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Identification of new glycosidic terpenols and norisoprenoids (aroma precursors) in *C. arabica* L. green coffee by using a high-resolution mass spectrometry database developed in grape metabolomics

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ABSTRACT

Grape aroma precursors have been extensively studied and many glycosidically-bound terpenols and C_{13}-norisoprenoids were identified. Instead, these compounds were scarcely investigated in green *Coffea arabica* where just few glycosidic compounds were identified so far. By resorting to knowledge of glycoside aroma precursors in grape and the possibility to identify their structures using a high-resolution mass spectrometry database constructed for grape metabolomics, *targeted* investigation of glycoside precursors in green *C. arabica* from different geographical origins, was performed. High linalool hexose-pentose was found in all the investigated samples and hexosyl-pentoside derivatives of geraniol, linalooloxide and another linalool isomer, were identified. Moreover, two putative norisoprenoid glycosides were characterized. β-Damascenone was detected in the volatile fraction of the examined *C. arabica* coffees only after acid addition, however no signals of β-damascenone glycosides, were found. Findings suggests that this important aroma compound could form by hydrolysis and dehydration of a putative 3-hydroxy-β-damascone glycoside precursor identified for the first time in coffee. Aglycones released during the roasting process contribute to enrich the coffee aroma with their positive sensory notes and the identification of these glycosides can contribute to disclose the coffee biology including biochemical, physiological and genetic aspects.

1. Introduction

Coffee is one of the most consumed beverages in the world and its success, in addition to the well-recognized functional properties, is largely due to the appreciated organoleptic qualities. The complex and unmistakable aroma of coffee is mainly due to the effects induced by the roasting process on the chemical compounds present in the raw bean that act as aroma precursors. The several hundreds of volatile organic compounds that make up the aroma of roasted coffee are thermally generated by a complex set of chemical reactions. However, several volatiles are already present in the green coffee bean and do not undergo chemical changes upon roasting. This is the case of terpenes and C_{13}-norisoprenoids usually detected in green coffee, roasted coffee and coffee brews (Czerny and Grosch, 2000; Clarke and Vitzthum, 2001; Flament, 2002; Bonnlaender et al., 2004; Akiyama et al., 2008; Yener et al., 2015), and well known to impart pleasant and appreciated flowery notes to the coffee beverage (Flament, 2002; Del Terra et al., 2013). These compounds are remarkably important contributors to the aroma of a wide range of important beverages and food products as well, including fruits such as kiwifruits, mangoes, lychees and tomatoes (Sefton et al., 2011; Maicas and Mateo, 2005; Marlatt et al., 1992) as well as tea (Yang et al., 2013) and grape and wine (Flamini and Traldi, 2010).

Grape aroma precursors have been extensively studied and many glycosidic terpenes and C_{13}-norisoprenoids, were identified (Flamini et al., 2014; Godshaw et al., 2019; Caffrey et al., 2020; Song et al., 2020; Wei et al., 2021). Many glycosidic monoterpenes were identified in both grape skin and pulp the which aglycones confer floral and citrus notes to the wines, and their qualitative/quantitative profile was depending on the variety. Grapes characterized by a middle-high contents of monoterpene glycosides (e.g., Muscats, Malvasia, Gewürztraminer, Riesling, Glera) are classified as aromatic or semi-aromatic varieties, instead

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those having low or not content are neutral grapes (Mateo and Jiménez, 2000).

C_{13}-norisoprenoids are the other main grape contributors to the wine aroma (Williams et al., 1989; 1992; Winterhalter et al., 1990; Winterhalter, 1992; Knapp et al., 2002; Versini et al., 2002). Compounds such as 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), vitispiranes, actinidols and β-damascenone confer to the wine kerosene, resinous/eucalyptus-like, woody and rose-like notes, respectively. Often, norisoprenoids constitute an essential part of aroma of wines produced using neutral grapes. For example, they confer floral and fruity notes to red wines such as Cabernet Sauvignon, Syrah, Grenache, Merlot, Pinot noir, and contribute to the aroma of white wines such as Chardonnay, Semillon, Sauvignon blanc (Flamini and Traldi, 2010; Ilc et al., 2016). Other grape compounds which contribute to aroma of wines are some benzenoids characterized by rose/sweet/fruity notes (e.g., benzyl alcohol, β-phenylethanol, zingerone), C6-aliphatic aldehydes and methoxypyrazines (herbaceous/green notes), S-compounds which confer the typical box-tree note and tropical fragrances to Sauvignon blanc wines, such as 4-mercapto-4-methyl-2-pentanone, 3-mercaptohexanol and 3-mercaptohexyl acetate (Flamini and Traldi, 2010). Glycosides are flavorless compounds but the aromatic aglycones are liberated during winemaking by the hydrolysis promoted by low pH of grape must and yeast glycosidases activity.

By using liquid chromatography/high-resolution multiple mass spectrometry (LC/HRMS) many terpene and norisoprenoid glycosides were identified in grape varieties such as Yellow Muscat, White Muscat, Muscat of Alexandria, Muscat of Hamburg, Pinot noir, Cabernet sauvignon, Riesling, Glera, Gewűrztraminer, Chardonnay, Sauvignon Blanc, and others (Flamini et al., 2014, 2018; Godshaw et al., 2019; Caffrey et al., 2020; Song et al., 2020; Wei et al., 2021). Particular important grape aroma precursors are terpenols and terpenediols linked to a sugar moiety, such as pentose-hexose, rhamnose-hexose, dipentose-hexose, hexose-deoxyhexose, or dihexose-pentose, and C_{13}-norisoprenoids linked to a hexose, hexose-hexose and pentose-hexose molecule. Moreover, some pentose-hexose monoterpenetriols and terpene malonylated glycosides were characterized in grape (Caffrey et al., 2020; Wei et al., 2021).

Differently from grape and wine, glycosidically-bound aroma precursors have been scarcely investigated in coffee. In our knowledge, the first investigations date back to 2002–2003 (Weckerle et al., 2002, 2003). In particular, from green coffee beans (a single sample of *Coffea arabica* from Ethiopia), two isolated terpenyl disaccharides were identified as 3(S)-linalool-3-*O*-β-D-glucopyranosyl-β-D-apiofuranoside and 3(S)-linalool-3-*O*-β-D-glucopyranosyl-α-L-arabinopyranoside (Weckerle et al., 2003) and three isolated acyl disaccharides were identified as 3-methylbutanoyl-1-*O*-β-D-glucopyranosyl-β-D-apiofuranoside, 3-methylbutanoyl-6-*O*-α-D-glucopyranosyl-β-D-fructofuranoside, and 3-methylbut-2-enoyl-1-*O*-β-D-glucopyranosyl-β-D-apiofuranoside (Weckerle et al., 2002). More than ten years later, the presence of 3-methylbutanoyl-6-*O*-α-D-glucopyranosyl-β-D-fructofuranoside was confirmed in several samples of green *C. arabica* from a single geographical origin (Guatemala) and two new acyl disaccharides were isolated and identified as 6′-*O*-(β-D-glucopyranosyl)-1′-*O*-[3-methylbutanoyl]-β-D-glucopyranose (Iwasa et al., 2015) and 6′-*O*-(β-D-glucopyranosyl)-1′-*O*-[3-methylbut-2-enoyl]-β-D-glucopyranose (Nakahara and Iwasa, 2016). Other than an investigation on carotenoid flavor precursors in coffee, where two glycosidically bound ionols (3-oxo-α-ionol and 3-oxo-7,8-dihydro-α-ionol) were identified in green coffee of unknown botanical species and geographical origin (Degenhardt et al., 2006), no further studies on glycosidically-bound volatiles in coffee have been reported.

