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Analysis of volatile compounds, α-dicarbonyl compounds, and acetic acid in Robusta coffee by soaking with D-xylose and D-ribose

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Abstract

Background The study investigated the impact of D-xylose and D-ribose soaking methods (autoclaved and non-autoclaved) on Robusta coffee's volatile compounds, α-dicarbonyl compounds (α-DCs), and acetic acid. Robusta coffees were soaked with D-xylose and D-ribose solutions, and the beans were dried until constant moisture content and lightly roasted.

Results The sugar treatment led to an 85.6% reduction in pyrazine levels and a 64.4% decrease in pyridine, while pyrroles and furans increased significantly by 84.4% and 16.4%, respectively ($p < 0.05$). The total concentration of α-DCs was decreased by 24.6–69.2%, with the autoclaved D-xylose sample exhibiting the lowest among all samples. Acetic acid concentration was lower in non-autoclaved samples compared to autoclaved samples ($p < 0.05$). Principal component analysis indicated autoclave-treated pentose pretreatment reduced pyrazines and increased in the levels of 1-furfurylpyrrole, methyl furfuryl disulfide, 4-ethyl-2-methoxy-phenol, 2-methoxyphenol, 2-acetylpyrrole, pyridine, furfuryl acetate, and acetic acid.

Conclusion This study, utilizing GC–MS, GC–NPD, and HPLC–UV for compound quantification, offers valuable insights into the changes of volatiles, α-DCs, and acetic acid in Robusta coffee soaking with D-xylose and D-ribose, suggesting potential applications in the coffee industry to modulate flavor profiles.

Keywords Robusta coffee, D-xylose, D-ribose, α-dicarbonyl compounds, Volatile compounds

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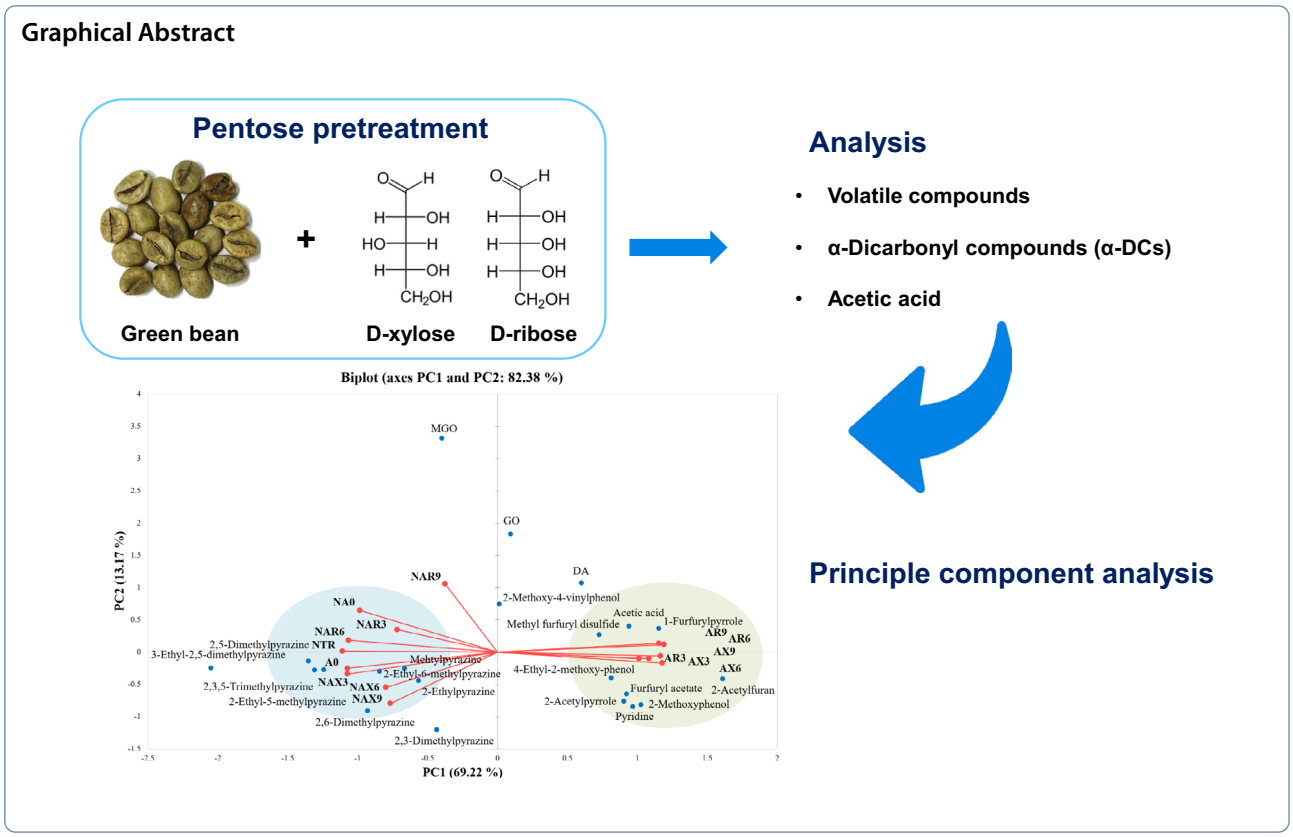

Introduction

As popularity of coffee has been grown over many years, the coffee consumption has been increased along with the soaring demand of the coffee. Green coffee bean mainly is composed of carbohydrates, lipids, and proteins [1]. Due to the chemical composition of the coffee, non-enzymatic browning reaction occurs during roasting process. The caramelization and Maillard reaction (MR), which are the main reaction of non-enzymatic browning, are the main chemical reaction and affect chemical changes including volatile compounds, brown color, and unpleasant toxic compounds through roasting process [2–4]. To control quality and safety of coffee, the investigation of those chemical changes on various coffee is necessary.

