review we focus on a number of the most important factors impacting green coffee chemistry as touched upon above, especially related to bean type (Robusta vs. Arabica), developmental influence and environmental/cultural practices. Roasted coffee bean chemistry is beyond the scope of this paper as this has already been extensively reviewed elsewhere (Bicho et al., 2013; Seninde & Chambers, 2020). What will become evident is our limited knowledge of green bean chemistry and hence our still poor understanding of the link between this and final cup quality.

### 1.2. Green bean anatomy and tissue chemistry: quality and circularity

The coffee industry continues to have a strong drive to improve coffee quality but also now a second goal is emerging – increased crop sustainability and circularity. Much waste, and especially the fruit pulp goes unused even though this huge volume of material, roughly equal to that of the green beans, may also contain valuable chemicals. Research in this field is increasing, particularly relating to bioactives extraction in a biobased economy context. We first consider the basic anatomy of the coffee berry and that of its incumbent beans as these different structures have clearly different chemistries. Next to the green bean, we include here also the so-called silverskin as well as the fruit pericarp (Fig. 1A). Although both should be removed before roasting the beans to make the beverage, each has its own chemistry directly and indirectly influencing final bean composition (Esquivel & Jiménez, 2012). Both also represent by-products of the industry which are valuable starting points for a circularity/biobased application for the production of high value chemicals for the food or non-food industries. For each tissue we draw attention to the main chemical constituents, their physiological *in vivo* role and how they might or might not be related to coffee cup flavour and quality.

## 2. The green bean

Each coffee berry contains 2 seeds (beans) which are usually green in colour although they may turn yellow-brown on drying. Beans take up ca. 50% of the volume of the fresh berry and anatomically, this is mainly endosperm tissue which is surrounded by the endocarp and testa (silverskin). A broad survey of the literature revealed that the main chemical compounds found in the green bean are alkaloids, phenolic compounds, carbohydrates, lipid soluble compounds, organic acids and proteins/amino acids. These groups are all relevant to cup quality and are now considered individually.

### 2.1. Green bean: alkaloids

Chou and Waller (1980) were able to identify most of the major alkaloids found in *C. arabica* tissues including leaves, roots, young seedlings and green beans. Caffeine, theobromine, theophylline, paraxanthine and scopoletin were detected, but notably others such as trigonelline were missing (Baeza et al., 2016). Physiologically, all have been demonstrated to be allelopathic agents from coffee trees and have also been considered to be causal agents of the decrease in production and quality of old coffee plantations (Chou & Waller, 1980). However later, it was recognised that caffeine and caffeine-related metabolites can also have the opposite effect and function as growth stimulants (Eira et al., 2006). Relatively high levels of caffeine are considered typical of both Arabica and Robusta beans and a protective function has been attributed to it (Baumann, 2006; de Melo et al., 2018) relating to protection of the germinating seedling against pests and pathogens at the plant's most vulnerable stage in its life cycle. Caffeine and the other alkaloid allelochemicals can leech out and reduce the germination of neighbouring seeds (Chou & Waller, 1980; Pham et al., 2019). They are also proposed to be "conditioning" agents in the soil rhizosphere, creating a more favourable microbial and physicochemical environment specifically suited for coffee plant development (Baumann, 2006).

Most research has focused on the alkaloids present at the highest concentrations and which are considered to be directly related to final product quality. Consequently, much information is to be found on caffeine and trigonelline and much less on other components of this chemical family. In relation to quality, the two most important compounds are, caffeine, which is by far the main methylxanthine present (99.8%) and trigonelline (0.2%) as determined in Arabica beans (Baeza et al., 2016). Significant differences in alkaloid concentrations where found between *C. arabica* and *C. canephora*, with the latter generally having higher levels of caffeine and lower amounts of trigonelline

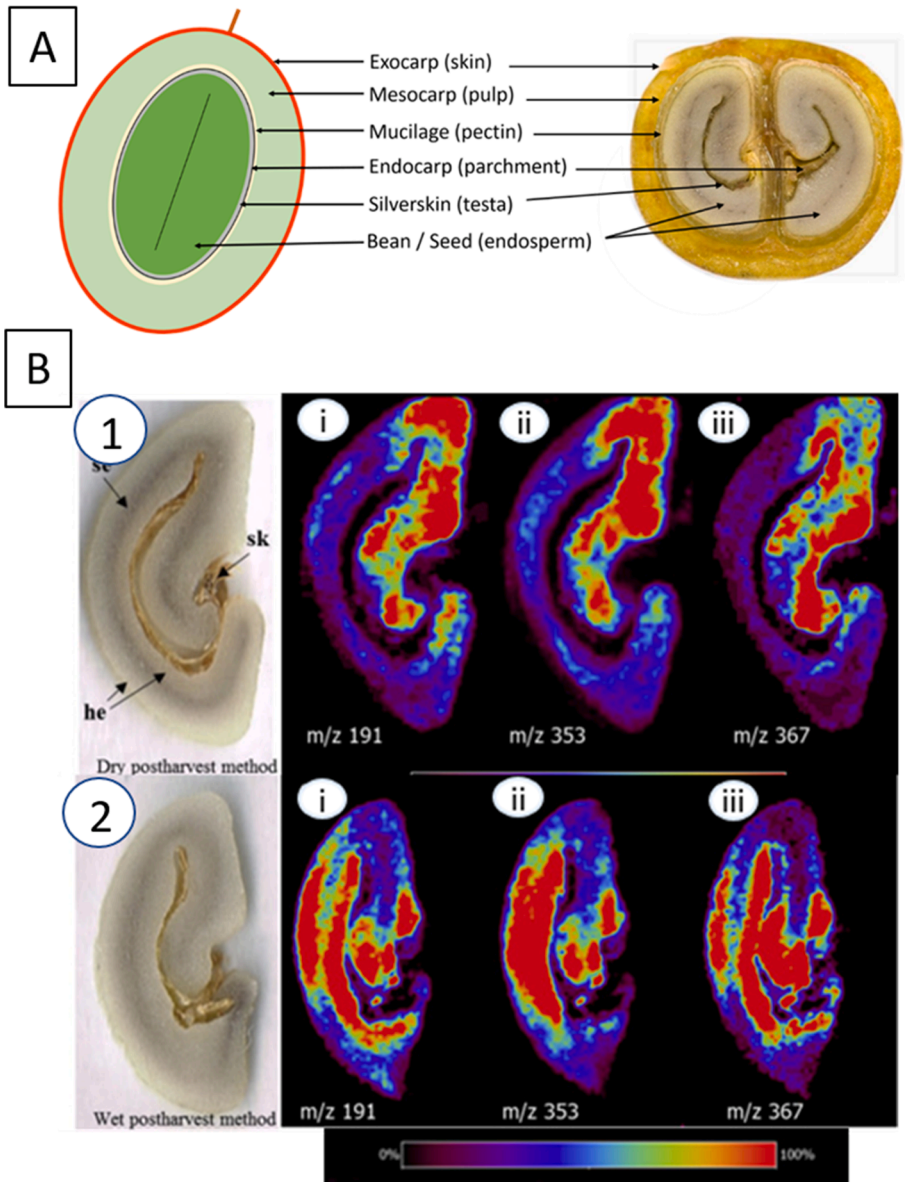


**Fig. 1. [A]** The anatomy of a coffee berry. Left – a schematic representation of a longitudinal cross-section and Right – a transverse section of a fresh coffee berry. **[B]** Cross sections of green coffee beans (1) processed by a dry post-harvest processing method or (2) a wet post-harvest processing method. Tissue coding: he: external hard endosperm region; se: internal soft endosperm region; sk: silver skin. DESI-MS (negative mode) ion images for each are presented for (i) *m/z* 191, quinic acid; (ii) *m/z* 353, caffeoylquinic acid; (iii) *m/z* 367, feruloylquinic acid to illustrate the non-homogeneous distribution of molecules across the endosperm. The colour bar ranges from low (Black) to high (Red). Modified and reproduced with permission from Garrett et al. (2016). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Barbosa et al., 2019; Caporaso, Whitworth, Grebby, & Fisk, 2018; Kwon et al., 2015). In absolute terms, caffeine content is found in the range of 7–18 mg·g$^{-1}$ (dry weight basis, dwb) in Arabica and 15–25 mg g$^{-1}$ (dwb) in Robusta. Trigonelline ranged from 6–20 mg·g$^{-1}$ (dwb) and 5–9 mg·g$^{-1}$ (dwb), for Arabica and Robusta respectively (Table 1). However, although these differences are considerable, the overlap in alkaloid concentration range between the two species means that species discrimination based only on alkaloid content as a marker of origin is unreliable. Regarding the minor alkaloids in green beans, Chou & Waller, (1980) reported theobromine and theophylline as well as scopoletin and paraxanthine being detectable and allelopathically bioactive in Arabica beans. Mehari et al. (2016) also found theobromine and theophylline in seven of the eight Robusta varieties tested but theophylline was always undetectable. Any relevance to quality has not yet been approached but considering the structural similarities between caffeine and theobromine it is likely that the latter will also be stable on roasting and hence may also impact sensory attributes like bitterness.

Regarding a potential relationship with coffee brew quality, caffeine has been described as a bitter-tasting compound but which has stimulatory effects on the human nervous system (Farah, 2012). Furthermore, by being thermostable, its concentration remains relatively constant during processing and it is not one of the components contributing to further aroma development (Barbosa et al., 2019; Caporaso et al., 2018). In contrast, trigonelline is thermolabile and its relevance to coffee taste relates to its degradation during processing leading to the formation of new sensory-relevant volatile compounds including pyrroles and pyridines (Caporaso et al., 2018). Several attempts have been made to determine if these two alkaloids are directly linked to bean quality. For example, trigonelline has been shown to be positively correlated with some sensory traits but negatively correlated with others (Gamboa-Becerra et al., 2019). For caffeine, Farah and Donangelo (2006) found correlation to a positive sensory impact while Barbosa et al. (2019) report the opposite. While it is thought that these differences may relate to the contrasting analytical protocols used, there is also a potential complicating factor in that trigonelline and caffeine cannot be considered independently as they have competing biochemical pathways (Baumann, 2006). Furthermore, there may be metabolic links with other metabolites which also positively correlate. More detailed research is needed to determine whether one or both of these compounds has a causal impact on coffee flavour.