Glycosidic aroma compounds are remarkably important in green coffee because the aglycones released during the roasting process greatly contribute to enrich the coffee aroma profile (Hattori et al., 2004; Xie et al., 2012), instead contribution of sugar moiety plays a minor role due to the high sucrose content (up to 8.5% w/w) of green *C. arabica* (Stredansky et al., 2018).

This lack of information on this interesting class of aroma precursors has largely stimulated the present study, aimed not only at confirming the presence of the compounds previously identified in few samples of *C. arabica* from only two different geographical origins, but also at ascertaining the possible presence of new compounds. In particular, by resorting to knowledge on glycoside aroma precursors in grape and the possibility to study their integer structures by using the liquid chromatography/high-resolution mass spectrometry (LC/HRMS) without using enzymatic artifacts (Flamini et al., 2014, 2018) their presence in *C. arabica* L. was investigated. *Targeted* search of glycosidic precursors in green coffee extracts was performed by using the extensive HRMS database previously constructed to study grape and wine metabolomics, which contains around 1.100 compounds including many glycosidic terpenoids and norisoprenoids (Flamini et al., 2013).

Headspace solid phase micro-extraction (HS-SPME) coupled with gaschromatography/mass spectrometry (GC/MS) analysis of the same samples was performed to add further information to the green *C. arabica* aroma composition.

2. Materials and methods

2.1. Samples and standards

Five green wet-processed coffee samples (*C. arabica* L.) from different geographic origins (Ethiopia, India, Nicaragua and Rwanda) were supplied by illycaffè S.p.A (Trieste, Italy). Two different commercial lots from Ethiopia were studied and named hereafter Ethiopia 1 and Ethiopia 2. The samples with zero primary and secondary defects, were selected on the basis of standard procedures of sorting and visual aspect, moisture content, screen size, and cup quality. After collection from jute bags, the coffee samples were immediately packed in high barrier plastic bags and stored at room temperature (22–24 °C). *n*-Heptyl-β-D-glucopyranoside was purchased from Sigma-Aldrich (Milan, Italy); methanol, acetonitrile, formic acid and hexane HPLC analytical grade from Romil LTD (Cambridge, UK). Molecule identity was complemented by the analysis of the pure chemical standards. Linalool, nerol, geraniol, isovaleric acid, 3-methyl-2-butenoic acid, α-terpineol, and β-damascenone were purchased by Sigma Aldrich (Milan, Italy).

2.2. UHPLC/QTOF analysis

Prior to perform sample preparation for analysis, 5 g of green coffee was defatted by 2 × 30 mL extraction using *n*-hexane by keeping sample under stirring for 30 min at room temperature. The residue was filtered through paper then extracted using 15 mL of H_2O/CH_3OH 20:80 (v/v) under stirring for 3 h. The sample was centrifuged at 4000 g for 15 min, the solution was added of 200 μL of heptyl-glucoside 40 mg/L as internal standard and filtered through Acrodisc 0.22 μm filter (PTFE membrane) by collecting the clear liquid in a vial for LC/MS analysis.

Analyses were performed using an Ultra-High Performance Liquid Chromatography (UHPLC) Agilent 1290 Infinity system coupled to Agilent 1290 Infinity Autosampler (G4226A) and Agilent 6540 accurate-mass Quadrupole-Time of Flight (QTOF) Mass Spectrometer (nominal resolution 40.000) equipped with Dual Agilent Jet Stream Ionization source (Agilent Technologies, Santa Clara, CA). Analyses were performed in negative ionization mode by recording data in full scan acquisition using Agilent MassHunter version B.04.00 (B4033.2) software and the experimental condition previously described (Flamini et al., 2014). Briefly, a Zorbax reverse-phase chromatographic column (RRHD SB-C18 3 × 150 mm, 1.8 μm) (Agilent Technologies, Santa Clara, CA), was used, by performing elution by mobile phase composed by A) 0.1% (v/v) aqueous formic acid, and B) 0.1% (v/v) formic acid in acetonitrile. Gradient elution program: 5% B isocratic for 8 min, from 5% to 45% B in 10 min, from 45% to 65% B in 5 min, from 65% to 90% in 4 min, 90% B 10 min isocratic; flow rate: 0.4 mL/min; sample

injection 10 μL; column temperature 35 °C. QTOF conditions were: sheath gas nitrogen 10 L/min 400 °C; dehydration gas 8 L/min at 350 °C; nebulizer pressure 60 psi; nozzle voltage 0 kV negative mode; capillary voltage −3.5 kV; signals recorded in the *m/z* 100–1700 range.

Data analysis was performed by using Agilent MassHunter Qualitative Analysis software B.05.00 (5.0.519.0). Overall identification score of the compounds was calculated by weighted average of the isotopic pattern signals. *Targeted* identification of metabolites was performed by using the homemade HRMS database *GrapeMetabolomics* containing the metabolites identified in grapes and wines (Flamini et al., 2013) using the algorithm "*Find by Formula*".

Targeted MS/MS of parent ions selected in the *m/z* 100–1700 range was performed using collision energies between 20 and 60 eV (acquisition rate 2 spectra/s). Each spectrum was manually interpreted to verify the assignment of the proposed molecular structure to the fragmentation pattern. As a further confirmation the putative structure *in-silico* fragmentation by Molecular Structure Correlator (MSC), was performed. The software assigns the structures based on the mass error of each fragment compared to the theoretical *m/z* value and the likelihood that the fragment forms calculated by utilizing a bond algorithm which generates all possible fragments from the precursor ion and ranks the possibility of formation of each fragment based on the bond strength and stability of the fragments (Flamini et al., 2014; Caffrey et al., 2020).