The Maillard reaction (MR) is normally explained by three stages; the initial, intermediate, and final stage (Figure S1). Commencing with a condensation reaction between an amino group and a reducing sugar, the MR unfolds in its initial stage. The intermediate stage commences with the Amadori/Heyns product, initiating the generation of sugar fragmentation products and the liberation of the amine group. Then, dehydration, fragmentation, cyclization, and polymerization with reparticipation of amino group occur in the final stage [5, 6].

Caramelization occurs when sugar is heated with high temperature without amino group and affected by pH and sugar concentrations [7]. Sugar isomerization and sugar degradation reaction are included in caramelization. In general, monosaccharides are initiated with enolisation and sugar degradation reactions occur in sequence [8]. 5-Hydroxymethylfurfural and α-dicarbonyl compounds are formed in both caramelization and the MR [9–13].

In the Spanish coffee market, there is a traditional practice known as Torrefacto coffee, where sucrose (not exceeding 15% by weight) is added directly to the coffee at the end of the roasting process. The addition of sugar results in bitter taste and decreases aroma of coffee [14]. To avoid burnt flavor and increase the aroma through the Maillard reaction and caramelization, pentose pretreatment was used by soaking in solution in this study. As for our knowledge, only hexoses have been used with soaking method and there are no studies on the impact of coffee treated with pentose [15, 16]. In this study, D-xylose and D-ribose were chosen, since they have higher browning development property [17].

The specific aim of this study was to investigate the impact of pentose pretreatment on Robusta coffee following the roasting process. Green Robusta coffee bean

was soaked with D-xylose and D-ribose solution (0, 3, 6, and 9% w/v) with and without autoclave (100 ℃, 30 min). Autoclave was used to compare the difference between non-autoclaved and autoclaved samples. Volatile compounds, α-dicarbonyl compounds, and acetic acid were analyzed in treated and non-treated roasted Robusta coffee beans.

Materials and methods

Chemical reagents and materials

Green coffee beans (*Coffea robusta* from Vietnam), D-(+)-Xylose (≥ 99%) [Sigma-Aldrich Chemical Co. (St. Louis, MO, USA)], D-Ribose (≥ 99%) [Sigma-Aldrich Chemical Co. (St. Louis, MO, USA)], and HPLC-grade water [J.T.Baker (Philipsburg, NJ, USA)] were used for the preparation of coffee samples.

3-Ethyl-2,5-dimethylpyrazine, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 1-furfurylpyrrole, 2-acetylpyrrole, 2-methoxy-4-vinylphenol, 4-ethyl-2-methoxy-phenol, methylglyoxal at a purity 40% and diacetyl at a purity 97%, 1-methylpyrazole, o-phenylenediamine, and acetic acid (≥ 99%) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). 2-Ethylpyrazine, 2-methoxyphenol, glyoxal at a purity 39%, and quinoxaline, were purchased from Tokyo Chemical Industry Co., Ltd. C7-C40 n-alkane standard and divinylbenzene/Carboxen/Polydimethylsiloxane (50 µm DVB/CAR/PDMS) solid-phase microextraction (SPME) fiber were purchased from Supelco Inc. (Bellefonte, PA, USA). Ethyl acetate, methanol, and HPLC-grade water were purchased from J.T.Baker (Philipsburg, NJ, USA). Hydrochloric acid (HCl), potassium phosphate monobasic, potassium phosphate dibasic, and phosphoric acid were purchased from Daejung Chemical & Metals Co., Ltd. (Gyeonggi-do, Korea). A 50 mM potassium phosphate buffer (pH 7.0) was formulated using potassium phosphate monobasic and potassium phosphate dibasic.

Pentose pretreatment of coffee samples

The pentose pretreatment of coffee samples is illustrated in Figure S2, and the corresponding samples are detailed in Table S1. Specifically, 200 g of green coffee beans were immersed in 200 mL of D-xylose and D-ribose solutions with varying concentrations (0%, 3%, 6%, and 9% w/v). Then, green coffee beans were soaked under two conditions; soaking under non-autoclaved and autoclaved condition (AC-60, HYSC, Seoul, Korea) at 100 ℃ for 30 min. After that, solution was drained and soaked green coffee beans were washed with 500 mL of HPLC-grade water. Drying was conducted at 50 ℃ until reaching the same moisture content (around 10.1 ± 0.1%) (LD-918, L'EQUIP, Seoul, South Korea).

Green coffee beans underwent roasting at 235 ℃ for 15 min using a coffee bean roaster (CBR-101A, Gene café, Korea) and were subsequently ground with a coffee grinder (Delonghi KG200, Treviso, Italy). Ground coffee samples were sealed in storage bag and stored at -80 ℃ before analysis. For extraction, 12.5 g of ground coffee powder was subjected to a process using 100 mL of filtered water through an espresso coffee machine (Delonghi ECO311, Treviso, Italy).