In conclusion, much research has been done on the importance of alkaloids in green coffee beans. However, almost all attention is still

**Table 1**
Concentration of the main constituents on Green Coffee Beans expressed in mg·g$^{-1}$ sample (dry weight basis), according to a selection of the literature*.

| | Caffeine | Trigonelline | CGAs | | | | Carbohydrates | | | Proteins | Amino acids | Lipid soluble compounds | Organic acids | Ashes | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Total | CQA | FQA | diCQA | Total | Sucrose | Reducing sugars | | | | | | |
| C. arabica | 9–13 | 6–20 | 41–79 | | | | 450–580 | 60–90 | 1 | 100–110 | 5 | 155–182 | 10 | 30–42 | (Farah, 2012) |
| C. arabica | 12.1–13.6 | | 40–80 | | | | | 62–69 | | 134–153 | | 159–167 | | | (Barbosa et al., 2019) |
| C. arabica | 7.3–10.7 | 6.3–9.1 | | | | | 682–709 | | | 145–161 | | 97–111 | | 46–49 | (Franca et al., 2005) |
| C. arabica | 13.4–18 | 6.8–10.4 | | | | | | 39–54 | | | | | | | (Caporaso et al., 2018) |
| C. arabica | | | 35–75 | | | | | | | | | | | | (Gawlik-Dziki et al., 2014) |
| C. arabica | | | 68.8 | 57.6 | 2.5 | 8.7 | | | | | | | | | (Trugo & Macrae, 1984) |
| C. arabica | | | 56.3 | 46.3 | 3.3 | 6.6 | | | | | | | | | (Clifford & Ramirez-Martinez, 1991) |
| C. arabica | | | 56.7 | 47.7 | 3.4 | 5.6 | | | | | | | | | (Clifford & Ramirez-Martinez, 1991) |
| C. arabica | | | 61.0 | 43.0 | 5.7 | 12.3 | | | | | | | | | (Correia, Leitão, & Clifford, 1995) |
| C. arabica | | | 56.5 | 48.4 | 2.8 | 5.3 | | | | | | | | | (Correia et al., 1995) |
| C. arabica | | | 78.5 | 56.7 | 7.9 | 13.9 | | | | | | | | | (Correia et al., 1995) |
| C. arabica | | | 52.5 | 42.0 | 2.8 | 7.7 | | | | | | | | | (Farah, Monteiro, & Trugo, 2005) |
| C. arabica | | | 57.3 | 46.0 | 2.9 | 8.4 | | | | | | | | | (Farah et al., 2005) |
| C. arabica (Wild) | 9.6–16.2 | 8.8–17.7 | 41.0 | 32.6 | 1.9 | 6.0 | | | | | | | | | (Ky et al., 2001) |
| C. canephora | 15–25 | 6–7 | 61–113 | | | | 539–640 | 9–40 | 4 | 110–150 | 8–10 | 72–108 | 10 | 44–45 | (Farah, 2012) |
| C. canephora | 15–24.8 | 5.6–9 | | | | | | 24.5–43 | | | | | | | (Caporaso et al., 2018) |
| C. canephora | | | 70–144 | | | | | | | | | | | | (Gawlik-Dziki et al., 2014) |
| C. canephora | | | 88.0 | 68.2 | 6.0 | 13.7 | | | | | | | | | (Trugo & Macrae, 1984) |
| C. canephora | | | 71.7 | 53.3 | 7.9 | 10.5 | | | | | | | | | (Clifford & Ramirez-Martinez, 1991) |
| C. canephora | | | 60.8 | 34.3 | 5.4 | 12.0 | | | | | | | | | (Correia et al., 1995) |
| C. canephora | | | 71.8 | 49.7 | 7.5 | 14.6 | | | | | | | | | (Correia et al., 1995) |
| C. canephora | | | 94.7 | 74.2 | 9.5 | 10.9 | | | | | | | | | (Farah et al., 2005) |
| C. canephora | | | 75.8 | 57.7 | 4.7 | 13.4 | | | | | | | | | (Farah et al., 2005) |
| Wild C. canephora | 15.1–33.3 | 7.5–12.4 | 113.0 | 76.6 | 14.3 | 23.1 | | | | | | | | | (Ky et al., 2001) |

*Where a blank cell is displayed no data regarding that parameter were found in the corresponding article.

being paid to the two most abundant compounds. From a sensory perspective, we should not continue to ignore the less abundant alkaloids such as putrescine, theophylline and theobromine as these may also play a significant role in bean physiology as well as in final product quality. As will become evident in this review, this trend of limited focus is recurrent for almost all the chemical families covered.

### 2.2. Green bean: phenolic compounds

Detailed analyses of extracts for the determination of phenolic compounds were already available at the end of the last century (Chou & Waller, 1980). These authors first identified the presence of caffeic, chlorogenic, vanillic, ferulic, p-coumaric, and p-hydroxybenzoic acids in Arabica coffee beans. Since then, advanced methodologies have discriminated up to 74 compounds from the phenolic family in green *C. canephora* beans (Jaiswal, Patras, Eravuchira, & Kuhnert, 2010) and approximately 40 in green *C. arabica* (Baeza et al., 2016). Others have described additional compounds, in either Arabica or Robusta, which were previously undetected (Alonso-Salces, Serra, Remero, & Heberger, 2009; Dziki et al., 2015). Although some of these investigations, performed in parallel, replicated or validated the results for total phenolic content, frequently total phenolics is observed to mask significant quantitative and qualitative differences. This underlines the considerable variability between the types of samples analysed, extraction procedure, analytical methods and detection sensitivity and that we are likely still to be underestimating the total number of phenolic structures actually present in green coffee.

The reported levels of total phenolic compounds in green beans ranges from 4% to 8.4% (dwb) for *C. arabica*, and from 7% to 14.4% (dwb) for *C. canephora* (Table 1). The majority comprises chlorogenic acid derivatives (CGAs) which is a large family of phenolic compounds derived from the esterification of trans-cinnamic acids (*e.g.*, caffeic, ferulic, and p-coumaric acids) with (−)-quinic acid (Clifford, Jaganath, Ludwig, & Crozier, 2017). The remainder represents just 1% of total phenolics (Farah & Donangelo, 2006) and comprises simple, free (non-conjugated) volatile and non-volatile compounds, including caffeic, vanillic, ferulic, p-coumaric, and p-hydroxybenzoic acids as well as a few, more complex phenolic molecules (Clifford, 2000; Moreira, Trugo, & De Maria, 2000). These can include anthocyanins, likely to be derived from pulp and skin residues (*e.g.* cyanidins, pelargonidins and one peonidin) and lignans such as secoisolariciresinol, lariciresinol, matairesinol and pinoresinol (Mazza & Miniati, 1993). Moreover, soluble and insoluble tannins may also be found in trace amounts, again perhaps as a residue from the pulp (Farah & Donangelo, 2006). Even though nowadays there is sufficient power to elucidate the exact composition of phenolics – using *e.g.* high resolution mass spectrometry - there is still a lack of research on green beans covering those compounds not belonging to the CGA family. Furthermore, much of the recent literature focuses more either on the composition and possible re-use of coffee production residues – including fruit pulp and spent coffee grounds - or on the major phenolic CGA component in the context of a potential role in human health. This again leaves a gap of knowledge on the lower abundant molecules which might now better be tackled with new state-of-the-art approaches with higher analytical sensitivity and/or high resolution untargeted metabolomics (Putri & Fukusaki, 2018; Souard et al., 2018).

Regarding the CGAs, this sub-class can be further divided according to the number, nature and esterification position of the substituents of the cyclohexane ring of the quinic acid moiety (Clifford, 2000). According to Alonso-Salces et al. (2009) this classification is proposed to comprise 10 classes of CGAs, while elsewhere five major classes are proposed (Baeza et al., 2016; Garrett, Rezende, & Ifa, 2016; Karpinska, Świsłocka, & Lewandowski, 2017). These are, based on abundance: 1: caffeoylquinic acids (CQAs), 2: dicaffeoylquinic acids (diCQAs), 3: feruloylquinic acids (FQAs), 4: p-coumaroylquinic acids (pCoQAs) and 5: caffeoyl-feruloylquinic acids (CFQAs) (Baeza et al., 2016; Garrett et al., 2016; Karpinska et al., 2017). Relative proportions, vary considerably per class. The CQAs represent up to 85.5% (of the total phenolic content) in green coffee beans. Within these, there are three main isomers: 5-caffeoylquinic acid (5-CQA), 4-caffeoylquinic acid (4-CQA) and acid 3-caffeoylquinic acid (3-CQA) which account for 62–69%, 8.5–11.4% and 4.4–6.8% respectively. 5-CQA is the most abundant and the most studied. It is also the only compound for which a commercial standard is available. In the literature it is often incorrectly referred to generically as 'chlorogenic acid'. DiCQAs and FQAs each represent 10% of the total phenolics, whereas the other groups together make up 1–2% (Karpinska et al., 2017; Mehari et al., 2016).

In relation to bean quality, a potentially relevant role for phenolics is to form complexes with caffeine and minor CGAs and most specifically, diCQAs. This complexing is considered to stabilize the alkaloid, helping its transport across the various tissues and avoiding autotoxicity (Baumann, 2006; Mondolot et al., 2006). Phenolic compounds were also identified in the endosperm boundary (Baumann, 2006) where they may reduce the diffusion of caffeine and other alkaloids out of the seed before imbibition. Work by Garrett et al. (2016) provided strong support for this hypothesis by using DESI-MS to map the distribution of phenolic acids across the green coffee endosperm (Fig. 1B). FQAs were mainly observed in the hard, external layer of the seed storage tissue, whereas CQAs and diCQAs were mainly located in the soft internal region.

Phenolic compounds have been directly and indirectly linked to coffee flavour quality. Generally, a higher level (qualitative and quantitative) of phenolics has been associated with green beans of lower quality (Barbosa et al., 2019; Farah, 2012; Farah & Donangelo, 2006; Farah, Monteiro, Calado, Franca, & Trugo, 2006; Franca, Mendonça, & Oliveira, 2005; Kurniawan, Andarwulan, Wulandari, & Rafi, 2017). This also matches the evaluation that Robusta beans have lower brew quality than Arabica beans. Some of the most studied CGAs have been associated with astringency and bitterness of the coffee brew and can act as precursors of catechols and other phenolic structures that can confer unpleasant sensory attributes (Gloess et al., 2013). CQAs and FQAs may undergo oxidation and degradation during storage and processing, which can also result in off-flavours and a lower quality (Farah & Donangelo, 2006). Oxidized and degraded chlorogenic acids are often found in defective/unripe beans, once again supporting the general consensus that low quality starting materials result in low quality end products. A full understanding of the role of each specific CGA isomer in the physiology and in the quality of coffee beans is lacking. Farah & Donangelo, (2006) trying to address this stated that in sour and black defective beans, 3-CQA, 4-CQA and 4-FQA increased by 25% when compared to levels in standard quality beans. However, this is only a limited evaluation of the entire role of CGA isomers in coffee and the situation is likely to be much more complex. Even if CGAs may be linked to low quality coffee this is not the full picture. For example, chlorogenic acids are known to be essential for roasted coffee pigmentation and aroma formation – as well as for astringency which is still required at low levels for a high-quality brew (Kurniawan et al., 2017). The link between phenolic content and the degree of quality is a complex one associated with both qualitative and quantitative differences within the overall biochemical profile (Barbosa et al., 2019; Zanin, Corso, Kitzberger, Scholz, & Benassi, 2016). These findings reiterate the need not to rely solely on chemical measurements as these must always be placed in the context of the coffee matrix as a whole as well as in the context of (local/cultural) flavour preferences. This is especially true in relation to *e.g.* astringency and bitterness attributes, where phenolics are major players.

### 2.3. Green bean: carbohydrates

Another important, quality-related metabolite group is the carbohydrates (CHO). Both free sugars and polysaccharides represent, on average, >50% of the total seed dry weight (Table 1) (Farah, 2012; Monteiro & Farah, 2012). The latter also accounts for the majority of

total CHO content (Poisson, Schmalzried, Davidek, Blank, & Kerler, 2009; Redgwell & Fischer, 2006). Generally, sugars are thought to be precursors of important coffee flavours and aromas which are present after roasting. Greatest attention has been given to sucrose. However, a link between high abundance and a high relevance for quality is over-simplified. It has been demonstrated that minor components such as 3-methylbutanoyl disaccharides, which are present in concentrations of ca. 10–35 $\mu g.g^{-1}$ is a significant store of sugar and might even be more relevant than sucrose, which occurs at ca. 80 $mg{\cdot}g^{-1}$, regarding coffee taste discrimination (Iwasa et al., 2015). This glycoside of 3-methylbutyric acid, contains glucose and fructose, and a clear correlation has been found with coffee aftertaste - an attribute which is usually positively perceived and considered by official tasters to give added value to coffee.