2.3. Solid phase micro extraction (SPME) - headspace GC/MS analysis

Green coffee samples (30 g) kept under liquid nitrogen, were ground by using an M20 Universal mill (IKA Werke GmbH). For each coffee sample two different preparations were performed: a) a 20-mL SPME vial containing 2.0 g of ground green coffee and 2.0 g of Milli-Q water was vortexed (2 × 15 s) at room temperature (no acid), b) a 20-mL SPME vial containing 2.0 g of ground green coffee, 1.0 g of citric acid and 2.0 g of Milli-Q water was vortexed (2 × 15 s) at room temperature (acid addition at pH ≈ 1.4). The vials were immediately inserted into the autosampler after preparation to keep under strict control the time gap at room temperature from sample preparation to analysis (whole time 30 min before SPME extraction). For the SPME analysis, a 75 μm carboxen/polydimethylsiloxane (CAR/PDMS) fiber (Supelco, Bellefonte, PA, U.S.A.) was used. The fiber was conditioned before use according to the instruction of the manufacturer. Each vial was loaded in the thermostatic autosampler tray and kept at 60 °C for 30 min; during this time, the SPME fiber was inserted into the sample vials and volatile organic compounds (VOCs) were collected. Temperature (60 °C) and stirring were kept constant throughout the extraction period. In the case of the sample preparation where citric acid was added, the consequent hydrolytic process was then performed for a total time of 30 min at room temperature and subsequent 30 min at 60 °C. It has to be highlighted that the citric acid, in addition to promote hydrolytic process, acts as preservative from browning of the sample. After extraction, the SPME fiber was removed and introduced for 10 min into the injector port of the gas chromatograph at 250 °C. Injection of blanks between samples showed no contamination of the fiber, confirming effective cleaning. Gas chromatographic (GC) analyses were performed with an Agilent 6890 gas chromatograph equipped with a 5975 Agilent mass spectrometer (Agilent, Palo Alto, CA, U.S.A.), equipped with an autosampler MPS2 (Gerstel, Mülheim an der Ruhr, Germany), 60 m ZB-WAX capillary column (film thickness 0.25 μm; internal diameter 0.25 mm, Phenomenex, Bologna, Italy). The GC injector was set in split mode (split ratio of 4:1), and the oven temperature, initially set to 50 °C for 3 min, was then increased to 200 °C at 4 °C/min, then again to the final temperature of 240 °C at a rate of 20 °C/min, and held for 5 min. The mass spectrometer was set to electron impact mode (EI) generated at 70 eV, and mass spectra were collected in both "full scan" and SIM mode. Identifications of *cis*-furanlinalool oxide and *trans*-furanlinalool oxide were carried out by mass spectra matching with the NIST11/Wiley10 libraries and the data from the literature (Cantergiani et al., 2001; Saw et al., 2015). Identification of compounds was complemented by the analysis of the pure chemical standards available.

3. Results and discussion

3.1. Identification of monoterpenyl and acyl glycosides in green C. arabica

Due to the relevant fat content of green coffee it was necessary to perform defatting of the samples using n-hexane. Reasonably, possible losses of the glycoside compounds under study were limited by their medium-high polarity. In general, these structures contain a small aglycone linked to a mono or disaccharide and are scarcely soluble also in low-polar organic solvents. For example, in SPE purification of grape extract using C18 cartridge the terpene glycosidic fraction cannot be eluted by dichloromethane but is recovered using methanol (Williams et al., 1982).

By performing *targeted* search of the metabolites previously identified in grape in the chromatograms recorded by Ultra-high performance liquid chromatography/quadrupole-time of flight mass spectrometry (UHPLC/QTOF) around 120 molecular formulae were identified in *C. arabica* extracts with id. score >95%. They include unknown compounds, structures containing caffeoylquinic, di-caffeoylquinic, *p*-coumaroylquinic, feruloylquinic, and caffeoylshikimic acids, di- and trimethoxy cinnamoylquinic and feruloylquinic acids, dimethoxycinnamoyl-hexose isomers, and feruloyl-sinapoylquinic acid (Supplemental Material Table S1). Moreover, some *N*-compounds previously found in coffee, such as caffeoyl-*N*-tryptophan, *p*-coumaroyl-*N*-tryptophan, feruloyl-*N*-tryptophan, and caffeoyl-*N*-tyrosine, were identified (Alonso-Salces et al., 2009a, 2009b; Baeza et al., 2016). Caffeic acid glucoside has also been identified; this compound is present in vegetables (Jaiswal and Kuhnert, 2014) and in the present work it has been detected in *C. arabica* for the first time.

LC-high resolution mass spectrometry (HRMS) analysis provides the direct identification of glycosidic aroma precursors without performing enzymatic hydrolysis, which is commonly used but can affect the results depending on the enzyme used. Moreover, this method provides information on the sugar residue linked to the aglycone which can be useful to select the more suitable enzymes for liberation of the aroma compounds. For example, it was found the type of terminal sugar on a glycoside is relevant for its hydrolysis during wine fermentation: apiofuranose sugars are not hydrolyzed by Saccharomyces glycosidases which instead have hydrolytic capabilities towards glucose, arabinose, and rhamnose (Delcroix et al., 1994).

Because standards of glycosidic monoterpenols and norisoprenoids studied are not commercially available, in previous studies their identification in grape was performed by crossing different orthogonal approaches, such as MS/MS experiments using different collision energies (CE), measurement of accurate masses of the fragments, and crossing data from LC/HRMS and GC/MS analysis performed before and after hydrolysis of grape extracts using glycosidase enzyme (Flamini et al., 2014, 2018). Moreover, the match between the MS/MS spectra and putative structures was studied *in-silico* fragmentation. As a consequence, the compounds were identified by following the recommendations for identification in MS-based metabolomics (Scalbert et al., 2009).

The UHPLC/QTOF chromatograms of *C. arabica* extracts showed an intense peak at retention time (Rt) 17.43 min corresponding to formate adduct ($[M + HCOO]^-$ ion) of putative linalool-hexose-pentose at *m/z* 493.2291 (mass error −0.7 ppm) and the $[M-H]^-$ ion at *m/z* 447.2238 in according to the previous identification of linalool in coffee reported by Weckerle et al. (2003). Moreover, in the 17.2–17.8 min range of chromatogram the peaks of other two monoterpene glycosides not identified in coffee were found. In particular, a putative isomer of linalool-hexose-pentose at *m/z* 493.2291 (mass error −0.1 ppm), previously not identified in grape, and geraniol hexose-pentose at *m/z* 493.2291 (error 0.1 ppm) which eluted in the chromatograms at

retention time (Rt) 17.30 min and 17.77 min, respectively (chromatogram and MS/MS spectra in Fig. 1). Moreover, at Rt 14.35 min the peak of a putative furan/pyran linalooloxide-hexose-pentose ($[M + HCOO]^-$ and $[M-H]^-$ ion signals at *m/z* 509.2240 and *m/z* 463.2187, respectively), were found. Identification of the compounds was confirmed by performing MS/MS fragmentation of $[M + HCOO]^-$ precursor ion. In general, the glycoside compounds were identified by checking the presence of the main hexose-pentose fragments at *m/z* 179.0561, 161.0455 149.0455 and 131.0350, respectively. The main fragments identified are reported in Table 1. Our results are consistent with a recent study in which the glycosyltransferases isolated from *C. arabica* showed to be able to perform glycosylation not only of linalool but also of geraniol and α-terpineol (Ida et al., 2021).