Analysis of volatile compounds in coffee by GC–MS

The volatile compounds in coffee samples were analyzed using Headspace Solid-Phase Microextraction–Gas Chromatography–Mass Spectrometry Detector (HS-SPME–GC-MSD) [4]. For this analysis, 10 mL of espresso coffee samples were placed in a 20 mL headspace vial containing 1 g of sodium chloride. Internal standard quinoxaline (10 µL of 1,000 µg/mL) and an n-alkane standard (20 µL of 10 µg/mL) were introduced into the samples. The vial was then heated on a hotplate at 70 ℃ for 10 min to reach equilibrium. The SPME fiber, Divenylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS), was introduced into the vial to adsorb volatile compounds in the headspace at 70 ℃ for 40 min. Subsequently, the volatile compounds were desorbed into the GC injection port at 230 ℃ for 10 min. It was performed using an Agilent 7820A GC with a 5977E MS detector (Agilent Technologies, Santa Clara, CA). A DB-WAX UI column (60 m × 250 µm × 0.25 µm, J&W Scientific, Folsom, CA) was employed to separate the peaks of volatile compounds. The GC oven temperature was initially held at 44 ℃ for 5 min, increased to 170 ℃ at a rate of 3 ℃/min, held for 10 min, and finally raised to 240 ℃ at 8 ℃/min for 5 min. Helium was used as the carrier gas at a constant flow rate of 1.0 mL/min. The ionization mode was electron impact at 70 eV, and the scan range was 50–550 m/z.

The identification of volatile compounds involved comparing retention indices (RI) using n-alkanes (C7-C40) with reference values (Kovat's index) on DB-WAX UI, analyzing mass spectrum data from reference libraries (NIST08, Wiley), and co-injection method. The quantification of volatile compounds was represented with peak area ratio (peak area of each compound/peak area of internal standard, quinoxaline).

Analysis of α-DCs in coffee by GC-NPD

The α-DCs in coffee samples were derivatized to quinoxalines using o-phenylenediamine, followed by a liquid–liquid extraction (LLE) procedure [18–21]. In a 20 mL headspace vial, 3 mL of coffee sample and 2 mL

of o-phenylenediamine solution (0.01 g/mL) were combined. The mixed solution was adjusted to a pH of 12 using sodium hydroxide, and the derivatization process was carried out by stirring for 2 h at 600 rpm. Subsequently, 5 mL of ethyl acetate and 20 µL of 1-methyl pyrazole (internal standard, 500 µg/mL) were introduced into the derivatized solution. Then, it was shaken at 280 rpm for 5 min to extract quinoxalines. Centrifugation was conducted (Combi 514R-refrigerated large-capacity centrifuge, Hanil Science Industrial Co. Ltd., Incheon, Korea) for 10 min at 1,259 xg at 4℃. The supernatant (1 µL) was collected, and quantitative analysis was conducted by gas chromatography–nitrogen-phosphorus (GC-NPD) detector.

The analysis of α-DCs was conducted using Agilent 6890 GC-NPD system (Agilent Technologies, Santa Clara, CA) equipped with an autosampler and DB-WAX column (30 m × 0.25 mm × 0.25 µm, J&W Scientific, Folsom, CA). The oven temperature was initially held at 40 °C for 2 min, then raised at 20 °C/min to 170 °C, and maintained for 15 min. The post-run was implemented at 230 °C for 15 min. The temperature of the injector was 260 °C and detector was 300 °C. Helium gas was used as the carrier gas at a constant flow of 1.5 mL/min at splitless mode. Nitrogen was used as the make-up gas at 5 mL/min. The ionization was held using air and hydrogen at 120 and 2 mL/min, respectively. Blos-bead (Agilent Technologies, Santa Clara, CA) was used as the NPD bead. The analysis of α-DCs was carried out when baseline of the signal was between 20 and 25 pA.

Analysis of acetic acid in coffee by HPLC

Solid-phase extraction (SPE) was conducted with Strata Sax (55 mm, 70 Å) 500 mg/3 mL (Phenomenex, Torrance, CA). 1 mL of espresso coffee sample was diluted with 2 mL of 50 mM potassium phosphate buffer (pH 7.0). Anion exchange cartridges were conditioned with 3 mL of methanol and 3 mL of HPLC-grade water. The cartridge was loaded with 3 mL of diluted coffee sample and washed with 2 mL of HPLC-grade water. The final solution was used for analysis after filtration through a 0.45-µm pore membrane filter (BioFACT, Seoul, Korea).

Acetic acid in coffee was analyzed using high-performance liquid chromatography (Agilent 1200 series, Agilent Technologies, Waldbronn, Germany) with a slight modification of [22, 23]. Separation was performed on an analytical Zorbax SB-C18 column (250 mm × 4.6 mm, 5 µm) at 25 ℃ with ultraviolet detection at 210 nm. Injection volume was 10 µL and all standards and coffee samples were injected in triplicate. The analysis was run in an isocratic mode, with mobile phases of 25 mM potassium phosphate buffer (adjusted to pH 1.8 with phosphoric acid) with methanol (96:4, v/v) at a flow rate of 0.64 mL/min. The solvents were filtered, degassed, and sonicated before analysis.

Measurements of pH and color value

pH values of grinded green coffee bean and roasted coffee bean powder were measured with pH meter (SevenEasy, Mettler Toledo Co., Ltd., USA) at room temperature in triplicate.