At the end of bean maturation, sucrose is the most abundant free sugar essentially functioning as a C/energy source (Garrett et al., 2016). However, it is also influential in the formation of sensory-relevant molecules after roasting (Campa et al., 2004; Geromel et al., 2006). Depending on species and variety, but also on environmental conditions during cultivation, sucrose concentration in green beans may vary up to 10 fold, from 9 to 90 $mg{\cdot}g^{-1}$ (dwb). Generally, Arabica coffee beans have a higher level than Robusta beans (Campa et al., 2004; Clarke & Vitzthum, 2008). According to Garrett et al. (2016), sucrose is mainly concentrated in the bean endosperm and has a relatively homogeneous distribution. Glucose and fructose are the two other major constituents, with the former being higher in concentration. Their levels at the end of bean maturation are generally between 0.03 and 0.05% (3–5 $mg{\cdot}g^{-1}$) (dwb) (Redgwell & Fischer, 2006; Rogers, Michaux, Bastin, & Bucheli, 1999) with *Arabica* showing higher levels than *Robusta*. However, in contrast to sucrose, both glucose and fructose appear mainly present in the perisperm (Redgwell & Fischer, 2006). Other oligosaccharides such as raffinose and stachyose as well as monosaccharides such as mannose, arabinose, and rhamnose have been detected in trace amounts in green coffee (Redgwell & Fischer, 2006) although no function or relationship with quality or physiology has yet been established.

Concerning the group of structural carbohydrates, galactomannans and mannans, arabinogalactans, hemicellulose and cellulose are the major components. Pectic polysaccharides and xyloglucans are usually only found in trace amounts (Oosterveld, Harmsen, Voragen, & Schols, 2003; Redgwell, Curti, Fischer, Nicolas, & Fay, 2002). Here we shall refer to arabinogalactans as arabinogalactan-proteins (AGPs), as the vast majority of these polysaccharides in coffee is present in complexes with proteins (Redgwell et al., 2002). Structural sugars fulfil their function mainly in the cell walls, where galactomannans account for $\leq$50% of all polysaccharides (Redgwell & Fischer, 2006). Even though galactomannans are the most abundant polymers, they are not equally distributed within the cell wall. A clear spatial heterogeneity was observed using antibody labelling, with higher level regions located close to the cell lumen and the middle lamella, while lower concentrations were evident in between (Sutherland, Hallett, MacRae, Fischer, & Redgwell, 2004). Similarly, AGPs appear to be mainly localised surrounding the cell lumen.

While the physiological and structural roles of cellulose and hemicellulose, pectins and xyloglucans etc is unlikely to be different than in all other plant structures, there are no reported links to a potential relevance for coffee quality. However, when other physical characteristics are relevant, such as the solubility of so-called 'instant coffee', these components may become important (Redgwell & Fischer, 2006). The ripening process is also important regarding the exact chemical composition of the cell walls and will be covered below.

Of all the chemical groups analysed, possibly the most publications focus on the potential correlation between carbohydrate composition and beverage quality. One hypothesis that regularly emerges regarding flavour precursors, is that complex and insoluble structures, like AGPs or mannan-cellulose complexes in green beans, are more relevant for aroma formation during roasting than *e.g.* soluble, free or more simple sugars (Poisson et al., 2009). These authors demonstrated a role for AGPs as key precursors of 2-furfurylthiol (FFT), one of the most important sensory-relevant thiol volatiles in roasted coffee. Free sugars in contrast, can work as repressors of the formation of alkyl-pyrazines, another family of compounds associated with coffee flavour. Free sugars can also work as precursors of 2-furaldehyde, another important volatile compound (Poisson et al., 2009). Such contrasting results emphasise the complex chemistry behind flavour formation where individual precursors present in the starting material can have a positive role on the formation of certain sensory-relevant compounds, while having a negative influence on others. The relevance of single components on overall quality of a coffee brew is usually small and difficult to evaluate within such complex mixtures and the ratios of constituents may be a more valuable way to address sensory variation. This appears to be the case for sucrose where apparently-contrasting findings is found in the literature where its concentration both is/is not positively correlated with coffee quality (Farah et al., 2006; Kwon et al., 2015). However, there is agreement about the relevance of the sucrose/TTA (Total Titratable Acidity) ratio for discriminating good quality green beans (Barbosa et al., 2019). More specifically, a high ratio is positively correlated with better quality. High sucrose and low acid contents, typical of Arabica beans, is associated with a higher quality brew and the opposite is associated with the lower Robusta quality.

Carbohydrates are also considered to be essential for the formation of coloured compounds – melanoidins – and the depth of pigmentation, another quality parameter not yet mentioned (Kurniawan et al., 2017). Melanoidins give a brown colour and are high molecular weight, heterogeneous polymers produced during bean roasting through reactions involving reducing sugars and amino acids present in the green beans during the Maillard process (Davídek et al., 2005). Early in this process, or when mild roasting conditions are used, Amadori rearrangements can occur leading to the appearance of Amadori compounds (Davídek et al., 2005). These are generally simple, non-enzymatic condensation products between a reducing sugar and an amino acid. Melanoidins play a central role in coffee quality determination and Amadori reaction products are considered to influence both coffee aroma and taste by adding specific sensory nuances (Davídek et al., 2005).

### 2.4. Green bean: lipid soluble compounds

Despite clear potential relevance to sensory attributes, only limited literature is available on the lipid content and profile of green coffee beans. Arabica generally has higher levels of lipid soluble compounds compared to Robusta, 15–17% and 7–10% (dwb) respectively (Table 1) (Farah, 2012). The triacylglycerols (TAGs) account for ca. 75% of the total lipid soluble fraction; followed by diterpenes (ca. 20%); sterols (ca. 5.5%); free fatty acids (1%); phospholipids (ca. 0.5%) and tocopherols (0.05%). In general, the majority of the fatty acids present, both free as well as esterified to glycerol (TAGs), is unsaturated with the main representatives being linoleic, oleic and linolenic acids (Kölling-Speer, Kurzrock, Gruner, & Speer, 2005). Lipids, in the strict sense (therefore, excluding the diterpenes, but including sterols and phospholipids), are mainly found as TAGs in the endosperm with only a small amount, 2–3%, being present outside the seed where they form the external protective wax layer (Franca et al., 2005). Lastly, the tocopherols, a less abundant sub-group of lipids, have been shown to work as ROS scavengers protecting the seed lipids from stress damage (DaMatta & Ramalho, 2006; Munné-Bosch & Alegre, 2002).

Overall, in *C. arabica* higher concentrations of diterpenes are detected compared to *C. canephora* (Monteiro & Farah, 2012). Among these, cafestol and kahweol are the main representatives and the most studied. However, many derivatives of these two molecules have also been identified including, ethylated molecules in Robusta beans (Kölling-Speer et al., 2005; Speer & Kölling-Speer, 2006) and salts and esters of fatty acids in both species (Cavin et al., 2002; Speer & Kölling-Speer, 2006). The two derivatives, 16-O-methylcafestol and 16-O-

methylkahweol, remain stable during processing. This may allow the discrimination between different coffee blends and their species composition, as 16-O-methylcafestol is mainly detected in Robusta and not/almost not in Arabica (Kölling-Speer et al., 2005; Speer & Kölling-Speer, 2006). Cafestol and kahweol are themselves generally considered to be less stable and the latter is less abundant as it has a lower stability at high processing temperatures when light and oxygen are present (Flament, Gautschi, Winter, Willhalm, & Stoll, 1968). Both Barbosa et al. (2019) and Novaes, Oigman, De Souza, Rezende, & De Aquino Neto, (2015) found a positive correlation between coffee quality, cafestol concentration and the cafestol/kahweol ratio. Higher levels of cafestol compared to kahweol, or a higher overall concentration of the former, leads to a higher quality beverage.

Possible crosstalk between the CGAs and diterpene pathways has been hypothesised based on a positive correlation between cafestol and CGA as highlighted by Barbosa et al. (2019). Other identified diterpenes are coffeadiol and arabiol-I. These are structurally similar to cafestol and kahweol but the furan ring is substituted differently (Speer & Kölling-Speer, 2006). Following their detection and characterization no further studies appear to have been performed on these molecules. Chu et al. (2016) detected nearly 90 ent-kaurane diterpenoids in coffee beans, however again no further information is available.

Despite cafestol and kahweol being known to influence coffee quality, lipids appear to be only partially involved in flavour production during roasting as they are generally relatively stable even at high processing temperatures. Indeed, lipids present in green beans can still be detected in roasted coffee (Farah, 2012). The lipid fraction can still lead to the production of sensory-relevant volatile compounds including aldehydes, ketones and alcohols during the roasting process (Sunarharum, Williams, & Smyth, 2014). However, it has been observed that higher levels of lipid soluble molecules in green coffee beans can be associated with a lower cup quality (Franca et al., 2005). This may seem contradictory, but many off flavours in coffee and indeed other foodstuffs, can result from the hydrolysis, oxidation and/or peroxidation of these molecules during non-optimal storage and processing (Kwon et al., 2015; Vila, Andueza, De Peña, & Cid, 2005).

In conclusion, green coffee beans generally have a low level of lipid soluble compounds relative to other sub-tropical tree crop seeds such as cacao (50–55%) (Caporaso, Whitworth, & Fisk, 2021) and coconut (ca. 60%) (Kumar, 2011). For this reason, it was long thought that the lipophilic fraction was less relevant than several other chemical classes regarding coffee quality.

### 2.5. Green bean: Organic acids

The major coffee aliphatic acids are citric, acetic, lactic, malic and γ-aminobutyric acid (GABA) (Kramer, Breitenstein, Kleinwchter, & Selmar, 2010). Of course, there are many more acidic compounds in the green bean, but these are usually either included in other families (*e.g.* fatty acids in the lipid soluble compounds group, chlorogenic acid in the phenolic compounds family) or they are present only in trace amounts (*e.g.* succinic, gluconic, fumaric acids as well as many others) (Bähre, 1996). Much of the literature covering this class of molecules only reports pH values or total titratable acidity (TTA) values and give little or no information on individual compounds. However, qualitative as well as quantitative differences are of importance from a quality/sensory perspective. Barbosa et al. (2019) reported TTA levels between 193.59 and 409.85 mL NaOH (0.1 mol $L^{-1}$) per 100 $g^{-1}$ in Arabica coffee, whereas Franca et al. (2005) detected TTA values ranging from 198.42 and 237.64 mL NaOH (0.1 mol $L^{-1}$) 100 $g^{-1}$, in the same species. Many other data are available in the literature - mainly for Arabica - and there is reasonable consensus between the results. The variation observed is most likely explained by genetic diversity, geographic origin, maturity level of the fruits and/or by suboptimal bean storage conditions. TTA has been negatively correlated with ripening, meaning that unripe fruits have higher acid contents compared to ripe fruits (Koshiro, Jackson, Nagai, & Ashihara, 2015; Rodrigues et al., 2007).

The effect of acids on coffee quality is well known and there is little contradiction between results across the literature. A higher TTA is directly related to a lower brew quality (Barbosa et al., 2019; Kwon et al., 2015), but also the ratio between sucrose and TTA is considered a potential determinant of green bean quality. This has been proposed to be a potentially more accurate predictor than acidity level alone (Barbosa et al., 2019) and typically sucrose/TTA ratios for Arabica are between 3.7 and 8.1. However, there is still a lack of knowledge regarding the impact of individual molecules. Identifying the specific molecules involved should become a priority, especially regarding the negative impact of aliphatic acids – are these perhaps direct precursors of off-flavour molecules?