In grape different pentose sugars can be present, such as arabinofuranose, apiofuranose, and xylopyranose (D'Ambrosio, 2019). It is possible that also in green coffee more isomers with different sugars and the same monoterpenic aglycone occur, which are not separated by the chromatographic conditions we used. Further characterization of monoterpenyl diglycosides could be performed by HRMS using chromatography columns more suitable for sugars separation, e.g., phenyl-hexyl or porous graphitic carbon (PGC) which have been already used to study grape (Caffrey et al., 2020).

In parallel, hydrolysis of the same green coffee samples was performed by addition of citric acid and the volatile fraction formed was studied by performing solid-phase micro extraction-gaschromatography/mass spectrometry (HS-SPME-GC/MS) analysis. Compounds whose peaks had a consistent increase after acid addition are reported in Table 2. In particular, the acidification induced a 4-8-fold increase of the linalool peak in Ethiopia, India and Nicaragua samples and 18-fold increase in Rwanda. Reasonably, it was induced by hydrolysis of the intense hexosyl-pentoside conjugate found in the UHPLC/QTOF chromatogram of these samples (peak 2 in Fig. 1).

Geraniol and two linalool oxide isomers were also identified in the GC/MS profiles of the hydrolyzed samples: while geraniol and *trans*-furan inalool oxide were found only after acidification the *cis*-furanlinalooloxide signal was initially present and acidification induced a marked increase.

Despite in the LC/QTOF chromatograms of coffee samples no putative signals of nerol (peak 3 in Fig. 1) and α-terpineol hexose-pentose derivatives, were found (which were identified in grape at Rt 17.58 min and 16.75 min, respectively, Flamini et al., 2014), these two aglycones α-terpineol were identified in the GC/MS chromatograms after citric acid addition.

It was found that acidic hydrolysis of hop (pH 2.7, 90 °C for 1 h) predominantly produced α-terpineol, terpinen-4-ol, linalool, β-damascenone, and geraniol (Sharp et al., 2017). The presence of these compounds in the volatile fraction of acidified coffee samples is consistent with other studies reporting that the acid hydrolysis induces intramolecular rearrangement of sugar released linalool according to the scheme in Fig. 2 (Di Stefano et al., 1992; Skouroumounis and Sefton, 2000; Maicas and Mateo, 2005) and these hydrolytic artifacts can also explain the not fully congruent match between GC/MS and LC/QTOF data.

Relative percentages of the $[M-H]^-+[M + HCOO]^-$ signal intensities sum of glycosidic terpenols identified in the *C. arabica* samples are reported in Table 3. Despite the absolute intensities of the signals of metabolites and the internal standard can differ mainly due to their different ionization yields, the normalization on the signals of heptylglucoside provided the alignment of data among the samples. As a consequence, the data do not provide absolute quantitation of the metabolites in coffee but allow to perform comparison among the different coffee samples. Two samples from Ethiopia showed the highest linalool-

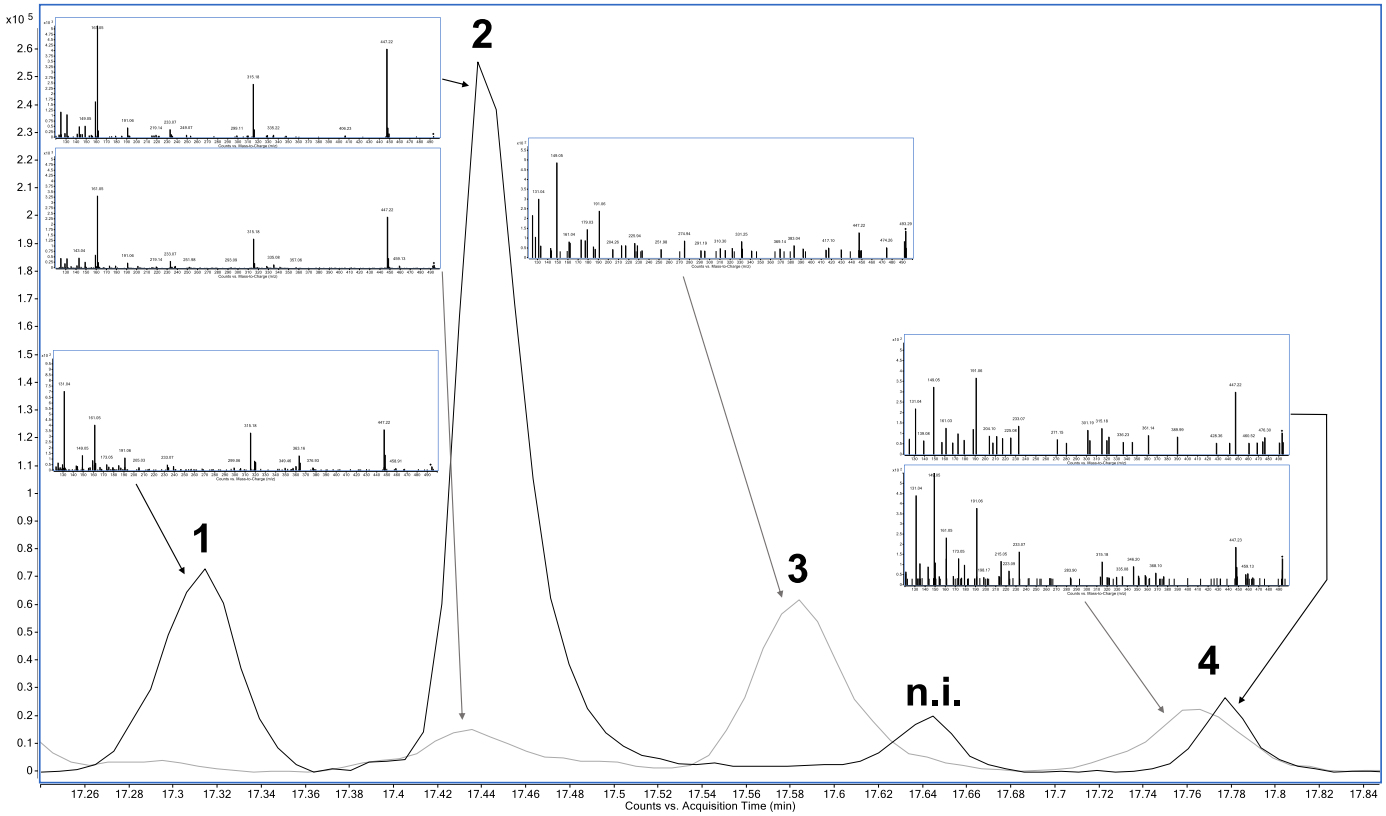

Fig. 1. Overlapping of extract ion chromatograms (EIC) of $[M-H]^-+[M + HCOO]^-$ signals and MS/MS spectra of glycosidic monoterpenes identified in extracts of green *C. arabica* from Ethiopia (black) and Glera *V. vinifera* grape (grey), respectively: **1**. linalool/geraniol hexose-pentose isomer, **2**. linalool hexose-pentose, **3**. nerol hexose-pentose, **4**. geraniol hexose-pentose. **n.i.**, isobaric compound not identified. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1
MS/MS fragments used for identification of monoterpene and C_{13}-norisoprenoid glycoconjugates in green *C. arabica*.