Colors of grinded green coffee bean and roasted coffee bean powder were measured with a color meter (NIPON DENSHOKU Industries CO., Ltd., Tokyo, Japan). The L* value [light (L* = 100) and dark (L* = 0)], a* value [red (+) and green (−)], and b* value [yellow (+) and blue (−)] were measured. The ΔE index was calculated from the Hunter–Schofield equation.

$$\Delta E = \sqrt{(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2}.$$

Statistical analysis

Experiments were replicated three times and quantitative data were expressed as mean ± standard deviation (SD). One-way analysis of variance (ANOVA) tests and Duncan's test were conducted by IBM SPSS Statistics 23 (IBM, Chicago, USA) were used for analysis. Principal component analysis (PCA) was performed with XLSTAT (v.2021, Addinsoft, Paris, France).

Results and discussion

Identification of volatile compounds in coffee samples

A total of 18 volatile compounds, comprising 9 pyrazines, 1 pyridine, 2 pyrroles, 3 furans, and 3 phenols, were analyzed in 15 samples of untreated and treated Robusta coffee. The chromatogram of non-treated Robusta sample is shown in Fig. 1. Kovat's retention index (KI), Wiley Library of mass spectrum, and co-injection with authentic chemicals were used to identify volatile compounds. Their Kovat's retention index, identification method, and aroma description are illustrated in Table 1. All values of the volatile compounds were represented as the peak area ratio (peak area of each peak/peak area of internal standard).

Analysis of volatile compounds in coffee samples by GC–MS

The levels of the total peak ratio of volatile compounds were in the range of 28 (NAR3) to 43 (NTR). The total amount of each group of volatile compounds is in Table 2. Pyrazines, pyridine, pyrroles, furans, and phenols were, respectively, ranged from 2.08 (AR9) to 14 (NTR), from 0.7 (NAR3) to 3.0 (NTR), from 3.71 (NA0)

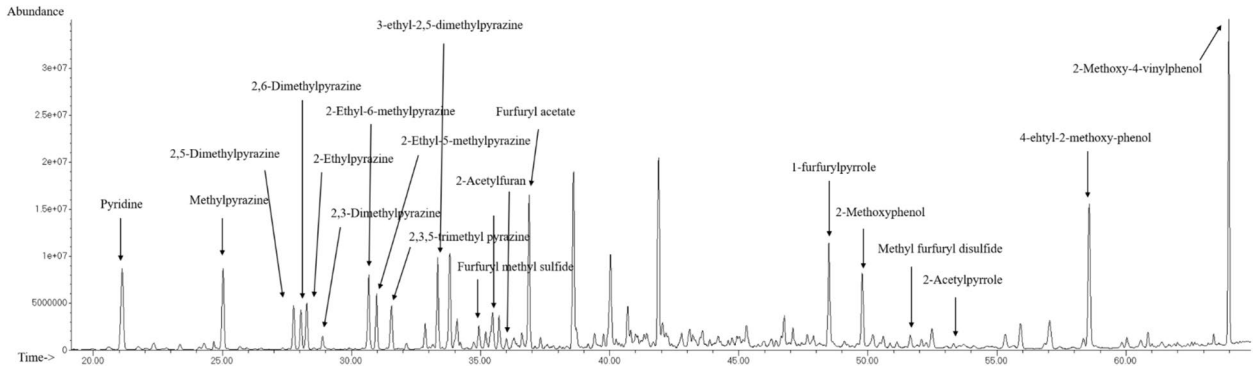

Fig. 1 Chromatogram of volatile compounds in non-treated Robusta (NTR) coffee sample

Table 1 Volatile compounds in roasted Robusta coffee samples non-autoclaved and autoclaved with D-xylose and D-ribose

No	Volatile compounds	KI	KI (Ref.)[a]	Identification method[b]	Aroma description
Pyrazine					
1	Methylpyrazine	1281	1281	MS, KI	Nutty, roasted, sweet, chocolatey
2	2,5-Dimethylpyrazine	1340	1339	MS, KI, CO	Roasted, cocoa, beefy
3	2,6-Dimethylpyrazine	1346	1346	MS, KI, CO	Nutty, sweet, fried
4	2-Ethylpyrazine	1351	1352	MS, KI, CO	Musty, nutty, peanut butter
5	2,3-Dimethylpyrazine	1364	1363	MS, KI, CO	Nutty, cocoa-like
6	2-Ethyl-6-methylpyrazine	1401	1402	MS, KI	Roasted baked potato
7	2-Ethyl-5-methylpyrazine	1409	1411	MS, KI	Coffee, roasted
8	2,3,5-Trimethylpyrazine	1422	1421	MS, KI	Baked potato, hazelnut
9	3-Ethyl-2,5-dimethylpyrazine	1463	1460	MS, KI, CO	Earthy, roasted
Pyridine					
10	Pyridine	1197	1196	MS, KI	Pungent, burnt, smoky
Pyrrole					
11	1-Furfurylpyrrole	1840	1838	MS, KI, CO	Cocoa, green, roast
12	2-Acetylpyrrole	1965	1966	MS, KI, CO	Bread, cocoa, hazelnut, licorice, walnut
Furan					
13	2-Acetylfuran	1517	1518	MS, KI, CO	Coffee-like
14	Furfuryl acetate	1546	1550	MS, KI, CO	Mild, ethereal-floral fruity
15	Methyl furfuryl disulfide	1910	1820	MS, KI	Slight sulfuraceous coffee-like meaty
Phenol					
16	2-Methoxyphenol	1876	1876	MS, KI, CO	Smoky, burnt, phenol, wood
17	4-Ethyl-2-methoxy-phenol	2051	2054	MS, KI, CO	Clove, phenol, spice
18	2-Methoxy-4-vinylphenol	2303	2230	MS, KI, CO	Spicy, clove-like roasted peanut