### 2.6. Green bean: amino acids and proteins

Relatively little research has been dedicated to the protein component of green coffee. Proteins account for ca. 13–16% of the bean dry weight (Table 1) and the majority are α- and β-legumin like storage proteins (Baú, Mazzafera, & Santoro, 2001). The remaining fraction includes enzymes, structural components, etc. From a sensory perspective, proteins are important as their amino acids are involved, together with free sugars, in Maillard reactions which occur during roasting and contribute to colour, aroma and flavour of coffee brews (Kitzberger, Scholz, Pereira, da Silva, & Benassi, 2016; Kitzberger et al., 2013). In addition, free amino acids and oligopeptides from protein degradation can participate in the Strecker degradation reactions during roasting leading to the formation of aldehydes (Rizzi, 2008). There are no indications that green beans of the two coffee species have clearly different overall protein contents or composition (Folstar, 1985; Franca et al., 2005). Overall protein content and a potential link with coffee quality has not received much attention. Barbosa et al. (2019) did report that a lower protein content was associated with higher quality although earlier, Franca et al. (2005) proposed the opposite. Consequently, as there are indications of a link between protein content and quality/sensory attributes, it would be valuable to re-address this in greater detail. Furthermore, we also know nothing regarding whether individual proteins or protein classes may be more influential than others on sensory impact.

The literature on free amino acid levels is more extensive. Arabica and Robusta differ in their total free amino acid content where Robusta has, on average, a higher level (ca. +21% dwb) compared to Arabica (Arnold, Ludwig, Kühn, & Möschwitzer, 1994). However qualitatively, the specific composition of the major and minor amino acids appears to be similar across the two species with a few exceptions such as glutamic acid and arginine (Arnold et al., 1994). These findings correlate well with the aforementioned difference in bean quality between Arabica and Robusta. As shown by Poisson et al. (2009), using a sophisticated method combining heavy isotope labelling with biomimetic spiking experiments in an “in green bean” approach, a higher total free amino acid content was seen to inhibit the production of certain flavour compounds such as 2-furaldehyde and other furanone derivatives during the roasting process. Other aroma compounds like diketones and compounds belonging to the alkylpyrazine family decreased in quantity in the absence of free amino acids, while 2-furfurylthiol (FFT) did not show any change as a result of total amino acid removal. However, when removal was only partial, no quantitative effect was seen except for 2-furaldehyde and other furanone derivates which increased. These results demonstrate that free amino acid levels can impact some flavour compounds and melanoidins which are linked to colour formation. However, too high concentrations can also be detrimental to final coffee quality.

Cysteine, one of the two S-containing amino acids, has been specifically linked to the appearance of sensory-relevant molecules. Addition of exogenous cysteine in the “in green bean” approach resulted in higher amounts of alkylpyrazines, diketones and FFT (Poisson et al., 2009).

However, free cysteine is naturally almost absent in beans (Arnold & Ludwig, 1996) which may suggest that cysteine derivatives, *e.g.* glutathione, or cysteine-rich-proteins may be the actual *in vivo* source of these flavour precursors, although other "S" sources cannot be excluded. In conclusion, while the importance of certain specific amino acids has been well researched, this is not the case for proteins. Considering the importance of proteins in the generation of Maillard products as well as being a storage unit for amino acids, more research is needed into the true importance of this class of compounds in final coffee bean quality.

## 3. The silverskin

The coffee silverskin is a thin integument surrounding the coffee bean which separates the true seed from the rest of the fruit (Fig. 1**A**). While it might seem relatively inconsequential, the silverskin has received considerable attention both in relation to its envisaged function within the fruit by influencing the chemical composition of the beans, as well as it being a potentially interesting biobased by-product of the coffee industry. Botanically, the silverskin originates from the perisperm, a storage tissue that atrophies during fruit maturation to produce a thin layer just a few cells thick. While for the initial steps of seed development its function is known, a biological and physiological role for the silverskin inside the ripe berry has not been demonstrated. The most accredited hypothesis refers to it being an outer protective layer of the green bean as its chemical composition might suggest (Bresciani, Calani, Bruni, Brighenti, & Del Rio, 2014; Narita & Inouye, 2012).

Silverskins are an important by-product of coffee roasting as ca. 75 kg is produced for each ton of roasted beans (Alves, Rodrigues, Antónia Nunes, Vinha, & Oliveira, 2017). With coffee farmers annually generating ca. 10 million tons of green beans (June 2020, International Coffee Organisation), this represents a significant bioresource for circularity goals. Silverskins are a rich source of phytochemicals such as (poly) phenolic compounds as well as caffeine and other alkaloids (Panusa, Zuorro, Lavecchia, Marrosu, & Petrucci, 2013; Regazzoni et al., 2016). Nevertheless, nowadays the silverskin component is usually discarded without being re-utilized. Many alternative uses have been proposed which vary from producing absorbent materials for the removal of potentially toxic metals from water, to providing input for biofuel production (Hijosa-Valsero, Garita-Cambronero, Paniagua-García, & Díez-Antolínez, 2018; Malara et al., 2018). Soil or livestock feed applications are unsuitable due to high levels of anti-nutritional compounds (Murthy & Madhava Naidu, 2012; Mussatto, Machado, Martins, & Teixeira, 2011). The most promising opportunity is potentially to use this material as biomass for the recovery of functional bioactives, such as phenolic or alkaloidal compounds which could be used in the cosmetic, food or pharmaceutical industries (Nzekoue et al., 2020; Wen, Zhang, Rai, Sun, & Tiwari, 2019).

Regarding the chemical composition of this tissue, the main classes of compounds detected are the same as those found in the green been (Tables 1 and 2) although not all classes have been investigated in such detail. However, it must be borne in mind that all the literature concerns roasted material and not dried/fresh tissue. Care must be taken on making direct comparisons, especially as key information is often lacking in publications where *e.g.*, it is not mentioned whether the beans were from Robusta or Arabica varieties, or which on-farm pre-processing method had been used.

### 3.1. Silverskin: alkaloids

As in beans, the main alkaloid in the silverskin is caffeine. Its level varies widely across the literature – more likely due to the use of different analytical protocols as well as the different origins of the analysed material. Levels range from 3.7 to 36.7 $mg{\cdot}g^{-1}$ (dwb) (Table 2). When comparing species, a significant and reliable difference has been detected with higher caffeine levels being present in Robusta (Panusa, Petrucci, Lavecchia, & Zuorro, 2017). The caffeine content in silverskin is essentially of the same order of magnitude as in the green bean. It has been claimed to be higher but again this may be a reflection of different methodologies and different extraction efficiencies being compared (Wen et al., 2019). Therefore, more precise, direct comparisons of specifically, fresh materials are needed for clarification. Few other alkaloids have been detected in silverskin and only in trace amounts (*e.g.* quinine) (Nzekoue et al., 2020). Other methylxanthines like theobromine and trigonelline, were not found although again, this is a likely consequence of using roasted material. In conclusion, knowledge of the alkaloid composition of silverskin is sparse, but what there is indicates differences with the other fruit tissues. Furthermore, differences between *C. arabica* and *C. canephora* are becoming evident and that interspecific differences are greater than those between tissues.

### 3.2. Silverskin: phenolic compounds

The phenolic composition of silverskin resembles that of green beans although roasting is particularly relevant here as the level of the roasting temperature influences the degree of phenolic compound degradation (Sulaiman, Moon, & Shibamoto, 2011). Accordingly, it is justifiable to conclude that silverskin material has a lower level of phenolic compounds compared to green beans which was found to vary between 0.42% and 3.6% (dwb) - roughly five times less than is typical of green beans (Tables 1 and 2) (Panusa et al., 2017). These authors were the first to compare Arabica and Robusta and equivalent to the green bean, *C. arabica* silverskin had ca. 50% lower levels of total phenolics compared to *C. canephora*. The most abundant compounds were again identified to be CGAs, with CQAs accounting for 78.5–96.8% (Bresciani et al., 2014; Nzekoue et al., 2020; Regazzoni et al., 2016; Wen et al., 2019). Furthermore, 5- and 3-CQA isomers are described as the major components, together comprising 23% of total phenolics (Bresciani et al., 2014). After CQAs, FQAs are the next main CGA components.

The presence of CQA lactones, which are common roasting products, was also demonstrated although the levels were less than predicted

**Table 2**
Concentration of the main constituents on Coffee Silverskin expressed in $mg{\cdot}g^{-1}$ sample (dry weight basis), according to different authors*.

| | *Caffeine* | *Total phenolics* | *Cgas* | *Carbohydrates* | *Reducing sugars* | *Proteins* | *Lipid soluble compounds* | *Ash* | *References* |
|---|---|---|---|---|---|---|---|---|---|
| *C. arabica* | | | | 621 | 2.1 | 186 | 22 | 70 | (Borrelli et al., 2004) |
| *C. arabica* | 4 | 22–36 | | 50–121 | 25–50 | 50–157 | | | (Narita & Inouye, 2012) |
| *C. arabica* | 10 | | 6 | | | | | | (Bresciani et al., 2014) |
| *C. arabica* | 32.7–36.7 | 5.8–6.4 | 5.8–6.4 | | | | | | (Wen et al., 2019) |
| *C. arabica* | 7.7–10.3 | | | | | | | | (Toschi, Cardenia, Bonaga, Mandrioli, & Rodriguez-Estrada, 2014) |
| *C. arabica* | 12.5 | | | | | | | | (Costa et al., 2018) |
| *C. arabica* | 10–35 | 4.2–5.6 | | | | | | | (Nzekoue et al., 2020) |
| *C. arabica* | 3.7 | 7.8 | 0.3 | | | | | | (Panusa et al., 2017) |
| *C. canephora* | 3.8 | 12.8 | 1.3 | | | | | | (Panusa et al., 2017) |

*Where a blank cell is displayed no data regarding that parameter where found in the corresponding article.

(Bresciani et al., 2014; Farah et al., 2006). Additional compounds from the hydroxycinnamate family have also been identified in trace amounts including a number of coumarylquinic acids (CoQAs) (Bresciani et al., 2014). In addition, unconjugated forms such as caffeic, ferulic and dimethoxycinnamic acids where identified by Panusa et al. (2017). Later, gallic, vanillic, syringic, p-coumaric, and trans-cinnamic acids were reported by Nzekoue et al. (2020). Tryptophane-conjugated phenolic acids, such as caffeoyl- and coumaroyltryptophan, the xanthone isogentisin, and the flavonoids rutin, quercetin, kaempferol, quercitin hyperoside, naringin and epicatechin were also found, typically at the $\mu g.g^{-1}$ level (Nzekoue et al., 2020).

Consequently, as for the green bean, a large variation in phenolic compounds has been reported in a few publications, but a few compounds dominate. The recent appearance of papers identifying new molecules not detected before, suggests that improved technologies are contributing greatly and we might predict that much is yet to be discovered. However, how the profiles actually look in fresh material is still a black box.

### 3.3. Silverskin: carbohydrates

Information on carbohydrates is limited and the data referred to in this section concern analyses mainly conducted on *C. arabica* (Borrelli, Esposito, Napolitano, Ritieni, & Fogliano, 2004; Bresciani et al., 2014) and only sporadically on Robusta (Alghooneh, Mohammad Amini, Behrouzian, & Razavi, 2017) or on silverskin mixtures of both types (Wen et al., 2019). Carbohydrates and more precisely, the polysaccharides, are the major components of the silverskin and account for $\leq$62% of the total dry weight (Table 2). The polysaccharide fraction is most likely mainly composed of galactomannans and arabinogalactans (Borrelli et al., 2004; Nunes & Coimbra, 2002b, 2002a). However, real evidence has yet to be provided. Pectins, inulins and oligofructans have also been identified as members of the soluble carbohydrate fraction and cellulose and hemicellulose were detected in the insoluble fraction, together with lignin (Borrelli et al., 2004). The high polysaccharide/fibre content of this tissue again suggests that silverskin mainly has a protective function. As for the less complex molecules, the levels of free reducing sugars and monosaccharides were not significantly different from those of the green bean, being ca. 0.2% (dwb) equivalent to 2 $mg{\cdot}g^{-1}$ (Borrelli et al., 2004; Bresciani et al., 2014; Pourfarzad, Mahdavian-Mehr, & Sedaghat, 2013; Wen et al., 2019).

