



Research article

Chemical and antioxidant characterization of *Dovyalis caffra* and *Dovyalis abyssinica* fruits in KenyaDaniel Mwangi Waweru^a, Joshua Mbaabu Arimi^a, Eunice Marete^b, Jean-Christophe Jacquier^c, Niamh Harbourne^{c,*}^a Department of Food Science and Technology, Meru University of Science and Technology, Meru, Kenya^b Department of Physical Sciences, Meru University of Science and Technology, Meru, Kenya^c School of Agriculture, Food Science and Veterinary Medicine, University College Dublin, Belfield, Dublin 4, Ireland

ARTICLE INFO

Keywords:

*Dovyalis caffra**Dovyalis abyssinica*

Chemical

Antioxidant

Kenya

ABSTRACT

This study aimed at chemical characterization of *Dovyalis caffra* (Hook.f. & Harv.) Sim. and *Dovyalis abyssinica* (A. Rich.) Warb. fruits from Kinamba Town (KT) in Laikipia county and Gitoro Forest (GF) in Meru county of Kenya. All analysed fresh fruit samples had low pH values averaging at 2.67. Other tests showed *D. abyssinica*-GF to be significantly inferior to *D. caffra*-GF and *D. caffra*-KT in terms of TSS, TSS:TTA ratio, and ascorbic acid content. Based on these parameters, *D. caffra*-KT presents itself with a higher potential for direct consumption as compared to *D. caffra*-GF. Proximate analysis of dried fruit pulps demonstrated *D. abyssinica*-GF to be significantly higher in ash content and significantly lower in protein and fat contents compared to the other two samples. There were insignificant difference in the fibre and carbohydrate contents of all the fruit samples. In phytochemical analysis, *D. caffra*-GF recorded the highest total polyphenol content of 1845 mg Gallic acid equivalent (GAE)/100 g while *D. abyssinica*-GF reported the lowest figure of 1128 mg GAE/100 g. Flavonoid and simple phenols fractions were in the range of 18.15–26.85% and 73.15–81.85% respectively in all fruit samples. As for antioxidant activity, *D. caffra*-GF recorded significantly high scores in both DPPH and CUPRAC assays, and *D. abyssinica*-GF the lowest. The range of DPPH and CUPRAC scores for all samples was 1995–4993 mg l-ascorbic acid/100 g and 1384–2303 mg l-ascorbic acid/100 g respectively. The current study presents the nutritional and health potential of *D. caffra* and *D. abyssinica* fruits. This forms a good basis for future adoption and exploitation of these fruits.

1. Introduction

Dovyalis caffra and *Dovyalis abyssinica* belong to the salicaceae family (Waweru et al., 2022). The former originated mainly from South Africa while the latter is native to East Africa (Cavalcante and Martins, 2005). *D. caffra* is a dioecious shrub that grows to a height of up to 5 m. It has thorny branches with simple leaves popping out in clusters. The tree bears fleshy, acidic, spherical berries containing approximately 12 hairy seeds arranged in circles (Aremu et al., 2019). The ripe fruit can be used in making wine (Minnaar et al., 2017), ready to drink fruit juices (Gore, 2005) and nectars (Du Preez et al., 2013). *D. abyssinica* on the other hand is a shrub that grows to a height of up to 3 m and has lesser thorns than *D. caffra*. The shrub bears acidic, apricot like fruits with a diameter of up to 25 mm. The ripe fruit can be used in making jelly and fruit punch (Cavalcante and Martins, 2005).

Despite these fruits being indigenous to the African continent, they remain largely underexploited for food purposes. Apart from a few *D. caffra* studies in South Africa and Egypt (Omotayo et al., 2019; Taher et al., 2018), very scanty information is available regarding the fruit's food potential in other African countries. In Kenya for example, other than one recent report on a *D. caffra* study in Narok County (Osano, 2019), substantive countrywide information on the fruit is basically absent. Overall, *D. abyssinica* has received the least attention and remains extremely unreported universally (Cavalcante and Martins, 2005).

The consumption of fruits and vegetables is generally linked to reduced risk of major diseases mainly due to their richness in health promoting compounds such as vitamin C, carotenoids and diverse phytochemicals (Vincente et al., 2014). Such compounds have been demonstrated to have antioxidant capabilities that prevent radical formation in our bodies and thus preventing onset of disorders such as aging, brain dysfunction, some cancers and cardiovascular diseases (Verma and Mishra, 2014).

* Corresponding author.

E-mail address: niamh.harbourne@ucd.ie (N. Harbourne).

Previous studies on *D. caffra* have accordingly demonstrated the fruit to be an excellent source of ascorbic acid (Du Preez et al., 2013; Loots et al., 2006; Nitcheu Ngemakwe et al., 2017) and a moderate source of β -carotene (Mpai et al., 2018). Besides consideration of the antioxidant activity of ascorbic acid and β -carotene in *D. caffra* fruits, additional phytochemicals such as polyphenols further amplify such potential. Composition wise, Loots et al. (2006) reported a total polyphenol content of 1013 ± 3.0 mg GAE/L in *D. caffra* fruit juice. Elsewhere in Egypt, a total polyphenol content of 2901 mg GAE/100 g dry weight (DW) was reported for the same fruit (Taher et al., 2018). The overall antioxidant activity associated with all these compounds can be estimated using different *in-vitro* assays. Such assays employ different mechanisms in their action such as, single-electron-transfer-based assays (2, 2-azinobis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS) radical cation, Ferric antioxidant power (FRAP) and DPPH assays) and one hydrogen-atom-transfer based assay (ORAC) (Sethi et al., 2020). Overall, the use of more than one assay is recommended in order to provide for the complexity of diverse plant chemicals (Sethi et al., 2020). In general however, a positive correlation has already been established between high levels of polyphenols and high antioxidant activities in *D. caffra* fruits (Loots et al., 2006; Taher et al., 2018).