[a] Kovats retention index (KI) on DB-WAX UI in NIST database

[b] Identification method: MS = Comparison with mass spectrum in Wiley Library; KI = Kovats Retention Index obtained from standard and literature values on DB-WAX; CO = Co-injection with authentic chemicals

to 8.9 (AX9), from 3.6 (NAR3) to 11.2 (AX9), and from 14 (NA0 and NAR3) to 19 (A0, AX9, and AR6). The phenol group showed the highest peak area ratio among the 5 volatile compound groups. In total level of pyrazines, the sample pretreated with 9% ribose solution and soaked using autoclave (AR9) was decreased by 85% after pretreatment compared to NTR (non-treated Robusta). In total pyridine, the sample pretreated with 3% D-ribose solution and soaked without using autoclave (NAR3) was decreased by 77% after pretreatment compared to NTR. In total pyrroles, the sample pretreated with distilled water and soaked without using autoclave (NA0) was decreased by 23% compared to NTR followed by the sample pretreated with 3% D-ribose solution and soaked

Table 2 Peak area ratio of volatile compounds in roasted Robusta coffee samples non-autoclaved and autoclaved with D-xylose and D-ribose

Compounds	NTR	Non-autoclaved						
		NA0	NAX3	NAX6	NAX9	NAR3	NAR6	NAR9
Methylpyrazine	2.60 ± 0.60^{j}	1.30 ± 0.10^{de}	1.40 ± 0.03^{ef}	1.40 ± 0.20^{efg}	2.20 ± 0.40^{h}	1.80 ± 0.30^{gh}	1.20 ± 0.07^{de}	1.05 ± 0.10^{bcde}
2,5-Dimethylpyrazine	1.20 ± 0.30^{f}	0.61 ± 0.06^{cd}	0.61 ± 0.03^{cd}	0.60 ± 0.10^{cd}	0.90 ± 0.10^{e}	0.70 ± 0.30^{cd}	0.56 ± 0.03^{cd}	0.44 ± 0.03^{bc}
2,6-Dimethylpyrazine	1.10 ± 0.20^{h}	0.49 ± 0.07^{cd}	0.66 ± 0.001^{ef}	0.70 ± 0.10^{ef}	1.00 ± 0.20^{g}	0.47 ± 0.07^{cd}	0.59 ± 0.03^{de}	0.48 ± 0.04^{cd}
2-Ethylpyrazine	1.40 ± 0.30^{h}	0.76 ± 0.08^{de}	0.88 ± 0.01^{ef}	0.90 ± 0.20^{ef}	1.20 ± 0.20^{g}	0.60 ± 0.10^{bcd}	0.79 ± 0.05^{de}	0.66 ± 0.07^{cd}
2,3-Dimethylpyrazine	0.39 ± 0.10^{f}	0.19 ± 0.02^{bc}	0.25 ± 0.02^{cd}	0.24 ± 0.07^{cd}	0.35 ± 0.05^{ef}	0.12 ± 0.02^{ab}	0.18 ± 0.03^{bc}	0.16 ± 0.03^{ab}
2-Ethyl-6-methylpyrazine	2.20 ± 0.40^{g}	1.20 ± 0.10^{de}	1.46 ± 0.02^{e}	1.40 ± 0.30^{e}	1.80 ± 0.20^{f}	1.00 ± 0.20^{cd}	1.28 ± 0.09^{de}	1.07 ± 0.13^{cd}
2-Ethyl-5-methylpyrazine	1.60 ± 0.30^{f}	0.83 ± 0.08^{d}	0.90 ± 0.01^{d}	0.90 ± 0.20^{d}	1.10 ± 0.10^{e}	0.60 ± 0.10^{c}	0.80 ± 0.05^{cd}	0.64 ± 0.08^{c}
2,3,5-Trimethylpyrazine	1.50 ± 0.30^{k}	0.72 ± 0.07^{gh}	0.79 ± 0.001^{hi}	0.80 ± 0.20^{h}	0.90 ± 0.10^{ij}	0.50 ± 0.10^{def}	0.66 ± 0.05^{fgh}	0.56 ± 0.07^{efg}
3-Ethyl-2,5-dimethylpyrazine	2.40 ± 0.50^{f}	1.10 ± 0.10^{cd}	1.07 ± 0.02^{cd}	1.00 ± 0.20^{bcd}	1.20 ± 0.10^{d}	0.70 ± 0.20^{b}	0.84 ± 0.07^{bc}	0.68 ± 0.10^{b}
Pyrazine	14.00 ± 3.00^{i}	7.20 ± 0.60^{fg}	8.02 ± 0.06^{g}	8.00 ± 1.00^{g}	11.00 ± 1.00^{h}	6.50 ± 0.80^{efg}	6.90 ± 0.50^{fg}	5.70 ± 0.60^{def}
Pyridine	3.00 ± 0.80^{g}	0.85 ± 0.07^{ab}	1.79 ± 0.04^{de}	1.60 ± 0.30^{cd}	2.20 ± 0.10^{def}	0.70 ± 0.10^{a}	1.08 ± 0.07^{ab}	1.30 ± 0.10^{bc}
Pyridine	3.00 ± 0.80^{g}	0.85 ± 0.07^{ab}	1.79 ± 0.04^{de}	1.60 ± 0.30^{cd}	2.20 ± 0.10^{def}	0.70 ± 0.10^{a}	1.08 ± 0.07^{ab}	1.30 ± 0.10^{bc}
1-Furfurylpyrrole	3.90 ± 0.50^{ab}	3.20 ± 0.30^{a}	3.90 ± 0.10^{ab}	5.00 ± 1.00^{cd}	5.20 ± 0.40^{cd}	3.60 ± 0.80^{ab}	4.10 ± 0.30^{abc}	4.40 ± 0.50^{bc}