### 3.4. Silverskin: lipid soluble compounds

In Arabica, the lipid fraction accounts overall for ca. 2% (dwb) or 20 $mg{\cdot}g^{-1}$ (Table 2), eight fold lower than is typical for the green bean (Panusa et al., 2017; Pourfarzad et al., 2013; Wen et al., 2019). Essentially all other information available, and more precisely, on the diterpenoids and their derivatives comes from a single paper (Panusa et al., 2017) which was the first to report atractyligenins and furokauranes in silverskins. These diterpenoids and their glycosides have been described as bitter-tasting. They likely have a protective function and may substitute for caffeine in some wild coffee species (Prewo, Guggisberg, Lorenzi-Riatsch, Baumann, & Wettstein-Bättig, 1990). Two different furokauranes glycosides were found and have been tentatively assigned as mozambioside and mascaroside. In contrast, many (ca. 12) distinct atractyligenins were detected but, due to lack of standards, none could be definitively identified. Nevertheless, clear qualitative and quantitative differences in abundance and presence of different atractyligenins between green beans and silverskins was clear, suggesting a tissue-specific chemical composition presumably related to a specific function. Furokauranes are more abundant in silverskin as compared to green beans, and higher concentrations were detected in Arabica than in Robusta. Atractyligenin levels were also higher in Arabica (Panusa et al., 2017).

### 3.5. Silverskin: other compounds

Due to lack of available information on other classes of molecules, the remaining findings can be summarized as follows: ash content was higher in silverskins than in green beans (Table 1 and 2) suggesting a higher C and/or mineral content. This may be related to the previously hypothesized protection function or to a storage role (Borrelli et al., 2004; Bresciani et al., 2014; Pourfarzad et al., 2013; Wen et al., 2019). The silverskin protein content was also high but comparable to levels in the green bean (Borrelli et al., 2004; Bresciani et al., 2014; Pourfarzad et al., 2013; Wen et al., 2019).

## 4. The pericarp

The pericarp, on drying is also known as the coffee husk. Anatomically, as shown in Fig. 1**A**, the pericarp comprises multiple tissues, from outside to inside: the exocarp, mesocarp and endocarp, often referred to as skin, pulp and parchment respectively. The most abundant of these three tissues is the pulp, comprising 30–40% of the whole fruit dry weight at maturity (Aristizábal-Marulanda, Chacón-Perez, Cardona Alzate, & Alzate, 2017; Bakker, 2013; Heeger, Kosińska-Cagnazzo, Cantergiani, & Andlauer, 2017). During coffee processing, the pericarp must first be removed using a dry, wet or semi-dry process as briefly discussed in Section 1.1. This produces ca. 0.8–1 ton of fruit waste for each ton of isolated green beans (Saenger, Hartge, Werther, Ogada, & Siagi, 2001). Pulp is the major by-product of the coffee industry (Murthy & Madhava Naidu, 2012) and has gained increasing interest in recent years, for having potential application as a biobased resource. Recent publications have proposed multiple opportunities to exploit this organic waste *e.g.* as a fertilizer, compost, fuel and livestock feed. Use as a substrate for mushroom cultivation has been suggested and tested (Heeger et al., 2017; Rodríguez-Durán et al., 2014; Torres-Valenzuela, Ballesteros-Gómez, & Rubio, 2020). However, the relatively high caffeine and phenolic contents can have a negative impact on the environment (Torres-Valenzuela et al., 2020) and currently limits application. The most promising use concerns the recovery of high value bioactives as a first step. Subsequently, the remaining organic matter can be used for the originally intended purposes with limited negative environmental impact (Rodríguez-Durán et al., 2014). The bioactive compounds obtained have potentially multiple applications in the food, pharmaceutical and cosmetic industries and are currently being investigated (Alves et al., 2017; Belščak-Cvitanovic & Komes, 2017; Janissen & Huynh, 2018). Literature on the berry pericarp is still limited compared to the green bean but is quickly increasing due to the growing chemical industry interest in biobased opportunities and indeed, the general desire of the coffee industry to become more sustainable.

### 4.1. The pericarp: alkaloids

Caffeine, theobromine, trigonelline and a number of other yet unidentified minor mono-methylxanthines and xanthine have been detected in coffee pericarp (Heeger et al., 2017; Koshiro, Zheng, Wang, Nagai, & Ashihara, 2006; Pandey et al., 2000; Torres-Valenzuela et al., 2020). The most abundant alkaloid is again caffeine, which has a concentration varying from 0.3 and 13 $mg{\cdot}g^{-1}$ (dwb), with no significant differences being observed between Arabica and Robusta (Table 3). The overall caffeine content is similar to that in the green bean (Tables 1 and 3). However, Koshiro et al. (2006) (not included in Table 3 as they used a different way of measurement), reported that in all analysed samples, 70–80% of the alkaloid was found in seed and 20–30% in pulp. Furthermore, a higher caffeine biosynthetic activity was also detected in the seed compared to the pulp. Potentially, these inconsistencies relate to the use of materials with distinctly different geographical origins and different extraction and analysis protocols. This calls for more detailed analysis and indeed for standardized protocols, in order to allow better comparison between results coming from different laboratories as well

**Table 3**
Concentration of the main constituents on Coffee Husk expressed in mg·g$^{-1}$ sample (dry weight basis), according to different authors*.

| | Caffeine | Trigonelline | Total phenolics | CGAs | Carbohydrates | | | Proteins | Lipid soluble compounds | References |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Total | Sucrose | Reducing sugars | | | |
| Not specified | 0.3–3.6 | 0.1 | | | | | | | | (Torres-Valenzuela et al., 2020) |
| Blend | 13 | | 10–14 | | 650–702 | | | 92–120 | 20–25 | (Pandey et al., 2000) |
| C. arabica | 13 | | | | 330–460 | | 124 | 90–110 | 20–170 | (Woiciechowski et al., 2000) |
| C. arabica | | | | | | 125–140 | 270–290 | | | (Geromel et al., 2006) |
| C. arabica | 6.5–6.8 | | 4.9–9.2 | | | | | | | (Heeger et al., 2017) |
| C. arabica | | | 2.96–6.49 | 2.34–5.90 | | | | | | (Rodríguez-Durán et al., 2014) |
| C. arabica | | | 3.6–27.0 | | | | | | | (Labat, Augur, Rio, Perraud-Gaimé, & Sayadi, 2000) |
| C. arabica | | | 2.5–4.5 | | | | | | | (Delgado et al., 2019) |
| C. arabica | | | 37 | | | | | | | (Ramirez-Coronel et al., 2004) |

*Where a blank cell is displayed no data regarding that parameter were found in the corresponding article.

as providing a proper set of meta-data for full evaluation.

The second most abundant alkaloid is again trigonelline, which has a concentration of ca. 0.1 mg·g$^{-1}$ (dwb) (Torres-Valenzuela et al., 2020). Interestingly Koshiro et al. (2006) reported that trigonelline biosynthetic activity is much higher in the pericarp than in the seed, even though its accumulation in the former is 10 to 100 times lower. It has therefore been hypothesised that after synthesis, this alkaloid is transported from the pericarp into the seed. There is no further information available on the rest of the detected alkaloids but this is likely to change quickly as biobased approaches, likely needing more detailed analyses of compounds actually present in pericarp waste, develop.

### 4.2. The pericarp: phenolic compounds

Even if the total amount of phenolic and polyphenolic compounds is relatively low, ranging between 2.5 mg·g$^{-1}$ and 37 mg·g$^{-1}$ tissue (dwb), this class of compounds is the most studied (Table 3). This is primarily due to their multiple envisaged applications as food, cosmetic and pharmaceutical ingredients. Regarding total phenolics, the value reported by Ramirez-Coronel et al. (2004) is a factor ca. 10 higher than most others reported. This difference appears to be due to the unique use of a particular extraction and sample preparation methodology based on thiolysis. This class of compounds in the pericarp is represented by five sub-groups: flavan-3-ols, hydroxycinnamic acids (HCAs), flavonols, anthocyanidins and simple phenols (Heeger et al., 2017; Ramirez-Coronel et al., 2004; Rodríguez-Durán et al., 2014). Of these, the flavan-3-ols and HCAs are most abundant, in roughly equal proportions. Together they represent 80 to 98% (dwb) of all phenolic compounds in coffee pulp.

Looking at the individual constituents, similar to green bean and silverskin, 5-CQA was the compound found at the highest concentration, followed by protocatechuic acid and gallic acid (Heeger et al., 2017; Rodríguez-Durán et al., 2014; Torres-Valenzuela et al., 2020). Almost the complete range of CGAs described in the green bean has also been reported for the pericarp, including many in the HCA family. Regarding flavan-3-ols, monomeric catechins (epicatechin, catechin) and proanthocyanidins (or condensed tannins) as well as protocatechuic acid and rutin have all been identified (Delgado, Arbelaez, & Rojano, 2019; Heeger et al., 2017; Pandey et al., 2000; Rodríguez-Durán et al., 2014). Flavonols, anthocyanins and other phenolics were much less prevalent. Cyanidin 3-*O*-rutinoside was the most abundant anthocyanin representing almost 80%, followed by cyanidin 3-glycoside (Prata & Oliveira, 2007). For the simple phenolic acids, caffeic, gallic, coumaric and ferulic acids were most regularly detected (Delgado et al., 2019; Heeger et al., 2017; Rodríguez-Durán et al., 2014).

Research has focused not only on the characterization of all the different compounds present and on their quantification, but also on where and how they were detected. Simple phenols were mainly found in the soluble fraction, although a small proportion of the ferulic and coumaric acids was present in the insoluble fraction (Rodríguez-Durán et al., 2014). Most polyphenolic compounds appeared covalently bound to the cell wall (Rodríguez-Durán et al., 2014). A function as defence molecules has been proposed, but it has also been hypothesised that they may act as a barrier to prevent caffeine diffusing outside the cells. The one clear qualitative difference to other tissues concerns the anthocyanins. These are typical pericarp compounds, present at highest concentrations in the outer layers of the red berry (Koshiro et al., 2007). Ripening coffee berries are often typified by developing dark red colours especially on the sun exposed sides. This correlates to a proposed physiological function of these pigments as being protective compounds by absorbing UV radiation, next to their signalling function to birds upon ripening (Pervaiz, Songtao, Faghihi, Haider, & Fang, 2017).

All the above findings refer specifically to *C. arabica*. Hardly any studies have looked into the differences in pericarp chemistry between Arabica and Robusta varieties. Potentially *C. canephora* has a higher phenolic and polyphenolic content but evidence is limited

(Koshiro et al., 2007; Rodríguez-Durán et al., 2014). One observation was that the C-glucosyl-xanthone, mangiferin, was detected in the Arabica exocarp and mesocarp but not in the endocarp and was not detected at all in Robusta (Campa et al., 2012).

In conclusion, once again there are remarkable contradictions or inconsistencies in the published data. A particular issue for the pulp is that this has often been analysed after processing (*i.e.* as a waste product) rather than as fresh material directly removed from the berries under controlled conditions. During (mechanical) pulp removal, fruit metabolites can readily undergo multiple enzymic and non-enzymic conversions involving *e.g.* (per)oxidation and deglycosylation, and fermentation reactions, with significant qualitative and quantitative chemical changes as a consequence (Heeger et al., 2017). A striking example here concerns the anthocyanins: there is clear agreement concerning their presence in the berry skin. However, only a few papers have quantified this reliably. These molecules are particularly susceptible to pH, temperature, oxidizing agents and enzymatic deglycosylation, and can quickly become undetectable in their native form when conditions are suboptimal (Prata & Oliveira, 2007).