Nutritionally, *D. caffra* fruits have been reported to be considerably high in carbohydrates (54.05% DW), crude fibre (16.3% DW) and moderate in protein (4% DW), ash (7.45% DW), moisture (15.5% DW) and fat (3% DW) (Taher et al., 2018). Amino acid profiling indicated that *D. caffra* fruit is a potential source of essential amino acids (Mpai et al., 2018; Taher et al., 2018). Micronutrient analysis demonstrates the fruit to be an appreciable source of minerals such as potassium, phosphorus and sodium as well as vitamins such as thiamine, riboflavin and niacin. Other micronutrients reported in moderate amounts include; copper, iron and calcium (Wehmeyer, 1966).

The *Dovyalis* fruits have considerable nutritional and health potential which warrant for their exploration and utilization across the globe, particularly in Africa where they are native. There being limited or no information on chemical properties of *D. caffra* and *D. abyssinica* fruits in Kenya, the current study aimed at filling the existing information gaps for these fruits. *D. caffra* fruits from two different geographical locations (Kinamba Town in Laikipia county and Gitoro forest in Meru county) were studied. A sample of *D. abyssinica* from Gitoro forest was also examined. Basic chemical properties such as pH, titratable acidity, total soluble solids and ascorbic acid were profiled as well as the proximate composition. Phytochemical composition and antioxidant capacities were also examined in the fruit samples. The findings of this research would be imperative in creating a scientific basis for future adoption of these fruits for food purposes in Kenya. More specifically, the findings may be useful to people such as, farmers, food processors, researchers, industrial manufacturers and clinical nutritionists amongst others.

2. Materials and methods

2.1. Sample collection and preparation

In Kenya, *D. caffra* and *D. abyssinica* fruits are wild in nature. Positive identification of the fruits prior to sampling was done with the help of a botanical expert (Dr. Paul Musili of the Kenya Museums, Nairobi herbarium). Individual batches of ripe (Approx. 10 °Brix) *D. caffra* fruits weighing 10 kg each were harvested on December 2019 from Kinamba Town (KT) of Laikipia county and Gitoro Forest (GF) of Meru county through collaboration with the Kenya Forestry Research Institute (KEFRI). A similar batch of *D. abyssinica* fruit was also obtained from the Gitoro forest. In each scenario, fruit collection was done from 7 shrubs distributed within a radius of 3 m. Ecologically, both Gitoro forest region and Kinamba town have a soil type largely consisting of a mixture of clay and loam; and experience average annual rainfall of between 1250–1600 mm and 740–900 mm respectively (County Integrated Development Plans, 2018). Once harvested, the fruits were packaged in cooler boxes

and transported by road to Meru University of Science and Technology (MUST), Kenya. On reception, the fresh fruits were stored in a cold room overnight (12 h) before analysis commenced.

The various batches of fresh fruits were independently sorted (Figure 1A), cleaned in cold water, rinsed and drained on racks to surface dryness. Three sets of 20 fruits were then randomly selected from individual batches and treated as replicates throughout the study. Such fruits were then cut into halves, deseeded and pulped (with their skin intact) using a blender (Ramtons, RM/259, China) for 1.5 min. Obtained pulps had their total titratable acidity, total soluble solids, ascorbic acid and pH measured before drying (Figure 1B) in an air oven (Biobase, bjpx-H160, Shandong, China) at 60 °C to constant weight. The dried samples (Figure 1C) were finally packed in sealed zip-lock bags and stored at room temperature (23 °C) prior to transportation by air to the University College Dublin (UCD) – Ireland, for further analysis. Such analysis commenced after six days.

2.2. Basic chemical properties of fresh *D. caffra* and *D. abyssinica* fruit pulp

The pH of fresh fruit pulp was measured at ambient temperature using a calibrated digital pH meter (Hanna-instruments, Woonsocket, United States of America).

The %TTA of fresh fruit pulp was determined by sample titration using 0.1N sodium hydroxide and phenolphthalein as an indicator according to Cavalcante and Martins (2005). The %TTA was expressed as % malic acid considering that it is the most abundant organic acid in *D. caffra* fruits (Taher et al., 2018).

TSS was measured using a portable refractometer (GFT-P50, Griff-Chem, China). The TSS was expressed as °Brix according to Augustyn et al. (2018). The ratio of TSS/TTA was also calculated according to Augustyn et al. (2018).

The Ascorbic acid content of fresh fruit pulps was determined by the 2, 6-dichloroindophenol titrimetric method as described by Mazumdar (2009). Standard reagent solution was prepared by first dissolving 50 mg of 2, 6-dichlorophenolindophenol and 42 mg of sodium carbonate in 200 ml of distilled water. For sample determination of ascorbic acid content, 5 g of fruit pulp was dispersed/extracted in 100 ml of 10 % TCA followed by indophenol titration against 10 ml drawn from such mixture. Sample blank was determined by indophenol titration against a mixture of 10 ml 10% TCA solution. Calculation of ascorbic acid content in mg/100 g of fruit sample was done as follows;

$$\text{Ascorbic acid content} = (A - B) \times C \times 100/10 \times 1/S \times 100$$

where; 100/10 = volume of sample extract used for determination, A = Volume in ml of the indophenol solution used for sample titration, B = Volume in ml of the indophenol solution used for blank titration, C = Mass in mg of ascorbic acid equivalent to 100 ml of standard indophenol solution and S = Weight of sample taken (g).

2.3. Proximate composition of dried *D. caffra* and *D. abyssinica* fruit pulp

The moisture content of dried fruit pulps was determined by following specifications provided by the AOAC International (1995), Method 925. 10-32.1.03. Samples were weighed before drying in a hot air oven (Biobase, bjpx-H160, Shandong, China) and after complete drying (constant weight). The weight difference was expressed as percentage moisture.