monoterpenes glycosides precursor ion [M + HCOO]⁻	Rt (min)	[M + HCOO]⁻id. score %	main *m/z* fragments		Formula	Error	putative ion
			experimental	theoretical		ppm	
furan/pyran linalool oxide hexose-pentose *m/z* 509.224	14.35	98.8	463.2182	463.2185	C21H35O11	−0.6	formate loss
			331.1761	331.1762	C16H27O7	−0.3	aglycone-hexose
			179.0557	179.0561	C6H11O6	−2.2	hexose frag.
			161.0459	161.0455	C6H9O5	2.5	hexose frag.
			149.0454	149.0455	C5H9O5	−0.7	pentose frag.
			131.0349	131.0350	C5H7O4	−0.8	pentose frag.
linalool/geraniol isomer hexose-pentose *m/z* 493.2291	17.30	99.9	447.2248	447.2236	C21H36O10	2.7	formate loss
			315.1823	315.1813	C16H27O6	3.2	aglycone-hexose
			161.0457	161.0455	C6H9O5	1.2	hexose frag.
			131.0351	131.0350	C5H7O4	0.8	pentose frag.
linalool hexose-pentose *m/z* 493.2291	17.43	98.9	447.2241	447.2236	C21H36O10	1.1	[M−H]⁻
			315.1806	315.1813	C16H27O6	−2.2	aglycone-hexose
			161.0458	161.0455	C6H9O5	1.9	hexose
			131.0353	131.0350	C5H7O4	2.3	pentose
geraniol hexose-pentose*m/z* 493.2291	17.77	99.5	447.2235	447.2236	C21H36O10	−0.2	[M−H]⁻
			315.1818	315.1813	C16H27O6	1.6	aglycone-hexose
			179.0564	179.0561	C6H11O6	1.7	hexose frag.
			161.0461	161.0455	C6H9O5	3.7	hexose frag.
			131.0354	131.0350	C5H7O4	3.1	pentose frag.
			149.0451	149.0455	C5H9O5	−2.7	pentose frag.
Acyl glycoside							
3-methylbut-2-enoyl-hexosyl-pentoside *m/z* 439.1457	12.48	92.2	293.0878	293.0878	C11H17O9	0.0	hexose-pentose frag.
			161.0453	161.0455	C6H9O5	−1.2	hexose
			149.0463	149.0455	C5H9O5	5.3	pentose frag.
			99.0459	99.0452	C5H7O2	7.0	aglycone
3-methylbutanoyl-hexosyl-pentoside *m/z* 441.1614	13.21	97.8	293.0875	293.0878	C11H17O9	−1.0	hexose-pentose frag.
			191.0555	191.0561	C7H11O6	−3.1	hexose-pentose frag.
			101.0608	101.0608	C5H9O2	0.0	aglycone
3-methylbutanoyl-hexosyl-hexoside *m/z* 471.1719	13.23	99.2	425.1656	425.1664	C17H29O12	−1.9	[M−H]⁻
			323.0977	323.0984	C12H19O10	−2.2	[M−aglycone−H]⁻
			101.0610	101.0608	C5H9O2	2.0	aglycone
C_{13}-norisoprenoid glycosides							
3-oxo-α-ionol/3-hydroxy-β-damascone hexosyl-pentoside *m/z* 547.2341	13.13	91.3	205.1238	205.1234	C13H17O2	2.0	agycone-H_2
			221.0674	221.0667	C8H13O7	3.2	hexose-pentose frag.
			161.0461	161.0455	C6H9O5	3.7	hexose frag.
			153.0926	153.0921	C9H13O2	3.3	damascone frag.
			152.0846	152.0843	C9H12O2	2.0	damascone rad.
			131.0355	131.0350	C5H7O4	3.8	pentose frag.
vomifoliol-hexoside *m/z* 431.1944	13.82	85.0	385.1869	385.1868	C19 H29 O8	0.3	formate loss
			205.1232	205.1234	C13H17O2	−1.0	aglycone-H_2O
			179.0558	179.0561	C6H11O6	−1.7	hexose frag.
			153.0925	153.0921	C9H13O2	2.6	damascone frag.

Table 2
SPME-GC/MS peak areas (arbitrary unit) of terpenols, norisoprenoids, and acyl glycoconjugate-related compounds identified in the volatile fraction of green *C. arabica* samples before and after citric acid addition. *, sample added by citric acid. nd, not detected.

volatile compounds	Ethiopia 1	Ethiopia 1*	Ethiopia 2	Ethiopia 2*	India	India*	Nicaragua	Nicaragua*	Rwanda	Rwanda*
linalool	370437	1705750	326682	1299166	31320	220773	58089	509232	28450	546098
α-terpineol	nd	250661	nd	202731	nd	48520	nd	85175	nd	91347
nerol	nd	72037	nd	52104	nd	nd	nd	21061	nd	23517
geraniol	nd	150832	nd	153870	nd	32554	nd	53998	nd	58035
β-damascenone	nd	132428	nd	121000	nd	93322	nd	180144	nd	151975
cis-furan linalool oxide	17851	54042	43831	99874	26691	56740	54497	58628	27336	51414
trans-furan linalool oxide	nd	14604	8878	25269	nd	13068	nd	12919	nd	11923
isovaleric acid	398135	2649207	290271	2099622	217381	1761377	193846	1475467	484366	1883866
3-methyl-2-butenoic acid	93716	318058	60271	248664	23971	60864	21794	72425	40911	107331

hexose-pentose and linalooloxide-hexose-pentose signals, instead geraniol-hexose-pentose was higher in the "Rwanda" sample. A previous study reported a high terpene content in Ethiopian *C. arabica* roasted coffee powder and coffee brews (Yener et al., 2015). As far as we know, it is the first time that linalool, linalooloxide isomers and geraniol glycosides were detected in coffee from geographic origins different from Ethiopia. In general, both LC/MS and post-hydrolysis GC/MS chromatograms of Ethiopia samples showed highest signals of glycosidic terpenols and of their aglycones (Tables 2 and 3) and despite probable rearrangements of linalool was promoted by acid hydrolysis linear correlation among the data, was found (Fig. 3).