### 4.3. The pericarp: carbohydrates

Depending on the analysis method, the total carbohydrate content is seen to vary between 40% and 60% (dwb) (Table 3) (Pandey et al., 2000; Pleissner et al., 2016; Woiciechowski, Pandey, Machado, Cardoso, & Soccol, 2000). Again, this large variation may be analytically related as well as depending on coffee variety and exact maturation stage. Of the total carbohydrates detected in mature berry pulp, fibres (mainly lignin, cellulose, hemicellulose) represent ca. 20% of the total husk dry weight, and pectins ca. 6.5% (dwb). The remaining carbohydrate fraction is made up of reducing sugars and sucrose, that, at berry maturity, can reach up to 280 $mg{\cdot}g^{-1}$ and 180 $mg{\cdot}g^{-1}$ (dwb), respectively, equal to 28% and 18% (dwb) (Geromel et al., 2006). Despite their important physiological role, no other information was found for this class of compounds.

### 4.4. The pericarp: lipid soluble compounds

The content of lipid soluble compounds in pulp is low compared to the green bean. Even though the content may vary a lot depending on the 'terroir' (see Section 6) and on the genotype, the concentration of lipid soluble compounds was generally found to be around 2–2.5% of the total pericarp dry weight (Table 3), with a few cases reporting a much higher level of 17% (Table 3) (Pandey et al., 2000; Woiciechowski et al., 2000). Ruesgas-Ramón et al. (2019) were the first to investigate in more detail certain specific compounds such as α-linolenic acid (ALA) and some ALA peroxidation derivatives (isoprostanes), and phytoprostanes (PhytoPs) and phytofuranes (PhytoFs). ALA level was revealed to be 160.7 $mg{\cdot}g^{-1}$ (dwb) (Ruesgas-Ramón et al., 2019) and PhytoPs were more abundant than PhytoFs (654.6 vs 543.2 $ng{\cdot}g^{-1}$ (dwb), respectively). Using a Micro-LC-QTRAP untargeted approach, Ent-16-F1t-PhytoP, 16-epi-16-F1t-PhytoP, 9-F1t-PhytoP, 9-epi-9-F1t-PhytoP, Ent-16-B1t-PhytoP, Ent-9-L1t-PhytoP, Ent-16(RS)-9-epi-ST-Δ14-10-PhytoF, Ent-9(RS)-12-epi-ST-Δ10-13-PhytoF, Ent-16(RS)-13-epi-ST-Δ14-9-PhytoF were additional isoprostanoids identified in coffee pericarp (Ruesgas-Ramón et al., 2019). Even though PhytoP levels appear quite low, it has been proposed that these are likely to be underestimated for analytical reasons. These molecules are usually associated with oxidative stress and their presence is used as an indicator of the level of stress resulting *e.g.* from cell injury (Cuyamendous et al., 2016; Imbusch & Mueller, 2000). It is not yet clear if the coffee processing steps used may have played an overly-influential role in the observed profiles of these (per)oxidation-derived compounds.

### 4.5. The pericarp: other compounds

Pericarp proteins and organic acids have practically been ignored. A few analyses report a protein content estimated to be 10–20% of the pericarp dry weight, whereas no estimates for the organic acids have been reported (Pandey et al., 2000; Pleissner et al., 2016; Woiciechowski et al., 2000). It has been reported that pulp resulting from processing is relatively acidic (Murthy & Madhava Naidu, 2012) although it is not clear if this is related to processes linked to spontaneous fermentation, bio-degradation and oxidation or if it is indeed an intrinsic feature of fresh berry tissue. The former is perhaps more likely with wet processing methods considering pulp fermentation usually takes up to 36 h for Arabica and 72 h for Robusta.

## 5. The potential influence of berry ripening stage on green bean chemistry

### 5.1. Berry development and ripening

Coffee berry composition is not constant. Next to important basic differences due to tissue type and genotype as described above, fruit ripening, and especially the exact moment of harvest, is of particular importance. Furthermore, how the collected fruits and beans are subsequently stored (in terms of humidity, temperature, duration, aeration etc) as well as the processing strategy used on-farm have also been identified as having significant impact on green bean chemistry. In this section we cover these developmental and post-harvest influencers and in the subsequent section we cover the other environmental component of importance – the 'terroir' on coffee production. Except when mentioned otherwise, the results described concern material of *C. arabica* as nearly all research has been performed using this species. Our knowledge of *C canephora* in this context is considerably limited. Most investigations have worked with whole fruits rather than individual tissues as it is difficult to isolate individual tissues from fruit at the younger stages. Some developmental effects may also be linked to environmental influences such as temperature fluctuation where *e.g.* higher altitudes/lower temperatures may result in a higher proportion of underdeveloped fruits and hence a lower quality as drawn attention to by Ribeiro et al. (2016).

### 5.2. Berry alkaloids

Studies on alkaloid composition during fruit ripening are scarce and limited to caffeine and trigonelline. Even if the final concentration of these two molecules, and their site of biosynthesis are different, their overall behaviour during development is largely similar (Koshiro et al., 2006). Both are already present in fruit primordia and in very young fruits, but at a low concentration (Smrke, Kroslakova, Gloess, & Yeretzian, 2015). Soon after, biosynthesis increases leading to higher concentrations during the intermediary growth stages while, at the later stages, synthesis dramatically slows down, even though the total levels of both alkaloids continue to increase slightly (De Castro & Marraccini, 2006; Smrke et al., 2015). This pattern of alkaloid production has been linked to the proposed main physiological role these compounds: protection against environmental threats (Eira et al., 2006). Once the alkaloids are produced, there seems to be little catabolism even on maturation. The presence of alkaloids in the ripe berry has led to the conclusion that these compounds likely also fulfil other functions in fresh coffee tissues - such as trigonelline being an NAD reserve compound for use during germination (De Castro & Marraccini, (2006) and Eira et al. (2006)).

### 5.3. Berry phenolic compounds

The total content of phenolic compounds, after increasing during the early stages of fruit development, is found to decrease significantly

during fruit ripening (Barbosa et al., 2019; Cheng et al., 2019). Qualitative shifts are observed and such changes are typical of fruits of diverse species such as raspberry and capsicum (Beekwilder et al., 2005; Estrada, Bernal, Díaz, Pomar, & Merino, 2000) where again it is considered that phenolics have an early role as protection/anti-grazing agents. This entails they have to be removed in order to ready the fruits to be eaten by birds and animals for effective seed dispersal. In addition, other phenolic and polyphenolic compounds have been identified as germination inhibitors and these would need to decrease as the seeds become ready for dispersal (Marambe, Ando, & Marambe, 1992). However, even though the major trend is an overall quantitative decrease in phenolic content, qualitative differences between individual compounds can change across the developmental stages. FQAs are the predominant CGAs in young berries but as these develop further, CQAs become predominant (Bertrand et al., 2003; Garrett et al., 2016; Koshiro et al., 2007). However, insights into the complexity and non-uniform distribution occurring in the seed and in the other berry tissues are limited. Quinic acid, a CGA component, had a high, but stable, level in the perisperm, and later on also in silverskin (Garrett et al., 2016; Koshiro et al., 2007). However, other authors report that its presence actually decreases with maturation (Bertrand et al., 2003; De Castro & Marraccini, 2006).

### 5.4. Berry carbohydrates

Berry carbohydrate composition and distribution starts relatively uniformly but soon becomes more tissue-specific as the different tissues become more functionally specialised. In the young berry, cellulose, arabinogalactans and pectins, to a lesser extent, represent almost the entire carbohydrate component and are mainly present in the cell wall (Garrett et al., 2016; Redgwell & Fischer, 2006). The simpler mono- and disaccharides are also present at lower concentrations and are located within the cells (Caporaso et al., 2018; Casal, Oliveira, Alves, & Ferreira, 2000). During development, storage tissues such as the perisperm and endosperm (in the seed), arabinogalactans and cellulose are substituted by mannans (Redgwell & Fischer, 2006). At the same time, the pectin content, in both the pericarp and the bean, drops dramatically but there is no evidence of its replacement by other polysaccharides. Cell wall carbohydrate composition during ripening varies significantly, both quantitatively and qualitatively (Caporaso et al., 2018; Clarke & Vitzthum, 2008), reflecting the physiological changes taking place during seed and fruit development. Particularly for the carbohydrates, the role of ethylene is considered of importance as coffee berries are climacteric fruits as discussed by Pereira, Galvão, Kobayashi, Cacao, & Vieira (2005). In the seed, for the simpler mono- and disaccharides, sucrose remains predominant over glucose and fructose regardless of the stage of development. However, in the pericarp glucose and fructose are prevalent early on (Fig. 2) but appear to be replaced by sucrose in mature seeds (Garrett et al., 2016; Geromel et al., 2006). The total polysaccharide content in the pericarp tends to remain constant during maturation but does show some decrease during the final phases of ripening. This is likely due to the degradation of the cell walls during fruit softening in preparation for eating and seed dispersal (Garrett et al., 2016). No particular trend was described during berry development for other sugars such as mannitol, raffinose and stachyose. These seem to remain constant but have been seen to vary due more to environmental or genetic factors than physiological ones (Caporaso et al., 2018).

### 5.5. Berry organic acids

Acidity is considered as a negative trait for coffee quality and as is often also seen for other fruits, organic acids are seen to decrease with coffee berry maturation (Barbosa et al., 2019). Individual compounds often behave differently, making functional interpretation difficult. It has been proposed that it is better to look at the sucrose/total acid ratio as a way to follow the behaviour of this class of compounds in order to reduce some variation caused by environmental and genetic factors (Barbosa et al., 2019). Results from this approach are more uniform and give less fluctuation and suggest that the sucrose/acid ratio increases during ripening likely relating to a simultaneous increase in sucrose mainly in the pericarp with a decrease in acid content.

### 5.6. Berry proteins

No evidence was found showing protein content changes in the coffee berry during development, even though its composition is known to vary considerably (Alves et al., 2016; Bandil et al., 2013; De Castro & Marraccini, 2006; Joët et al., 2009; Montavon, Duruz, Rumo, & Pratz, 2003; Salmona et al., 2008). The most abundant proteins in ripe fruit are globulins and their presence in young fruit is low. Biosynthesis does start at the earliest developmental stages and is mainly associated with the perisperm, but its accumulation occurs mainly in endosperm and is completed only in ripe fruits when the perisperm atrophies (Alves et al., 2016). Perturbations in individual protein classes likely show direct functional relationships to the physiological status of the different developmental stages. For example, in young fruits chitinases and β-tubulin were highly present and are known to be associated with cell division, expansion and microtubule formation (Alves et al., 2016; De Castro & Marraccini, 2006; Montavon et al., 2003). Later, during maturation these enzymes almost disappear and others appear such as polyphenol oxidases and laccases, needed for protection against ROS and other oxidative stresses caused by (a)biotic stresses (Alves et al.,

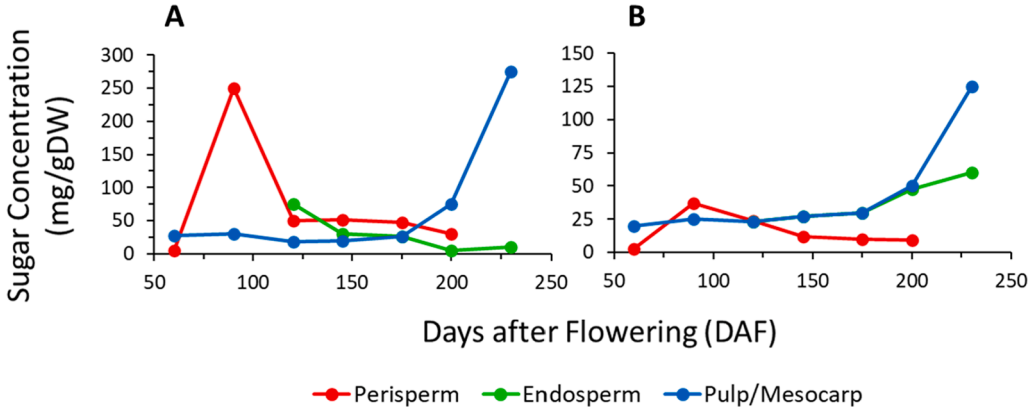


**Fig. 2.** Changes in carbohydrate composition in different fruit tissues of green Arabica coffee berries following anthesis: Perisperm (Red); Endosperm (Green), Pulp/Mesocarp (Blue) values for (A) Reducing sugars and (B) sucrose. Reproduced with permission from Geromel et al. (2006). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2016; Turlapati, Kim, Davin, & Lewis, 2011). Information on free amino acid content during coffee fruit development appears absent.