Percentage nitrogen content of dried fruit pulps was analysed by the Kjeldahl method as described by the AOAC International (1995) Method 20.87–32.1.22. The fruit sample (~1 g) was weighed into a digestion flask jointly with a catalyst consisting of 5 g K₂SO₄ and 0.5 g CuSO₄ and 15 ml of concentrated H₂SO₄ acid. The mixture was heated in a fume hood until the end of the digestion process before being cooled, transferred to a 100 ml volumetric flask and topped up to 100 ml with distilled

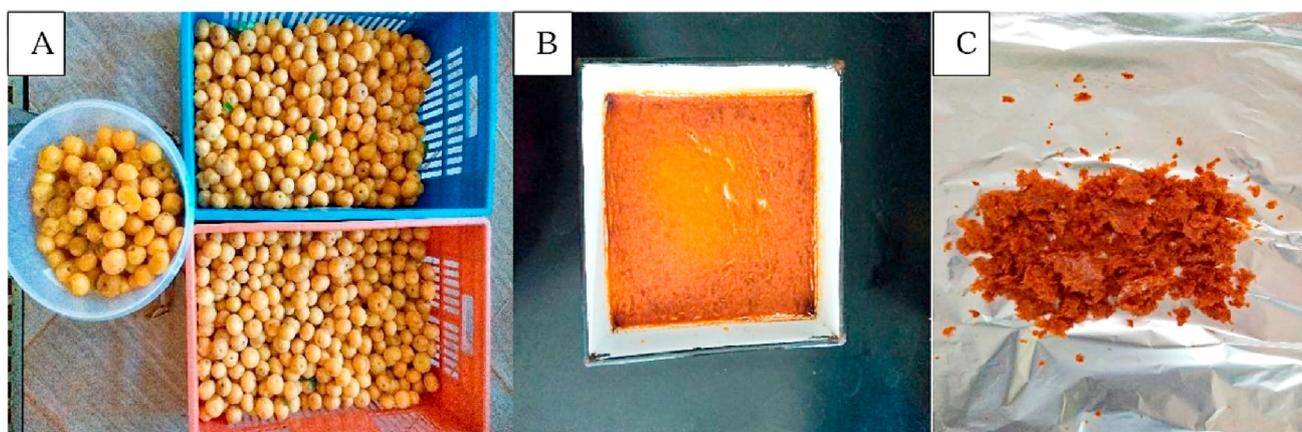


Figure 1. A = Sorting of *Dovyalis caffra* fruits, B = Ongoing drying process of *Dovyalis caffra* fruit pulp, C = Dried *Dovyalis caffra* fruit pulp ready for packing and further analysis.

water. 10 ml of the diluted digest was neutralized with 15 ml of 40% NaOH before distilling down to a volume of about 60 ml distillate. The distillate was titrated using 0.02 N-HCl to an orange colour. Calculations were done using the following formulae;

$$\text{Nitrogen \%} = (V1 - V2) \times N \times f \times 0.014 \times 100/V \times 100/S$$

where: V1 = Titre for sample (ml); V2 = Titre for blank (ml), N = Normality of standard HCl solution (0.02), f = Factor of standard HCl solution, V = Volume of diluted digest taken for distillation (10 ml), S = Weight of sample taken (g), Protein % = Nitrogen \times protein factor. Protein factor = 6.25.

Percentage fat content of dried fruit pulps was determined by the Soxhlet extraction technique of the AOAC International (1995), Method 920.85-32.1.13. Ground pulp samples (~5 g) were weighed into extraction thimbles. Initial weight of the extraction flasks were taken prior to the transfer of 90 ml of petroleum ether into each flask. Flasks were then attached to the soxhlet extraction apparatus and analysis carried out. Extraction was performed at 61.5 °C for 8 h. The extraction solvent in the flask was then completely evaporated and the extracted fat dried in a hot-air oven (Biobase, bjpx-H160, Shandong, China) for 15 min before the final weight of the flask with the extracted fat was recorded. Calculation of % fat was done as follows;

$$\text{Fat \%} = \text{Weight of fat extracted} \times 100/\text{Weight of sample}$$

The total ash content of dried fruit pulps was determined by dry-ashing method using a ceramic muffle furnace (SX3/SX4/SX4-P, Japan) as described by the AOAC International (1995), Method 923.03-32.1.05. Total crude ash was calculated by expressing the weight of acquired ash as a percentage of the sample weight.

Crude fibre of dried fruit pulps was determined by the acid, alkaline digestion and solubilisation technique (AOAC International, 1995), Method 920.86-32.1.15. Approximately 2 g (W) of dried fruit pulp was weighed into a 500 ml conical flask. 200 ml of boiling 1.25% H₂SO₄ was added and the sample was heated under reflux for 30 min. After filtration under vacuum with Pyrex glass filter (crucible type) and washing with boiling water, the sample was then alkali digested by adding 200 ml of boiling 1.25% NaOH to the washed residue. It was then heated under reflux for another 30 min. The residue was filtered, using a Pyrex glass filter, by rinsing with boiling water followed by 1% HCl and finally washing with boiling water to rinse off the acid. The residue was then washed twice with alcohol and three times with ether before being dried in a hot-air oven at 105 °C in a porcelain dish to a constant weight (W1). Incineration was done in a muffle furnace at 550 °C for 3 h and the final weight (W2) taken. Calculation was done as follows;

$$\% \text{ Crude fiber} = (W1 - W2)/W \times 100$$

where; W1 = weight of acid and alkali digested sample, W2 = weight of incinerated sample after acid and alkali digestion and W = weight of sample taken.

The total carbohydrate content of dried fruit pulps was determined by difference method as follows: %Total digestible carbohydrates = 100 – [Total ash + fibre + fat + protein + moisture].

2.4. Phytochemical analysis

2.4.1. Sample extraction

D. caffra and *D. abyssinica* extracts were prepared by extracting 1 g of dried fruit pulp sample in 100 ml water at 60 °C for 1 h. This was followed by vacuum filtration using a No.1 Whatman filter paper. Unused extracts were stored in sealed containers at –20 °C for later use.