Moreover, the signals of three putative acyl-glycosides (not identified in grape) were found in coffee. They are in agreement with three compounds previously identified by Iwasa et al. (2015) and Nakahara

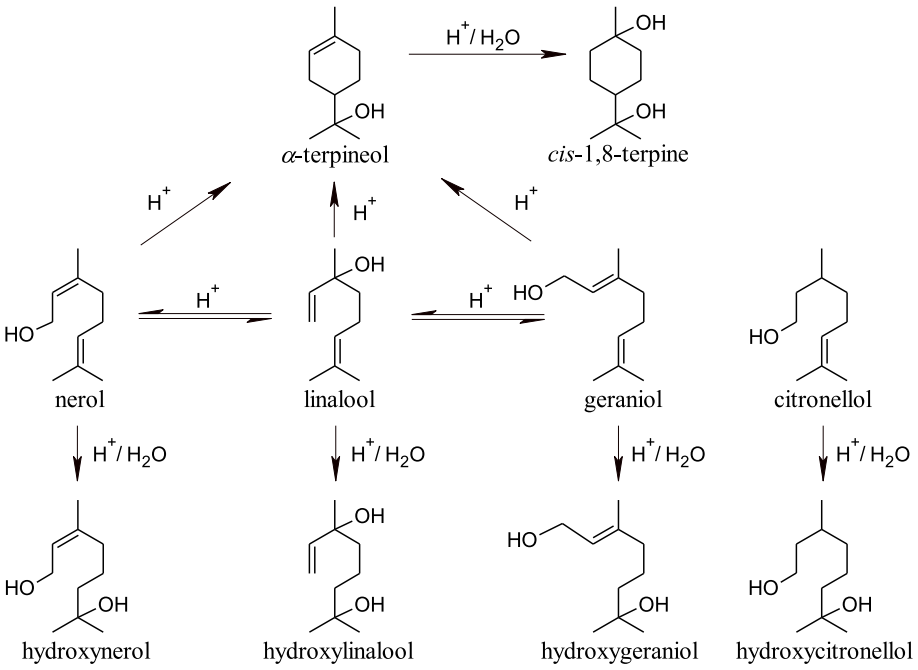

Fig. 2. Rearrangements of linalool promoted by acid conditions (by Di Stefano et al., 1992; Skouroumounis and Sefton, 2000; Maicas and Mateo, 2005).

Table 3
$[M-H]^-+[M + HCOO]^-$ signal intensities and relative percentages (rel.%) of aroma glycoconjugate precursors identified in extracts of *C. arabica* from different geographical origins (signals normalized to the IS; SD, standard deviation of four samples).

	C. Arabica geographical origin														
	Ethiopia 1			Ethiopia 2			India			Nicaragua			Rwanda		
	signal	SD	rel. %	signal	SD	rel. %	signal	SD	rel. %	signal	SD	rel. %	signal	SD	rel. %
monotepenyl glycosides															
linalool-hexose-pentose isomer	183752	25046	92	199168	39755	**100**	33427	2712	17	30723	2674	15	92180	28603	46
linalool-hexose-pentose	720480	148887	93	778828	168487	**100**	110257	8599	14	214026	24148	27	241271	65299	31
geraniol-hexose-pentose	58301	2157	57	63568	6944	62	75368	4281	73	94786	5849	92	102909	16958	100
trans/cis furan/pyran linalool oxide-hexose-pentose	136770	21544	83	164759	28415	**100**	25242	2437	15	36343	1442	22	49894	16921	30
acyl glycosides															
3-methylbut-2-enoyl-hexosyl-pentoside	159523	7498	41	149443	19472	39	195902	8245	51	137263	11460	36	385477	99654	**100**
3-methylbutanoyl-hexosyl-hexoside	989013	168023	**100**	931558	177346	94	327609	21587	33	220526	22234	22	760420	241471	77
3-methylbutanoyl-hexosyl-pentoside	426558	61219	86	465123	79446	94	290388	12696	58	164677	16917	33	497254	148881	**100**
C_{13}-norisoprenoid glycosides															
3-oxo-α-ionol/3-hydroxy-β-damascone pentosyl-hexoside	56942	4646	70	81469	23966	**100**	47778	4780	59	44369	9952	54	51411	5465	63
vomifoliol-hexoside	616459	15939	**100**	606072	60192	98	545750	24734	89	475469	33466	77	422021	96009	68

and Iwasa (2016), such as 3-methylbut-2-enoyl-hexosyl-pentoside, 3-methylbutanoyl-hexosyl-pentoside, and 3-methylbutanoyl-hexosyl--hexoside. In particular, the fragments at *m/z* 425.167, *m/z* 323.098, and *m/z* 161.044 match with those observed by Iwasa et al. (2015) in the HR-MS/MS spectrum of $[M + HCOO]^-$ precursor ion at *m/z* 471.171 of 3-methylbutanoyl-hexosyl-hexoside (Table 1).

In Table 3 their relative percentages in the samples calculated on the $[M-H]^-+[M + HCOO]^-$ intensities, are reported. Previously, these compounds were found in *C. arabica* from Ethiopia and Guatemala (Weckerle et al., 2002; Iwasa et al., 2015) and have been indicated as possible causative metabolites determining coffee quality and key compounds useful for green bean selection. Differences in provenance affect the concentrations of several potent odorants in roasted *C. arabica* (Mayer et al., 1999). Different geographical origins infer different environment, agronomical practices, post-harvest treatments and storage conditions which can remarkably affect the composition of non-volatile raw coffee components acting as aroma precursors.

The presence of these compounds in coffee samples from India, Nicaragua and Rwanda is here reported for the first time and this fact is particularly interesting for both biological implications and quality assessment purposes. It is noteworthy to stress that after citric acid addition, the peaks of 3-methyl-2-butanoic acid and isovaleric acid in the GC/MS chromatograms increased markedly reasonably due to hydrolysis of the glycoconjugates (Table 2). It has to be highlighted the

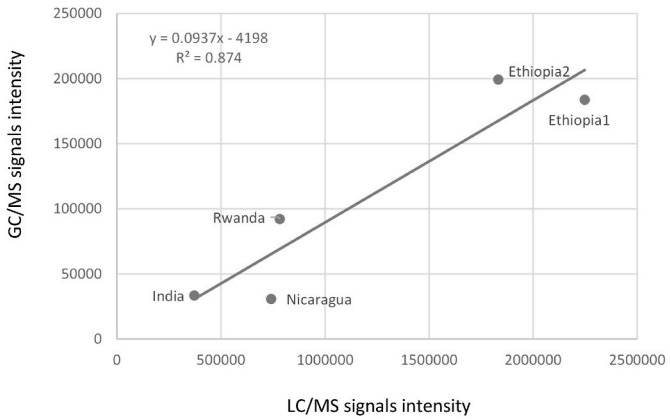

Fig. 3. LC/MS *vs* post-hydrolysis GC/MS normalized signals of the glycosidic terpenols and their aglycones identified in coffee samples (sum of the signals, is reported).

high signals of 3-methylbut-2-enoyl-hexosyl-pentoside, 3-methylbutanoyl-hexosyl-pentoside, isovaleric acid and geraniol-hexose-pentose found in *C. arabica* from Rwanda make this sample a fertile ground for further studies.