### 5.7. Berry: other compounds

No literature was found on the relationship between berry ripening and lipid soluble compounds. For volatile compounds including various alcohols, ketones, aldehydes and esters, Kulapichitr et al. (2017) were able to show clear differences between green beans from ripe and unripe berries from the same Arabica plantation in Thailand.

In conclusion, coffee berry chemistry is dynamic during fruit development with changes at the final stages of ripening being particularly important. This emphasises how influential the exact stage of fruit ripening can be on the biochemical composition of the harvested material be it for beverage production (beans) or for biomass applications (pulp, silverskin).

## 6. The impact of post-harvest processing on berry chemistry

After harvesting, ripe coffee berries undergo a number of treatment steps, firstly on the farm and later during transportation and storage before delivery to the factory. Depending on regionality and local cultural practice, berry treatments can follow three contrasting procedures referred to as: dry, semi-dry (or semi-wet) and wet processing. The first involves sun-drying of the bulk harvested fruits, which are usually laid out on tables or on the ground, before the separation of the seeds from the dried pericarp (Esquivel & Jiménez, 2012). This procedure is also called 'natural', because this is the traditional procedure used since ancient times. In strong contrast, wet processing involves mechanically dehulling most of the pericarp (pulp) from the ripe berries after which the remainder is fermented in water at ambient temperature for 24–36 h in the case of Arabica, or up to 72 h for Robusta. Any remaining pericarp residue can then easily be mechanically removed from the beans, which are then usually again dried in the sun before packaging and transportation (Murthy & Madhava Naidu, 2012; Pandey et al., 2000). The third, semi-dry (or semi-wet) method falls between the previously-mentioned procedures. As with wet processing, berries are separated by hand or using water and are then mechanically dehulled but are then not exposed to further fermentation before sun-drying (Montavon et al., 2003). In recent years it has become increasingly evident that differences in post-harvest methods can significantly impact final brew quality (Ribeiro et al., 2016). Beshah, Kitaw, Tirufat, & Dejene, (2013) even state that the uncompetitive prices and poorer quality of Ethiopian coffees is primarily due to the sub-optimal harvesting and on-farm processing practices commonly used. The literature mainly covers comparisons between dry processing and wet processing. The semi-dry procedure has generally been ignored but is also much less applied. A thorough review of the impact of post-harvest processing has already been provided by de Melo Pereira et al. (2019), specifically related to volatiles, so here we shall concentrate on key papers making specific links to green bean chemistry.

A higher coffee quality can be obtained when beans are processed using the wet procedure, but no clear link with seed chemistry could be highlighted (Da Silva, Toorop, Van Aelst, & Hilhorst, 2004). However, it was proposed that this effect was driven mainly by the starting material used. In wet processing often only the mature homogeneous berries are selected and used, whereas dry processing generally involves the whole harvest – a mixture of unripe, ripe and over-ripe fruits. This pre-selection of beans may result in a more uniform product after wet processing. Coffee displaying off-flavours following dry processing is believed to linked to the inclusion of over- and under-ripe fruits (Bytof et al., 2007; Da Silva Taveira et al., 2014). Nevertheless, Figueroa Campos, Sagu Tchewonpi, Saravia Celis, & Rawel, (2020) later showed that the wet processing phase itself significantly alters the sucrose, phenolic and amino acid levels in Arabica green beans and this may have a direct impact on cup quality.

Research comparing treatments using the same initial materials and performed specifically to test the different processing methods, has demonstrated that the processing method itself does impact bean chemistry and subsequent quality. For example, beans obtained from the dry processing method outperformed those from the wet processing method (Bytof et al., 2007; Ribeiro et al., 2016; Selmar & Bytof, 2007). Here also, certain biochemical traits could be correlated to quality: dry processed beans generally had higher sucrose levels, lower trigonelline and 3-CQA contents as compared to wet processed beans (Caporaso et al., 2018; Ribeiro et al., 2016). The effect on sucrose levels is considered to be of particular significance (Ribeiro et al., 2016). In addition, alkaloids, carbohydrates and phenolic compounds, as well as amino acids were also influenced by the different processing procedures (Bytof, Knopp, Schieberle, Teutsch, & Selmar, 2005; Selmar, Bytof, & Knopp, 2001). However, for these compounds, while the total content appeared stable, qualitative differences between individual compounds were evident (Casal, Oliveira, Alves, & Ferreira, 2001; De Castro & Marraccini, 2006). Duarte, Pereira, & Farah, (2010) in a rare direct comparison between wet and semi-dry processing methods, also reported significant differences in sucrose, alkaloids and chlorogenic acids although unfortunately these green beans were not subsequently tested for sensory differences. Such qualitative perturbations can of course have significant sensory impact if they concern (the precursors of) flavour/aroma molecules. Consequently, despite the small number of analyses performed to date, it is clear that the choice of berry processing method does influence a broad spectrum of chemical families in the green beans. This was particularly evident from some preliminary work reported by De Vos et al. (2007) who used untargeted metabolomics to follow the biochemical changes occurring during the dry processing procedure. Here it became clear that both qualitative and quantitative shifts in metabolic profile typify beans at different stages during the drying process.

There are of course exceptions – (Rodriguez, Guzman, & Hernandez, 2020), using a speciality Columbian coffee reported that while dry, wet and semi-dry methods did influence *e.g.* caffeine level, other chemical parameters and sensory scores appeared unaffected suggesting that the method of processing is irrelevant to quality. The influence of this step was previously recognised (Lee, Cheong, Curran, Yu, & Liu, 2015) and as a result, work started into determining if we can better understand the dynamics of the fermentation processes involved in wet processing (De Bruyn et al., 2017; Zhang, De Bruyn, Pothakos, Contreras, et al., 2019; Zhang, De Bruyn, Pothakos, Torres, et al., 2019). Furthermore, there is a strong desire to gain greater influence over this step – for example through the use of more specific (controlled) fermentation conditions. The use of microbial starter cultures has been considered to replace or supplement the natural microbial communities traditionally used. Here, the specific aim is to direct the fermentation process deliberately, make this more uniform and the outcome more predictable in order to be able to deliver coffee beans with enhanced sensorial quality (Haile & Kang, 2019; Wang, Sun, Lassabliere, Yu, & Liu, 2020). Also, the length of the fermentation step (which regularly varies from farm to farm and between harvest times) has been demonstrated to influence green bean composition with longer fermentation times being associated with a fruitier and more acidic cup.

The potential impact of the storage conditions of the dried green beans should also not be under-estimated (Rendón, Salva, & Bragagnolo, 2014). Decreases in key components such as fatty acids and certain phenolic compounds have been observed with increased storage time, and these changes have been associated with oxidative processes. Oxidation of fatty acids has long been known to be related to the appearance of off-flavours in foods (Frankel, 1980). Such post-harvest deviations observed in the biochemical composition of coffee beans following different processing and storage treatments have been reported to be explained by perturbations in (living) seed physiology and metabolism (Knopp, Bytof, & Selmar, 2006; Ribeiro et al., 2016). Coffee seeds are considered to have an intermediate behaviour between

recalcitrant and orthodox seeds and after harvesting are still metabolically active. During wet processing, due to pulping and high-water availability, the embryo may be exposed to environmental conditions which are commensurate to the induction of germination, and hence, germination-associated metabolism (Knopp et al., 2006; Selmar & Bytof, 2007; de Melo Pereira et al., 2019). This has also nicely been illustrated by Bytof et al. (2007) who looked at parameters related to the onset of cell division in beans subjected to the two most contrasting processing methods. They revealed that clear differences arose during the processing of beans via the wet and dry methods (Fig. 3). It is well known that germination initiates a paradigm shift in seed metabolism: "Green coffee is alive!" (Selmar & Bytof, 2007) and hence it can be anticipated that wet and dry processed seed will have contrasting metabolic profiles. During dry processing fewer chemical changes might be anticipated as both the pericarp and the seed undergo a continuous dehydration phase. Nevertheless, even their composition is not 'frozen' in time and chemical shifts during drying clearly do occur (De Vos et al., 2007). Furthermore, dry processing generally takes significantly longer. Once again, the specific conditions 'on-farm' at the time of harvest and the parameters of drying will have considerable impact on final green bean composition and can also represent an additional source of variation in green bean quality.

## 7. The influence of geographical location: Is there a coffee terrior?

For wine grape production it is well known that, next to the grape variety, the specific environmental conditions in the area of cultivation is of huge importance to the quality of the final product (Anesi et al., 2015). These conditions relate to many interacting factors such as soil type, drainage, rainfall, temperature fluctuations, direction of the sun, the farmer practices etc. The impact of genotype × environment is of prime importance as the right choice of variety to match a specific location is key to successful production. This phenomenon has become known as the 'terroir-effect'. Effectively, the same is also true for coffee where key environmental factors - including those already mentioned above - but for coffee also altitude is of particular significance to success. This section gives a brief overview of some of the key environmental factors known to influence green bean quality.

### 7.1. Altitude of cultivation

The influence of plantation altitude is perhaps the most studied environmental factor. The elevation at which coffee plantations are located has direct influence on average temperatures, humidity, radiation and many other environmental factors which influence both tree characteristics and fruit composition (Avelino, Barboza, Davrieux, &