2.4.2. Total polyphenol content (TPC)

The total polyphenol content of dried *D. caffra* and *D. abyssinica* fruit pulp extracts was determined by the Folin-Ciocalteu method with a slight modification of the procedure described by Singleton and Rossi (1965). A 0.2 ml of extract, blank or standard was added to ~6.0 ml of distilled water in a 10 ml volumetric flask. 0.5 ml of Folin-Ciocalteu reagent was then added and mixed. After 1 min and before 8 min, 1.5 ml of 20% sodium carbonate solution was added and the volume adjusted to 10 ml with distilled water. The colour generated after 2 h was read at 760 nm using a UV-Vis Spectrophotometer (UV mini-1240, Shimadzu, Kyoto, Japan). The total phenolic content was calculated using a Gallic acid standard curve (Figure 2) and results expressed as mg of Gallic acid equivalents (GAE) per 100 g sample.

2.4.3. Separation of phenolic groups in dried *D. caffra* and *D. abyssinica* fruit pulp extracts

The tannin (TT) and non-tannin (NT) fractions of *D. caffra* and *D. abyssinica* fruit extracts were separated by slight modification of the precipitation method described by Harboun et al. (2009). 1 ml of these extracts were then mixed with 1 ml of 0.5% cinchonine in micro-centrifuge tubes, shaken very well and centrifuged at 13,000 rcf for 5 min. The supernatant (NT fraction) produced was transferred into a new tube leaving the ‘tannin residue’ (TT fraction) at the bottom. Such residue was re-dissolved in 2 ml of an ethanol +10% hydrochloric acid (HCl) mixture 50:50 (v:v). Further separation was done by adding 0.5 ml formaldehyde solution +0.5 ml HCl (10%) to 1 ml of the NT and TT fractions to yield simple phenols and ‘hydrolysable tannins’, respectively. After separation all fractions were quantified using the Folin-Ciocalteu procedure (described above). The content of ‘condensed tannins’ and flavonoids was calculated by difference.

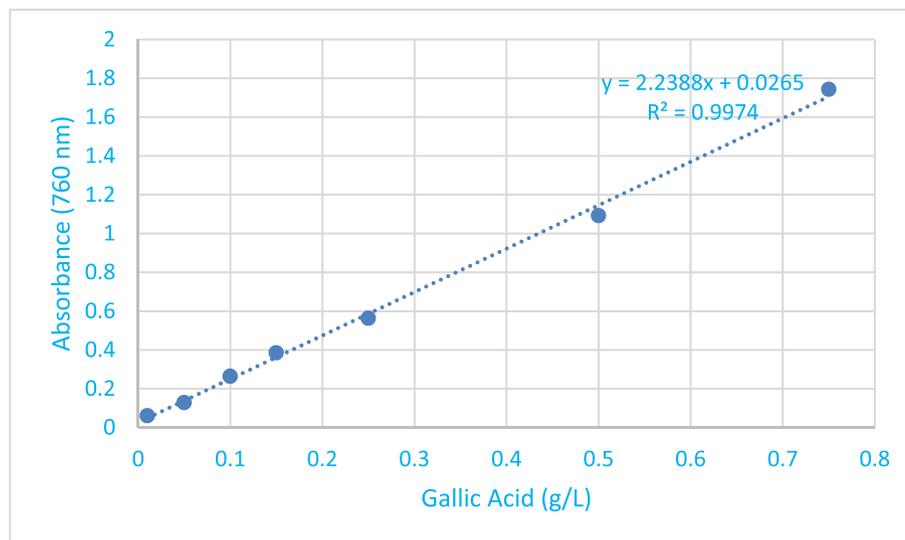


Figure 2. Standard curve for Gallic acid.

2.4.4. Antioxidant activity (AA)

The DPPH assay of *D. caffra* and *Dovyalis abyssinica* fruit extracts was carried out by a slight modification of the method described by Papoutsis et al. (2018). Firstly, a stock solution was prepared by dissolving 24 mg DPPH in 100 ml of methanol. A working solution was then prepared by mixing 10 ml of the stock solution with 45 ml of methanol to obtain an absorbance of 1.1 ± 0.02 at 515 nm. Subsequently, 2.85 ml of the working solution was mixed with 0.15 ml of sample and left in the dark at room temperature for 30 min before measuring the absorbance at 515 nm using a UV-Vis spectrophotometer (UV mini-1240, Shimadzu, Kyoto, Japan). The antioxidant capacity was calculated using an L-ascorbic acid standard curve and results expressed as mg of L-ascorbic acid equivalents per 100 g of sample (mg L-ascorbic acid equivalents/100 g).

The CUPRAC assay of *D. caffra* and *D. abyssinica* fruit extracts was carried out by a slight modification of the method described by Papoutsis et al. (2018). Briefly, 1 ml of 10 mM CuCl_2 solution was first mixed with 1 ml of 7.5 mM neocuproine solution. To this mixture, 1 ml of NH_4Ac buffer (pH 7.0) solution was added and finally 1.1 ml of sample extract. The mixture was then left in the dark at ambient temperature for 1.5 h before measuring its absorbance at 450 nm using a UV-Vis spectrophotometer (UV mini-1240, Shimadzu, Kyoto, Japan). The antioxidant capacity was calculated using an L-ascorbic acid standard curve and results expressed as mg of L-ascorbic acid equivalents per 100 g of sample (mg L-ascorbic acid equivalents/100 g).

2.5. Data management and analysis

For every fruit batch, all sample preparations, extractions and chemical analysis were conducted in triplicate. Data obtained was subjected to one way Analysis of Variance (ANOVA) using GenStat statistical package. Mean comparisons for treatments was done using Duncan's Multiple Range Tests. Significant difference was accepted at $P < 0.05$ (Steel et al., 1980).