3.2. C_{13}-norisoprenoid glycosides

In the UHPLC/QTOF chromatograms of coffee extracts the peaks of two putative C_{13}-norisoprenoid glycosides, were found. The signals correspond to 3-oxo-α-ionol hexose-pentose (the aglycone was previously reported in coffee), or alternatively to the isobar 3-hydroxy-β-damascone pentosyl-hexoside, and vomifoliol-hexoside (roseoside if the glucose molecule is linked at C9) which was found also in grape. Overlapping of vomifoliol-hexoside peaks and the mass spectra in green *C. arabica* from Ethiopia and Glera grape extracts are shown in Fig. 4. In general, norisoprenoids form by degradation of carotenoids according to the scheme Fig. 5. Carotenoids in green coffee have been the subject of previous studies, and possible precursors of norisoprenoids have been quantified in green coffee (Simkin et al., 2010). In a recent study, the $[M + HCOO]^-$ precursor ion of vomifoliol-hexoside at *m/z* 431.1944 was characterized in grape by HR-MS/MS and main fragments were observed at *m/z* 385.1868, *m/z* 179.0561, *m/z* 205.1234, and *m/z* 153.0921 (Wei et al., 2021). The putative $[M + HCOO]^-$ ion of 3-oxo-α-ionol/3-hydroxy-β-damascone pentosyl-hexoside (*m/z* 547.2341) was characterized according to the fragmentation pattern proposed in Fig. 6. Identification of these compounds in coffee is here reported for the first time (Table 1). Anyway, future studies will need to confirm the identification and distinguish between the two isomers.

Previously, also 3-oxo-7,8-dehydro-β-ionol was reported in coffee (Degenhardt et al., 2006) but the UHPLC/QTOF chromatograms of our samples did not show any signal corresponding to this compound or its hexose or pentose-hexose derivative. Both 3-oxo-α-ionol and 3-hydroxy-β-damascone are precursors of β-damascenone which is an important aroma compound characterized by very low sensory threshold (0.002 ppb) and floral note (Skouroumounis and Sefton, 2002). In Riesling wine, 3-hydroxy-β-damascone and β-damascenone are usually present with 1:9 ratio (Versini et al., 2002).

In general, signal intensity of 3-oxo-α-ionol/3-hydroxy-β-damascone in coffee extracts was higher than in grape, and the signals of glycosidic norisoprenoids in the two Ethiopia samples were higher with respect to the others *C. arabica* samples (Table 3). The SPME-GC/MS chromatograms of the coffee samples after citric acid addition showed the peak of β-damascenone which was not present before the acidification (Table 2). In the LC/QTOF chromatogram of coffee extracts any putative peak corresponding to a hexose or pentose-hexose derivative of this compound, was found, but only that of putative 3-hydroxy-β-damascone

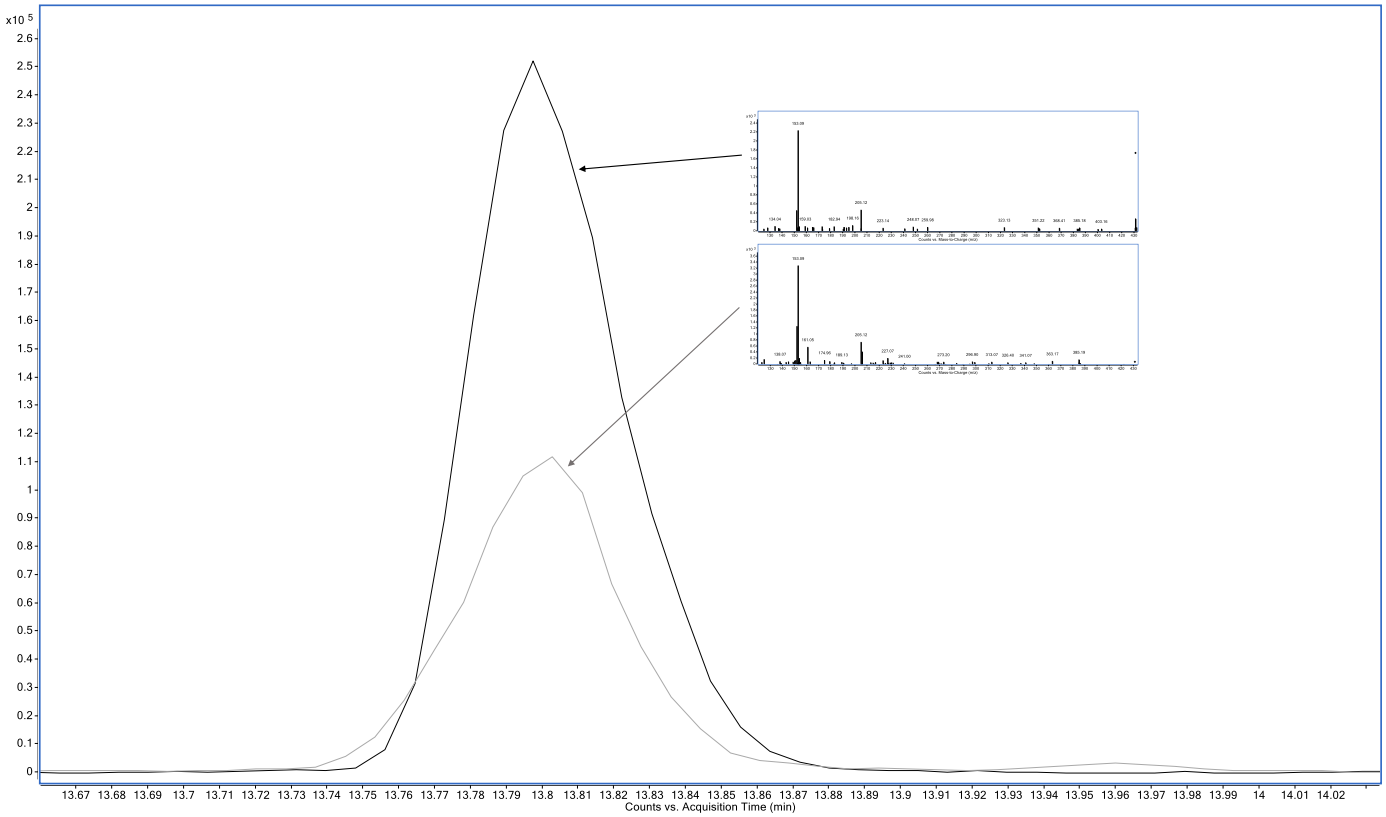

Fig. 4. Overlapping of $[M-H]^-$+$[M + HCOO]^-$ EICs and MS/MS spectra of vomifoliol-hexoside identified in extracts of Ethiopia green *C. arabica* (black) and Raboso *V. vinifera* grape (grey), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