2-Acetylpyrrole	0.90 ± 0.10^{cdefg}	0.50 ± 0.06^{a}	0.70 ± 0.06^{abcd}	0.90 ± 0.10^{defg}	1.30 ± 0.30^{ij}	0.50 ± 0.10^{a}	0.59 ± 0.02^{ab}	0.67 ± 0.06^{abc}
Pyrrole	4.81 ± 0.50^{bc}	3.71 ± 0.30^{a}	4.61 ± 0.20^{abc}	6.10 ± 1.00^{de}	6.50 ± 0.60^{efg}	4.11 ± 0.70^{ab}	4.70 ± 0.30^{bc}	5.10 ± 0.50^{bc}
Furfuryl methyl sulfide	0.80 ± 0.10^{bc}	0.44 ± 0.04^{a}	0.94 ± 0.02^{c}	0.90 ± 0.10^{c}	1.20 ± 0.10^{d}	0.44 ± 0.09^{a}	0.63 ± 0.04^{ab}	0.80 ± 0.10^{bc}
2-Acetylfuran	1.00 ± 0.20^{de}	0.55 ± 0.05^{ab}	0.77 ± 0.01^{bcd}	0.90 ± 0.20^{cde}	1.40 ± 0.10^{f}	0.50 ± 0.08^{a}	0.76 ± 0.05^{bcd}	0.71 ± 0.08^{abc}
Furfuryl acetate	4.30 ± 0.90^{bcd}	2.20 ± 0.20^{a}	4.20 ± 0.10^{bcd}	4.40 ± 0.90^{cde}	5.60 ± 0.70^{fg}	2.10 ± 0.50^{a}	3.50 ± 0.30^{bc}	3.40 ± 0.40^{b}
Methyl furfuryl disulfide	0.60 ± 0.10^{abc}	0.50 ± 0.05^{a}	0.75 ± 0.01^{bcde}	0.80 ± 0.20^{cdef}	0.78 ± 0.08^{cdef}	0.51 ± 0.08^{a}	0.59 ± 0.04^{ab}	0.70 ± 0.10^{bcd}
Furan	7.00 ± 1.00^{bc}	3.70 ± 0.40^{a}	6.70 ± 0.20^{bc}	7.00 ± 1.00^{bc}	9.00 ± 1.00^{de}	3.60 ± 0.70^{a}	5.50 ± 0.40^{b}	5.60 ± 0.70^{b}
2-Methoxyphenol	2.50 ± 0.50^{d}	1.30 ± 0.10^{ab}	2.34 ± 0.03^{d}	2.50 ± 0.40^{d}	3.30 ± 0.40^{e}	1.10 ± 0.20^{a}	1.70 ± 0.10^{bc}	1.90 ± 0.20^{c}
4-Ethyl-2-methoxyphenol	5.70 ± 0.60^{cd}	3.90 ± 0.40^{a}	6.70 ± 0.20^{cdef}	7.00 ± 1.00^{de}	7.30 ± 0.40^{e}	3.90 ± 0.50^{a}	4.50 ± 0.30^{ab}	5.50 ± 0.50^{bc}
2-Methoxy-4-vinylphenol	9.20 ± 0.40^{c}	9.20 ± 0.50^{c}	8.70 ± 0.50^{c}	10.80 ± 0.90^{d}	9.20 ± 0.80^{c}	8.50 ± 0.60^{c}	8.90 ± 0.20^{c}	8.40 ± 0.50^{bc}
Phenol	17.00 ± 1.00^{bcd}	14.00 ± 1.00^{a}	17.70 ± 0.70^{bcd}	21.00 ± 4.00^{e}	20.00 ± 1.00^{de}	14.00 ± 1.00^{a}	15.10 ± 0.60^{ab}	15.80 ± 0.90^{abc}
Total	43.00 ± 5.00^{cd}	29.00 ± 2.00^{a}	36.00 ± 1.00^{bc}	42.00 ± 7.00^{cd}	46.00 ± 4.00^{d}	28.00 ± 3.00^{a}	32.00 ± 2.00^{ab}	32.00 ± 3.00^{ab}
Compounds	**NTR**	**Autoclaved**						
		A0	**AX3**	**AX6**	**AX9**	**AR3**	**AR6**	**AR9**
Methylpyrazine	2.60 ± 0.60^{i}	1.70 ± 0.20^{fg}	1.13 ± 0.04^{cde}	0.80 ± 0.10^{abc}	0.70 ± 0.08^{ab}	0.95 ± 0.08^{bcd}	0.73 ± 0.03^{ab}	0.48 ± 0.02^{a}
2,5-Dimethylpyrazine	1.20 ± 0.30^{f}	0.78 ± 0.08^{de}	0.31 ± 0.02^{ab}	0.18 ± 0.02^{a}	0.15 ± 0.01^{a}	0.31 ± 0.002^{ab}	0.19 ± 0.01^{a}	0.11 ± 0.004^{a}
2,6-Dimethylpyrazine	1.10 ± 0.20^{h}	0.78 ± 0.08^{f}	0.45 ± 0.02^{cd}	0.28 ± 0.04^{ab}	0.23 ± 0.02^{a}	0.41 ± 0.03^{bc}	0.27 ± 0.01^{ab}	0.17 ± 0.01^{a}
2-Ethylpyrazine	1.40 ± 0.30^{h}	1.00 ± 0.10^{fg}	0.68 ± 0.02^{cd}	0.48 ± 0.09^{abc}	0.45 ± 0.04^{ab}	0.62 ± 0.04^{bcd}	0.49 ± 0.03^{abc}	0.34 ± 0.03^{a}
2,3-Dimethylpyrazine	0.39 ± 0.10^{f}	0.28 ± 0.03^{de}	0.18 ± 0.03^{bc}	0.14 ± 0.04^{ab}	0.14 ± 0.03^{ab}	0.19 ± 0.02^{bc}	0.12 ± 0.01^{ab}	0.09 ± 0.01^{a}
2-Ethyl-6-methylpyrazine	2.20 ± 0.40^{g}	1.80 ± 0.40^{f}	0.92 ± 0.02^{bc}	0.68 ± 0.14^{ab}	0.55 ± 0.04^{a}	0.91 ± 0.06^{bc}	0.66 ± 0.04^{ab}	0.46 ± 0.04^{a}
2-Ethyl-5-methylpyrazine	1.60 ± 0.30^{f}	1.10 ± 0.10^{e}	0.45 ± 0.02^{b}	0.28 ± 0.06^{ab}	0.23 ± 0.02^{a}	0.43 ± 0.02^{b}	0.28 ± 0.02^{ab}	0.19 ± 0.02^{a}
2,3,5-Trimethylpyrazine	1.50 ± 0.30^{k}	1.00 ± 0.10^{j}	0.40 ± 0.01^{cde}	0.26 ± 0.05^{abc}	0.22 ± 0.01^{ab}	0.38 ± 0.02^{bcd}	0.26 ± 0.01^{abc}	0.17 ± 0.01^{a}