3. Results and discussion

3.1. Basic chemical properties of fresh *D. caffra* and *D. abyssinica* fruit pulp

From a general observation in Table 1, it is quite clear that *D. caffra* and *D. abyssinica* fruits have both considerable similarities and differences. For instance, both fruit species recorded low pH levels with no significant difference $P < 0.05$ between respective values. The corresponding total titratable acidity of the fruits was also not significantly different between *D. abyssinica*-GF and *D. caffra*-GF. *D. caffra*-KT however, recorded significantly lower %TTA. Such differences may be attributed to the different geographical zones, soil conditions and variety/species variation amongst other factors. A study by Taher et al. (2018) reported higher acidity levels of 3.49 in *D. caffra* fruits from Egypt. Similarly, Minnaar et al. (2017) registered an equally high TTA of 144.01 g/L in the same species of fruit in South Africa. With regard to the total soluble solids TSS, *D. caffra* fruits from both Kinamba Town and Gitoro Forest scored significantly higher than the *D. abyssinica*-GF species. Accordingly, the corresponding TSS/TTA values of these batches were also significantly higher than the *D. abyssinica*-GF sample. The ratio of TSS/TTA is used to express the correlation between the fruits' total sugars and acids, constituting a crucial parameter that dictates the taste of the fruit. The higher the ratio the more the sweetness or rather the lesser the sourness of fruits (Augustyn et al., 2018). Based on such concept it is clear from results presented in Table 1 that *D. caffra*-KT would be the least sour hence most preferable for direct consumption followed by *D. caffra*-GF and finally *D. abyssinica*-GF species. Similar variations were also reported among *D. caffra* fruits from different regions of South Africa (Augustyn et al., 2018). *D. caffra* and *Dovyalis abyssinica* fruits have been considerably reported as excellent sources of ascorbic acid (Cavalcante and Martins, 2005; Ntcheu Ngemakwe et al., 2017). The current study is in agreement with these studies as

Table 1. Basic chemical properties of fresh *Dovyalis caffra* and *Dovyalis abyssinica* fruit pulp.

Sample	Parameter				
	pH	TTA (%)	TSS ($^{\circ}$ Brix)	TSS/TTA	Ascorbic Acid (mg/100 g)
<i>Dovyalis caffra</i> - KT	2.72 ± 0.04^a	2.30 ± 0.03^a	10.97 ± 0.12^b	4.76 ± 0.07^c	162.95 ± 7.01^c
<i>Dovyalis caffra</i> - GF	2.65 ± 0.07^a	2.49 ± 0.02^b	10.87 ± 0.12^b	4.36 ± 0.06^b	142.44 ± 5.43^b
<i>Dovyalis abyssinica</i> - GF	2.65 ± 0.01^a	2.50 ± 0.02^b	10.37 ± 0.15^a	4.14 ± 0.08^a	109.07 ± 3.97^a

Data presented as means \pm standard deviation (n = 3). Means in columns with the same superscript are not significantly different ($P > 0.05$), KT = Kinamba Town, GF = Gitoro Forest.

demonstrated in Table 1. The batch from Kinamba Town significantly registered the highest levels of this antioxidant vitamin followed by *D. caffra*-GF and finally *D. abyssinica*-GF (Table 1). Overall, the range of ascorbic acid content recorded in the current study is notably higher compared to previous studies on *D. caffra* fruits e.g., 65.8 mg/100 g (Loots et al., 2006) and 83 mg/100 g (Taher et al., 2018). As for the *D. abyssinica*-GF species, the ascorbic acid content registered agrees well with the report of Cavalcante and Martins (2005). Physicochemical parameters are in general very useful in defining fruit quality, maturity and suitability for processing or direct consumption (Cavalcante and Martins, 2005). In Kenya, such information has been missing for *D. caffra* and *D. abyssinica* fruits.

3.2. Proximate composition of dried *D. caffra* and *D. abyssinica* fruit pulp

Based on proximate composition (Table 2), various inter and intra-species differences and similarities were observed in all the three fruit batches. Interestingly there was no significant difference in both the fibre and total carbohydrate contents of all the fruits. On average these fruits registered a mean fibre content of 16.63% and a carbohydrate content of 53.79%. Such figures are in agreement with those reported for dried *D. caffra* fruits in Egypt i.e. 16.3% and 54.05% respectively (Taher et al., 2018). With regard to the protein and fat content, both batches of *D. caffra* fruits were shown to be significantly higher than in the *D. abyssinica*-GF species. Such difference could be attributed to variation in the genetic makeup of different species. In general however, the range of protein (3.11–4.32%) and crude fat (2.55–3.16%) recorded for all samples in the current study agree fairly well with the findings of Taher et al. (2018), who established a protein value of 4% and fat value of 3% in dried *D. caffra* fruits. As shown in Table 2, the ash and moisture content of *D. abyssinica*-GF are significantly higher than *D. caffra*-GF despite being from the same geographical location. This may as well be attributed to differences in the genetic makeup of different fruit species. In general, the average ash and moisture content recorded in current study agree fairly well with the report of Taher et al. (2018) i.e. 7.45% and 15.5% respectively. Apart from Taher et al. (2018), there is roughly no other study that utilized dried *D. caffra* fruit samples in such analysis. From a food scientist perspective, drying of the *Dovyalis* fruit pulp is a reliable way of preserving the fruit for longer periods. Dried fruit is also less bulky hence easier to handle, transport and market. The technique should be considered for future commercial production of dried *Dovyalis* fruit products e.g. fruit leathers.

3.3. Phenolic content in dried *D. caffra* and *D. abyssinica* fruit pulp as a percentage of the total phenols

The first column in Table 3 shows the total polyphenol content - TPC in (mg GAE/100 g) of the various fruit samples. *D. caffra*-GF recorded a significantly high quantity of TPC as compared to *D. caffra*-KT and *D. abyssinica*-GF. Numerically however, TPC contents of all the samples fell within a range of 1128–1845 mg GAE/100 g DW, which is fairly close to the figures reported in previous studies for *D. caffra* fruit. For instance, De Beer (2006) reported a TPC range of 521–1990 mg GAE/100 g DW in different fruit parts while Taher et al. (2018) reported a TPC of 1850 mg

GAE/100 g DW in fruit flesh. It is worth noting that above studies used different extraction methods and solvents from the one used in current study and hence a possible source of variation in reported TPC. Apart from extraction conditions, other factors that may contribute to TPC variations in fruits include but not limited to; soil conditions of fruit source, fruit species, fruit variety, fruit maturity and ripeness and general post-harvest handling of the fruit (Trebichalský et al., 2015).