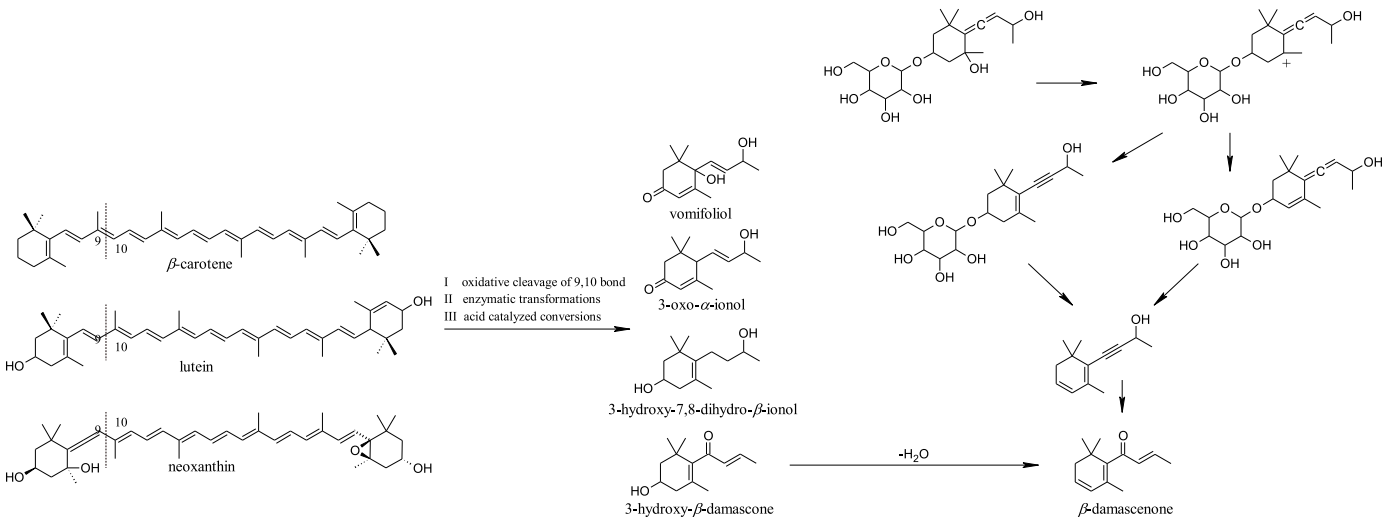

Fig. 5. Formation of β-damascone from putative C_{13}-norisoprenoid precursors identified in green *C. arabica* (Williams et al., 1982; Wirth et al., 2001; Versini et al., 2002).

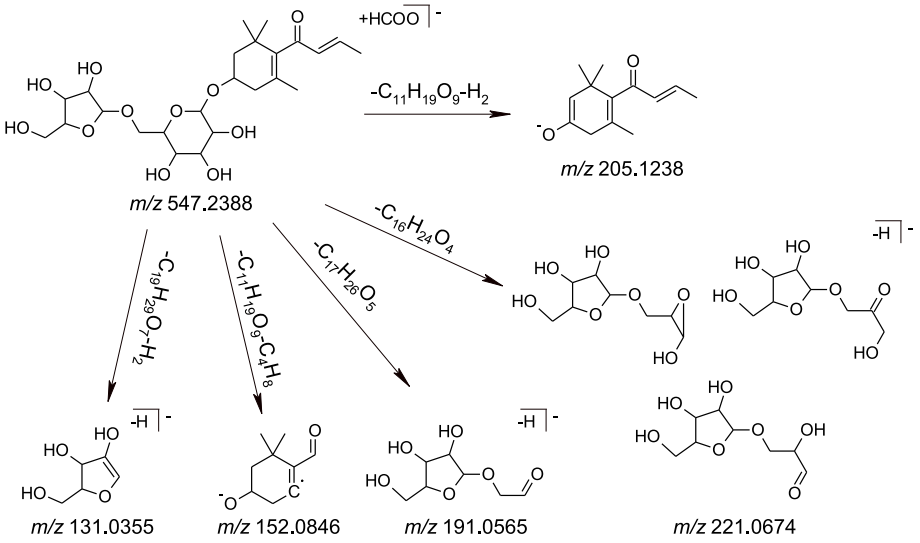

Fig. 6. Fragmentation proposed for 3-hydroxy-β-damascone hexose-pentose putatively identified in *C. arabica*.

hexosyl-pentoside. Reasonably, the formation of β-damascenone in the volatile fraction of coffee could occur by hydrolysis and dehydration of this precursor according to the scheme in Fig. 5 (Williams et al., 1982; Wirth et al., 2001).

4. Conclusions

The present study enlarges the panorama of glycoside aroma precursors in green *C. arabica* which were detected in samples from different geographical origins. This botanical species contains mainly terpenols and norisoprenoids as disaccharide glycosides with a hexose sugar directly bound to the aglycone similarly to grape, and it has considerable amount of linalool stored as hexosyl-pentoside derivative. In addition, other three monoterpenyl glycosides were identified for the first time, such as geraniol hexosyl-pentoside, furan/pyran linalooloxide hexosyl-pentoside, and another linalool-hexosyl-pentoside isomer, and two C_{13}-norisoprenoid glycosides, such as 3-hydroxy-β-damascone (or 3-oxo-α-ionol) hexosyl-pentoside, and vomifoliol-hexoside. Because no signals of β-damascenone glycosides, were found, reasonably the presence of this aroma compound in the volatile fraction of green coffee after acid addition originates by hydrolysis and dehydration of 3-hydroxy-β-damascone glycoside precursor.

It has to be highlighted that study of glycosidic aroma compounds in green coffee is remarkably important for at least two reasons: because the aglycones released during the roasting process greatly contribute to enrich the coffee aroma profile (to this regard the influence of the coffee geographical origin is strongly related to its quality), and because glycosides are the result of biosynthetic pathways not yet completely disclosed in coffee and their identification can shed light on biochemistry, physiology, and genetic aspects.

Findings of this study are therefore useful in terms of deepening of knowledge on possible new green *C. arabica* molecular markers and provide objective tools to assess coffee quality.

CRediT authorship contribution statement

Mirko De Rosso: Methodology, Data curation, Software, Validation. **Valentina Lonzarich:** Methodology, Data curation, Software, Validation. **Luciano Navarini:** Conceptualization, Funding acquisition, Writing – original draft, Data curation. **Riccardo Flamini:** Conceptualization, Funding acquisition, Writing – original draft, Data curation.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.crfs.2022.01.026.

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