Table 2 (continued)

Compounds	NTR	Autoclaved						
		A0	AX3	AX6	AX9	AR3	AR6	AR9
3-Ethyl-2,5-dimethylpyrazine	2.40 ± 0.50^{f}	1.50 ± 0.20^{e}	0.265 ± 0.01^{a}	0.11 ± 0.02^{a}	0.08 ± 0.01^{a}	0.26 ± 0.01^{a}	0.12 ± 0.01^{a}	0.07 ± 0.001^{a}
Pyrazine	14.00 ± 3.00^{i}	10.00 ± 1.00^{h}	4.80 ± 0.10^{cde}	3.20 ± 0.60^{abc}	2.80 ± 0.20^{ab}	4.50 ± 0.30^{bcd}	3.10 ± 0.20^{abc}	2.08 ± 0.09^{a}
Pyridine	3.00 ± 0.80^{g}	2.00 ± 0.20^{de}	1.99 ± 0.07^{de}	2.60 ± 0.40^{f}	2.20 ± 0.30^{ef}	1.80 ± 0.10^{de}	2.00 ± 0.10^{de}	1.80 ± 0.10^{de}
Pyridine	3.00 ± 0.80^{g}	2.00 ± 0.20^{de}	1.99 ± 0.07^{de}	2.60 ± 0.40^{f}	2.20 ± 0.30^{ef}	1.80 ± 0.10^{de}	2.00 ± 0.10^{de}	1.80 ± 0.10^{de}
1-Furfurylpyrrole	3.90 ± 0.50^{ab}	4.50 ± 0.50^{bc}	5.90 ± 0.04^{de}	6.00 ± 1.00^{e}	7.80 ± 0.70^{f}	5.60 ± 0.30^{de}	6.40 ± 0.30^{d}	5.90 ± 0.50^{de}
2-Acetylpyrrole	0.90 ± 0.10^{cdefg}	0.69 ± 0.06^{abcd}	1.00 ± 0.20^{fgh}	1.20 ± 0.20^{hi}	1.10 ± 0.20^{gh}	0.72 ± 0.07^{abcde}	0.95 ± 0.04^{efgh}	0.80 ± 0.05^{bcdef}
Pyrrole	4.81 ± 0.50^{bc}	5.20 ± 0.50^{cd}	6.90 ± 0.20^{efg}	7.50 ± 1.00^{g}	8.90 ± 0.70^{h}	6.30 ± 0.30^{ef}	7.30 ± 0.30^{fg}	6.70 ± 0.40^{efg}
Furfuryl methyl sulfide	0.80 ± 0.10^{bc}	1.20 ± 0.10^{d}	1.28 ± 0.04^{d}	1.60 ± 0.40^{ef}	1.70 ± 0.10^{f}	1.36 ± 0.09^{de}	1.40 ± 0.10^{de}	1.40 ± 0.10^{de}
2-Acetylfuran	1.00 ± 0.20^{de}	0.79 ± 0.07^{bcd}	1.05 ± 0.01^{e}	1.60 ± 0.30^{f}	2.50 ± 0.30^{h}	1.00 ± 0.07^{de}	1.55 ± 0.07^{f}	2.00 ± 0.10^{g}
Furfuryl acetate	4.30 ± 0.90^{bcd}	4.50 ± 0.50^{de}	4.62 ± 0.04^{def}	5.10 ± 1.00^{defg}	6.00 ± 0.60^{g}	4.80 ± 0.30^{def}	5.40 ± 0.30^{efg}	4.60 ± 0.50^{def}
Methyl furfuryl disulfide	0.60 ± 0.10^{abc}	0.90 ± 0.07^{efg}	0.80 ± 0.10^{defg}	0.90 ± 0.20^{efg}	0.95 ± 0.08^{fg}	0.59 ± 0.03^{ab}	0.98 ± 0.08^{g}	0.90 ± 0.07^{efg}
Furan	7.00 ± 1.00^{bc}	7.40 ± 0.70^{cd}	7.80 ± 0.10^{cde}	9.00 ± 2.00^{e}	11.20 ± 1.00^{f}	7.70 ± 0.40^{cde}	9.40 ± 0.60^{e}	8.90 ± 0.60^{de}
2-Methoxyphenol	2.50 ± 0.50^{d}	2.70 ± 0.20^{d}	2.62 ± 0.03^{d}	3.50 ± 0.50^{e}	3.50 ± 0.20^{e}	2.60 ± 0.10^{d}	3.20 ± 0.20^{e}	2.60 ± 0.10^{d}
4-Ethyl-2-methoxyphenol	5.70 ± 0.60^{cd}	7.80 ± 0.90^{e}	6.80 ± 0.10^{def}	8.00 ± 1.00^{e}	7.90 ± 0.70^{e}	7.40 ± 0.50^{e}	7.70 ± 0.30^{e}	6.00 ± 0.50^{cde}
2-Methoxy-4-vinylphenol	9.20 ± 0.40^{c}	8.50 ± 1.00^{c}	8.30 ± 0.60^{bc}	7.20 ± 0.30^{ab}	7.80 ± 0.80^{bc}	8.10 ± 1.00^{bc}	8.00 ± 0.10^{bc}	6.00 ± 0.06^{a}
Phenol	17.00 ± 1.00^{bcd}	19.00 ± 2.00^{de}	17.70 ± 0.80^{bcd}	18.00 ± 2.00^{cde}	19.00 ± 2.00^{de}	18.00 ± 1.00^{cde}	19.00 ± 0.50^{de}	14.63 ± 0.02^{a}