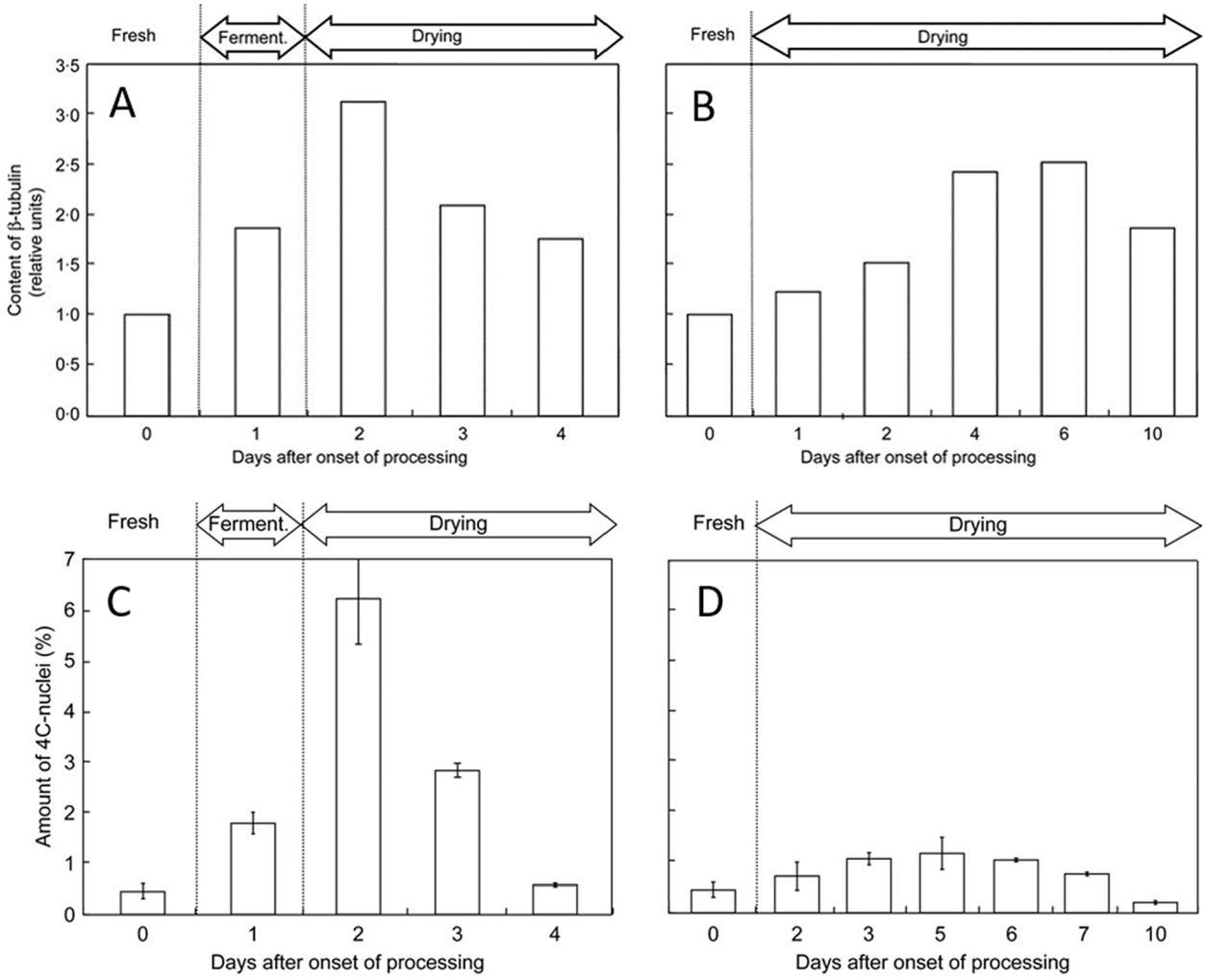


**Fig. 3.** Evidence of differences in the initiation of germination processes in green Arabica coffee beans processed by the wet processing method (Left, A and C) or the dry processing method (Right, B and D). Changes in b-tubulin levels (Upper, A and B) and in the occurrence of 4C nuclei (Lower, C and D) – both indicators of cell division activity - are given. (Modified and reproduced with permission from Bytof et al. (2007).

Guyot, 2007; Bertrand et al., 2006; Vaast et al., 2005). A cooler climate, associated with a higher altitude is considered the main driver of compositional variation in coffee berries (Bertrand et al., 2012, 2006; DaMatta & Ramalho, 2006). This relationship between elevation and chemical composition of berries has even led to the general consensus that superior bean quality is associated with trees cultivated at higher altitudes (Heeger et al., 2017; Worku, de Meulenaer, Duchateau, & Boeckx, 2018). Ribeiro et al. (2016) carried out one of the most detailed studies and concluded that the Arabica variety Yellow Burbon, when cultivated $>$ 1200 m, as compared to $\leq$ 1000 m, had higher levels of trigonelline and 3-CGA in green beans which subsequently appeared to be linked to a higher sensorial quality of the final beverage. The physiology behind this is not understood but it may be that at lower average temperatures, fruit/bean maturation time is longer which in turn may allow the fruits to produce and accumulate more sensory and quality-relevant metabolites (Muschler, 2001). The generally larger temperature differences between day and night at higher altitudes may also be influential.

Sucrose concentration and total acidity in coffee berries seem to increase in coffee plantations located at higher altitudes (Vaast et al., 2005; Worku et al., 2018). Lipid soluble compounds followed the same pattern, but there is a general lack of knowledge on which subclasses of molecules are linked to this variation (Bertrand et al., 2006; Decazy et al., 2003). Nevertheless, despite some clear associations there is still much inconsistency in other results. Some researchers observed increased CGAs and alkaloids (*e.g.* caffeine and trigonelline) at higher altitudes (Avelino et al., 2007; Sridevi & Giridhar, 2013) whereas others highlighted the opposite trend (Tolessa, D'heer, Duchateau, & Boeckx, 2017; Worku et al., 2018). Gebrekidan et al. (2019) found only a weak positive correlation between caffeine and trigonelline content and altitude in Ethiopian coffee beans although the species used is not mentioned. These contradicting results may suggest that the altitude effect on coffee berry biochemical composition has not properly been elucidated and that other local growing conditions as well as cultivar are also of importance in a typical genotype $\times$ environment effect. Most of the research mentioned here was done using *C. arabica*, but the information on the cultivars and the provenance of the materials used was often quite disparate.

### 7.2. Rainfall and drought

Water availability and drought stress is currently a major issue in coffee cultivation and in poor seasons can result in up to 80% yield loss (DaMatta & Ramalho, 2006). Opportunities for irrigation are also often limited or non-existent in coffee growing areas. This problem is likely to become even more serious in the near future as a result of global warming (Melke & Fetene, 2014). It has been proposed (Pinheiro, DaMatta, Chaves, Fontes, & Loureiro, 2004) that drought in coffee should be seen as a generalist term in nature and should be approached as a multidimensional stress problem. This is because drought, as is typical for tropical and subtropical agriculture, next to being a water deficit, is often paired with high temperatures and excess radiation. This represents a significant and combined environmental insult which, if not managed properly, can devastate yield potential and indeed, crop survival.

Once again, most research to date on this topic has focused on Arabica. It has been possible to identify some consequences of the separate individual stress factors giving us a more precise insight into the resulting chemical changes. The single environmental factors which have been investigated are water deficit, temperature and radiation. Regarding water availability, differences in acidity, odour, colour and flavour were observed by Melke & Fetene, (2014) after using different irrigation regimes for both Arabica and Robusta genotypes. Ronchi et al. (2005) and Vinecky et al. (2017) described a decrease in starch content in the green bean following a dry period of exposure. Soluble and reducing sugars appear to increase with decreasing water availability, although stable sugar levels were observed irrespective of the intensity of the stress experienced (Vinecky et al., 2017). Lipid-soluble compound levels in coffee berries were observed to decrease with prolonged rainfall (Decazy et al., 2003; Vinecky et al., 2017). Nevertheless, other papers describe contrasting results where concentrations appeared to be stable in irrigated and non-irrigated fields (Da Silva, 2005). A more detailed analysis revealed that even if the total content does not change, individual chemical composition can vary, *e.g.* the diterpenoid kahweol increased in concentration in irrigated plants as compared to non-irrigated ones (Marcheafave et al., 2020).

For phenolic compounds, levels appear to remain constant even when plants have been exposed to severe water stress (Cheng et al., 2019; Heeger et al., 2017). Again the literature is inconsistent as Marcheafave et al. (2020) and Vinecky et al. (2017) report finding higher levels of phenolics in Arabica beans from fields with higher water availability. Contradiction has also been observed for caffeine where some articles have shown a positive relationship with an increasing duration of the dry period (Da Silva, 2005; Marcheafave et al., 2020) while others observed a negative correlation (Da Silva, 2005; Vinecky et al., 2017). Finally, protein, amino acid and total nitrogen contents were found to be higher in Arabica beans from regions where rainfall was infrequent as compared to those from more humid areas (Bertrand et al., 2012; Joët et al., 2010)

Unexpectedly, while water stress significantly modified bean composition, the effect of temperature stress on bean components such as GABA, carbohydrates, amino acids and CGAs was insignificant (Bertrand et al., 2012; Joët et al., 2010; Kramer et al., 2010). No differences in total levels of lipid soluble compounds, sugars, phenolic compounds and caffeine were observed in beans from plants growing at different temperatures (Joët et al., 2010; Kramer et al., 2010). However, for all classes of molecules, qualitative compositional changes linked to increasing temperature were detected (Bertrand et al., 2012). Levels of polyunsaturated fatty acids (18:2 and 18:3) decreased with increasing temperature whereas their monounsaturated form, oleic acid (18:1) increased. The influence of high solar radiation levels closely matched that for high temperature (Pereira Baliza et al., 2012). Nonetheless, this qualitative, but not quantitative, effect of high temperature and radiation does not seem to show any peculiar modification that could determine lower bean quality. This is however, refuted by Flament, (2001) and Grosch, (2001), who observed that green beans from areas of elevated temperatures and high radiation positively correlate with the appearance of negative sensory attributes such as acidity and earthy flavour. These undesirable sensory attributes were linked to the presence of particular known volatiles, mainly alcohols (butan-1,3-diol and butan-2,3-diol), but also aldehydes, hydrocarbons and ketones. This exemplifies how higher environmental temperatures and solar radiation can have direct detrimental effects on coffee beverage quality while a colder climate, *e.g.* due to shade-grown coffee at a higher altitude, can have a positive effect.

In conclusion, despite inconsistent results, mainly regarding the effects of water deficit and temperature, in general, water availability appears to be a limiting factor for both carbon and nitrogen metabolism (DaMatta & Ramalho, 2006). In addition, high temperatures, especially under dry conditions cause a developmental acceleration of coffee fruit maturation which is accompanied by the appearance of negative factors reducing quality (Worku et al., 2018).

## 8. Concluding remarks and future perspectives

Coffee cup quality starts with the green bean. From the albeit limited results available in the literature on green coffee, some patterns are already emerging. However, it is evident that for many aspects, our knowledge of green bean physiology and chemistry is still lacking or non-existent and is often limited to individual or even unnamed varieties. This is remarkable considering the economic importance of this global crop which also delivers a commodity where quality of the final

product is of paramount importance. New advances in analytical potential, in terms of mass resolution, detection sensitivity, metabolite identification, *in vivo* location etc. are beginning to help significantly to improve this situation and help close our knowledge gap. The application of the more traditional, targeted analytical approaches used to date, in association with upcoming more comprehensive untargeted metabolomics approaches (Hall, 2014; Putri & Fukusaki, 2018), should become a powerful combination to help us broaden our chemical knowledge, map metabolic networks and ultimately link bean chemistry with cup sensory attributes. We can then start to get a better grasp of the chemistry behind both general coffee quality and even consumer preference.

Untargeted metabolomics approaches, including the detection of yet unidentified (unknown/novel) coffee compounds, also offer us a greater opportunity to help identify the potential importance of individual compounds or compound families which may not previously have been considered as being of relevance and hence have not yet been 'targeted'. A key issue often overlooked is that green beans are both living and metabolically-active tissues in contrast to the roasted products and hence seed and cell physiology are especially sensitive to environmental perturbations, both pre- and post-harvest. This entails that cultivation, postharvest processing treatments and storage conditions are potentially even more important at the green bean stage than following roasting. There are also indications that even germination-related biochemical processes can be initiated during on-farm wet processing treatments which inevitably will impact subsequent green bean chemical composition. Such changes might be less prevalent when farmers use dry processing methods which should more rapidly close down metabolic processes - although longer drying times must then also be considered. However, this and other so-called 'metadata' are often not available to the commercial factory and hence the on-farm processing choice can prove to be an undesired source of chemical variation. This can be translated into quality differences arising during roasting and further factory processing. All these points emphasise the need for an improved mechanistic understanding of the (bio)chemical processes involved in the natural development, pre and post-harvest treatments of coffee green beans as well as what happens thereafter during roasting and storage before consumer consumption. The literature is strewn with apparently conflicting results and it is often not possible to ascertain the true nature of these discrepancies as the full details of the origin and past history of the materials used are absent or at best, fragmented. We therefore call out for a more controlled research approach where the materials used are fresh, directly taken from the experimental fields or farmer plantations so that a complete metadata reference resource can be compiled to support the experimental results. These should include all information such as variety/genotype, geographical location, growth season, harvesting regime, storage time etc. In many of the papers published, such information is essentially lacking, presumably as this was also not gathered by the researchers when obtaining the experimental materials. The origin of the many apparent discrepancies in published results is likely to be associated with the genetic and environmental history of the green beans used, the importance of which has been the topic of this review.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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