As shown in Table 3, separation of polyphenols indicated that *D. caffra*-GF had significantly higher percentage of simple phenols and corresponding lower flavonoids in comparison to the rest of the samples. No significant difference was reported in these parameters between *D. caffra*-KT and *D. abyssinica*-GF. The overall range of simple phenols and flavonoids for all fruit samples was established to be 73–81% and 18–26% respectively. Tannins were not detected in all fruit samples. Health-wise, flavonoids are said to be highly bioactive compounds with potential to impart various health promoting benefits such as antioxidant, antimicrobial, anticancer and anti-inflammatory amongst other properties (Asaduzzaman and Asao, 2018). In addition, phenolic acids are in general said to be further useful in nutrient uptake, structural components, enzymatic activity and protein synthesis (De Beer, 2006). In such regard, the range of phenolics reported for *D. caffra* and *D. abyssinica* in current study, indicate a great potential of these fruits in imparting the health benefits associated with these compounds. From a health perspective, these fruits can be justifiably recommended for inclusion in the daily diets as new sources of phytochemicals to boost public health.

3.4. Antioxidant activity of dried *D. caffra* and *D. abyssinica* fruit pulp

As shown in Table 4, all fruit batches are potential electron donors as their extracts were able to reduce the copper (II)-neocuproine chelate as well as to quench DPPH radicals. *D. caffra*-GF registered significantly higher antioxidant capacity in both DPPH and CUPRAC assays as compared to *D. caffra*-KT and *D. abyssinica*-GF. Significant difference was also observed between the antioxidant capacity of *D. caffra*-KT and *D. abyssinica*-GF. Numerically, each of the two batches of *D. caffra* species was shown to contain roughly twice the amount of antioxidant capacity recorded for the *D. abyssinica*-GF in both DPPH and CUPRAC assays. Such discrepancy indicates that fruit species maybe a key influential factor in fruit composition. It is also worth noting that, different assays of antioxidant determination in fruits and vegetables yield different results among different crops. This is presumably due to divergent reaction pathways among different plant bio-actives. Since no single assay can absolutely characterize the total antioxidant profile of a particular food, the use of more than one analytical method is usually recommended for more accurate inferences (Sethi et al., 2020). The current study settled on (DPPH) and (CUPRAC) assays for their reliability. Previous reports indicate that DPPH is potentially applicable in a wide array of matrices such as; wines (Di Lorenzo et al., 2017), lemon pomace waste (Papoutsis et al., 2016), cereal grains (Žilić et al., 2011) and other complex biological systems (Kedare and Singh, 2011). CUPRAC on the other hand is also considerably reliable with capability of assaying both lipophilic and hydrophilic antioxidants (Apak et al., 2007).

Notably, several studies have previously reported the antioxidant activity of *D. caffra* fruits (Augustyn et al., 2018; Mpai et al., 2018; Taher

Table 2. Proximate composition of dried *Dovyalis caffra* and *Dovyalis abyssinica* fruit pulp.

Sample	Parameter (g/100 g)					
	Moisture	Protein	Fat	Ash	Fibre	Carbohydrate
<i>Dovyalis caffra</i> - KT	15.74 ± 0.3 ^{ab}	4.32 ± 0.01 ^b	3.09 ± 0.03 ^b	6.46 ± 0.19 ^{ab}	16.86 ± 1.20 ^a	53.54 ± 1.05 ^a
<i>Dovyalis caffra</i> - GF	15.58 ± 0.2 ^a	4.56 ± 0.03 ^c	3.16 ± 0.02 ^b	6.68 ± 0.03 ^a	16.95 ± 0.08 ^a	53.07 ± 0.16 ^a
<i>Dovyalis abyssinica</i> - GF	16.45 ± 0.21 ^b	3.11 ± 0.04 ^a	2.55 ± 0.04 ^a	7.05 ± 0.09 ^b	16.08 ± 0.1 ^a	54.77 ± 0.1 ^a

Data presented as means ± standard deviation (n = 3). Means in columns with the same superscript are not significantly different (P > 0.05), KT = Kinamba Town, GF = Gitoro Forest.

Table 3. Phenolic groups in dried *Dovyalis caffra* and *Dovyalis abyssinica* fruit pulp extracts as a percentage of the total phenols.

Sample	Parameter				
	Total Polyphenols (mg GAE/100 g)	Simple Phenols (%)	Flavonoids (%)	Hydrolysable Tannins (%)	Condensed Tannins (%)
<i>Dovyalis caffra</i> - KT	1203 ± 53 ^a	73.15 ± 1.48 ^a	26.85 ± 1.48 ^b	ND	ND
<i>Dovyalis caffra</i> - GF	1845 ± 35 ^b	81.85 ± 0.80 ^b	18.15 ± 0.80 ^a	ND	ND
<i>Dovyalis abyssinica</i> - GF	1128 ± 60 ^a	75.39 ± 0.26 ^a	24.61 ± 0.26 ^b	ND	ND

Data presented as means ± standard deviation (n = 3). Means in columns with the same superscript are not significantly different (P > 0.05), ND = Not Detected, KT = Kinamba Town, GF = Gitoro Forest.

Table 4. Antioxidant capacity of dried *Dovyalis caffra* and *Dovyalis abyssinica* fruit pulp.

Sample	Parameter	
	DPPH (mg L-Ascorbic acid/100 g)	CUPRAC (mg L-Ascorbic acid/100 g)
<i>Dovyalis caffra</i> - KT	3638 ± 18 ^b	2275 ± 7 ^b
<i>Dovyalis caffra</i> - GF	4993 ± 25 ^c	2303 ± 14 ^c
<i>Dovyalis abyssinica</i> - GF	1995 ± 14 ^a	1384 ± 6 ^a

Data presented as means ± standard deviation (n = 3). Means in columns with the same superscript are not significantly different (P > 0.05), KT = Kinamba Town, GF = Gitoro Forest.

et al., 2018). However, no such study has used cupric ion reducing antioxidant (CUPRAC) assay in quantifying the antioxidant capacity of the said fruit. Furthermore, the few reported studies on 2, 2-Diphenyl-1-picrylhydrazyl (DPPH) assay have only estimated the IC₅₀ and not the actual quantification of antioxidant capacity in (mg L-Ascorbic acid/100 g) like demonstrated in the current study. Comparison of present findings with such studies is therefore impossible. In general, the DPPH values registered by the two *D. caffra* species (Table 4.) are fairly comparable to those of dried *Prunus domestica* L. (3112 mg AAE/100 g DW), *Vaccinium oxycococcus* L. (3079 mg AAE/100 g DW) and *Prunus armeniaca* L. (3846 mg AAE/100 g DW) (Chang et al., 2016). These fruits are categorised among the best natural sources of antioxidants. On the other hand, the DPPH value registered by *D. abyssinica* compares pretty well with moderate antioxidant fruits such as *Pyrus communis* L. (1301 mg AAE/100 g DW), *Vitis vinifera* L. (1346 mg AAE/100 g DW) and *Prunus persica* (L.) Stokes (1442 mg AAE/100 g DW) (Chang et al., 2016).

In broad terms the high antioxidant activity exhibited by *D. caffra* and *D. abyssinica* fruits illustrates their potential use as natural antioxidants in food products e.g., prevention of lipid oxidation. Industrially, health promoting extracts may also be optimally extracted from the fruits and sold to consumers as supplements.

4. Conclusion and recommendation

In the present study, apart from the ash content, *D. caffra* fruits were shown to be superior to *D. abyssinica* species in terms of overall chemical and antioxidant characteristics. *D. caffra* species from different geographical zones showed significant variations in various parameters. The samples from Kinamba Town were superior in TSS/TTA, ascorbic acid and % flavonoids while the ones from Gitoro Forest were superior in %TTA, protein, ash, TPC, % simple phenols and antioxidant capacity (DPPH and CUPRAC). The variations in composition indicate that the fruits from Gitoro forest are the most suitable for consumption in a health perspective and the ones from Kinamba the most suitable for direct consumption in an organoleptic perspective.

Based on the demonstrated favourable chemical and antioxidant characteristics of *D. caffra* and *D. abyssinica* fruits, adoption of such fruits for food purposes in Kenya is highly recommended. For more detailed understanding of the fruits, further chemical profiling in terms of specific phenolic compounds present, carotenoids, total volatiles, chlorophyll, sugars, amino acids, minerals, organic acids and vitamins is also highly

recommended. In-vivo studies on specific health impacts of *D. caffra* and *D. abyssinica* fruits consumption should as well be considered for further investigation. Future research on aspects such as, pre-harvest fruit properties, harvesting methods, postharvest handling, effect of processing on chemical properties and value addition of these fruits is also encouraged.

Declarations

Author contribution statement

Daniel Mwangi Waweru: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Joshua Mbaabu Arimi, Eunice Marete, Jean-Christophe Jacquier, Niamh Harbourne: Conceived and designed the experiments; Wrote the paper.

Funding statement

This work was supported by the European Union through the Erasmus+ International Credit Mobility programme (2018-1-IE02-KA107-000603) between Meru University of Science and Technology, Kenya and University College Dublin, Ireland.

Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interest's statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Acknowledgements

We would like to extend our appreciation to the Kenya Forestry and Research Institute (KEFRI) for facilitating sample acquisition from the restricted forest region. We are also thankful to Dr. Paul Musili of the Kenya Museums - Nairobi herbarium, for his botanical assistance in the positive identification of the two different fruit species used in the study.

References

- AOAC International (Ed.), 1995. Official Methods of Analysis of AOAC International. AOAC International, Arlington, Va.
- Apak, R., Güçlü, K., Demirata, B., Özyürek, M., Karademir Çelik, S., Bektaşoğlu, B., Berker, K., Ozyurt, D., 2007. Comparative evaluation of various total antioxidant capacity assays applied to phenolic compounds with the CUPRAC assay. *Mol. Basel Switz.* 12, 1496–1547.
- Aremu, A.O., Ncama, K., Omotayo, A.O., 2019. Ethnobotanical uses, biological activities and chemical properties of Kei-apple [*Dovyalis caffra* (Hook.f. & Harv.) Sim]: an indigenous fruit tree of southern Africa. *J. Ethnopharmacol.* 241, 111963.

- Asaduzzaman, M., Asao, T., 2018. Introductory Chapter: Phytochemicals and Disease Prevention.
- Augustyn, W.A., Regnier, T., De Jager, K., Hajari, E., Du Preez, R., Nonyane, D., 2018. A preliminary study on the chemical characteristics of Kei apple (*Dovyalis caffra*), an undervalued South African fruit. *South Afr. J. Bot.* 117, 268–275.
- Cavalcante, Í.H.L., Martins, A.B.G., 2005. Physical and chemical characterization of *Dovyalis caffra* fruits. *Int. J. Fruit Sci.* 5, 39–46.
- Chang, S.K., Alasalvar, C., Shahidi, F., 2016. Review of dried fruits: phytochemicals, antioxidant efficacies, and health benefits. *J. Funct. Foods* 21, 113–132.
- County Integrated Development Plans, 2018. WWW Document. URL: <https://www.co.gov.ke/cog-reports/category/106-county-integrated-development-plans-2018-2022>. accessed 3.11.22.
- De Beer, T., 2006. Polyphenols, Ascorbate and Antioxidant Capacity of the Kei-Apple (*Dovyalis Caffra*). North-West University. Thesis.
- Di Lorenzo, C., Badea, M., Colombo, F., Orgiu, F., Frigerio, G., Pastor, R., Restani, P., 2017. Antioxidant activity of wine assessed by different *in vitro* methods. *Bio Web Conf.* 9, 04008.
- Du Preez, R.J., de Jager, K., Welgemoed, C.P., Maphanga, O., Mhlophe, S.D., Hansmann, C., 2013. Preliminary investigation into the potential for commercialization of indigenous fruits in rural communities: survey, fruit composition, propagation and product development. *Acta Hort.* 613–626.
- Gore, M.J.C., 2005. Development of a Functional Beverage from the Kei Apple Fruit *Dovyalis Caffra*. North-West University. Thesis.
- Harbourne, N., Marete, E., Jacquier, J.C., O'Riordan, D., 2009. Effect of drying methods on the phenolic constituents of meadowsweet (*Filipendula ulmaria*) and willow (*Salix alba*). *LWT-Food Sci. Technol.* 42, 1468–1473.
- Kedare, S., Singh, R., 2011. Genesis and development of DPPH method of antioxidant assay. *J. Food Sci. Technol.* 48, 412–422.
- Loots, D.T., van der Westhuizen, F.H., Jerling, J., 2006. Polyphenol composition and antioxidant activity of Kei-apple (*Dovyalis caffra*) juice. *J. Agric. Food Chem.* 54, 1271–1276.
- Mazumdar, B., 2009. *Methods on Physico Chemical Analysis of Fruits*. Daya Publishing House, Delhi.
- Minnaar, P.P., Jolly, N.P., Paulsen, V., Du Plessis, H.W., Van Der Rijst, M., 2017. *Schizosaccharomyces pombe* and *Saccharomyces cerevisiae* yeasts in sequential fermentations: effect on phenolic acids of fermented Kei-apple (*Dovyalis caffra* L.) juice. *Int. J. Food Microbiol.* 257, 232–237.
- Mpai, S., du Preez, R., Sultanbawa, Y., Sivakumar, D., 2018. Phytochemicals and nutritional composition in accessions of Kei-apple (*Dovyalis caffra*): southern African indigenous fruit. *Food Chem.* 253, 37–45.
- Nitcheu Ngemakwe, P.H., Remize, F., Thaoge, M.L., Sivakumar, D., 2017. Phytochemical and nutritional properties of underutilised fruits in the Southern African region. *South Afr. J. Bot.* 113, 137–149.
- Omotayo, A.O., Ncama, K., Aremu, A.O., 2019. Exploring the diverse potential of underutilized Kei-apple [*Dovyalis caffra* (Hook.f. & Harv.) Sim]: a multi-purpose fruit tree. *Hum. Ecol.* 47, 613–618.
- Osano, A., 2019. Analysis of Selected Nutrient Levels at Different Growth Stages of *Dovyalis caffra* (Kei-apple) Fruits, vol. IV, pp. 2454–6194.
- Papoutsis, K., Pristijono, P., Golding, J.B., Stathopoulos, C.E., Bowyer, M.C., Scarlett, C.J., Vuong, Q.V., 2018. Optimizing a sustainable ultrasound-assisted extraction method for the recovery of polyphenols from lemon by-products: comparison with hot water and organic solvent extractions. *Eur. Food Res. Technol.* 244, 1353–1365.
- Papoutsis, K., Pristijono, P., Golding, J.B., Stathopoulos, C.E., Scarlett, C.J., Bowyer, M.C., Vuong, Q.V., 2016. Impact of different solvents on the recovery of bioactive compounds and antioxidant properties from lemon (*Citrus limon* L.) pomace waste. *Food Sci. Biotechnol.* 25, 971–977.
- Sethi, S., Joshi, A., Arora, B., Bhowmik, A., Sharma, R., Kumar, P., 2020. Significance of FRAP, DPPH, and CUPRAC assays for antioxidant activity determination in apple fruit extracts. *Eur. Food Res. Technol.* 246.
- Singleton, V.L., Rossi, J.A., 1965. Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. *Am. J. Enol. Vitic.* 16, 144–158.
- Steel, R.G.D., Torrie, James, Hiram, 1980. *Principles and Procedures of Statistics a Biometrical Approach*, second Ed. McGraw-Hill, New York.
- Taher, M.A., Tadros, L.K., Dawood, D.H., 2018. Phytochemical constituents, antioxidant activity and safety evaluation of Kei-apple fruit (*Dovyalis caffra*). *Food Chem.* 265, 144–151.
- Trebichalský, P., Molnárová, J., Bajčan, D., Timoracká, M., Musilová, J., Harangozo, L., 2015. Total polyphenols content in fruits of selected cultivars of strawberries in relation to concentrations of cadmium and lead in soil. *Potravinárstvo* 9.
- Verma, P., Mishra, S., 2014. *Antioxidants and Disease Prevention*.
- Vincente, A.R., Manganaris, G.A., Ortiz, C.M., Sozzi, G.O., Crisosto, C.H., 2014. Chapter 5 - nutritional quality of fruits and vegetables. In: Florkowski, W.J., Shewfelt, R.L., Brueckner, B., Prussia, S.E. (Eds.), *Postharvest Handling*, third ed. Academic Press, San Diego, pp. 69–122.
- Waweru, D.M., Arimi, J.M., Marete, E., Jacquier, J.-C., Harbourne, N., 2022. Current status of utilization and potential of *Dovyalis caffra* fruit: major focus on Kenya - a review. *Sci. Afr.* 16, e01097.
- Wehmeyer, A.S., 1966. The nutrient composition of some edible wild fruits found in the Transvaal. *South Afr. Med. J. Suid-Afr. Tydskr. Vir Geneesk.* 40, 1102–1104.
- Žilić, S., Hadži-Tašković Šukalović, V., Dodig, D., Maksimović, V., Maksimović, M., Basić, Z., 2011. Antioxidant activity of small grain cereals caused by phenolics and lipid soluble antioxidants. *J. Cereal. Sci.* 54, 417–424.