Total	43.00 ± 5.00^{cd}	42.00 ± 4.00^{cd}	37.20 ± 0.90^{bc}	38.00 ± 5.00^{bc}	42.00 ± 4.00^{cd}	37.00 ± 2.00^{bc}	39.00 ± 1.00^{bc}	32.00 ± 1.00^{ab}

All values are shown as mean ± S.D. (standard deviation) ($n = 3$)

Lowercase letters (series "a-k") indicate significant (Duncan's range test, $p < 0.05$) differences in the same row

The abbreviations for the samples are as follows

NTR Non-treated Robusta (Coffea Robusta), *NA0* Sample pretreated with distilled water and soaked without using autoclave,

NAX3, 6, 9: Sample pretreated with 3, 6, and 9% D- xylose solution and soaked without using autoclave

NAR3, 6, 9: Sample pretreated with 3, 6, and 9% D-ribose solution and soaked without using autoclave

A0: Sample soaked with distilled water and autoclaved

AX3, 6, 9: Sample pretreated with 3, 6, and 9% D-xylose solution and soaked with using autoclave

AR3, 6, 9: Sample pretreated with 3, 6, and 9% D-ribose solution and soaked with using autoclave

without using autoclave (NAR3) which was decreased by 15%. In total furans, the sample pretreated with 3% D-ribose solution and soaked without using autoclave (NAR3) was decreased by 48% compared to NTR. In total phenols, the sample pretreated with distilled water and soaked without using autoclave (NA0) was decreased by 18% compared to NTR followed by the sample pretreated with 9% D-ribose solution and soaked with using autoclave (AR9) which was decreased by 14%. On the other hand, the sample pretreated with 9% D-xylose solution with autoclave (AX9) had the highest level of pyrroles, furans, and phenols increased by 85%, 60%, and 12%, respectively, compared to the control (NTR).

The significant decrease of pyrazines pyridine, pyrroles, and furans compared to NTR can be attributed to the loss of water-soluble precursors during pretreatment ($p < 0.05$). The decrease of pyrazine also occurred in the study treated with sugars, and it can be explained by excessive sugar which can affect the reactant ratio [15]. This result can also be inferred by low pH values after pentose pretreatment. According to a previous study, pyrazines were not detected in low pH conditions [24]. Meanwhile, the peak area ratio of 1-furfurylpyrrole increased after pentose pretreatment. The study of peptide-xylose Maillard reaction [25] has suggested the formation pathway of 1-(2-furanylmethyl)-1H-pyrrole, D-xylose can be formed in two ways. One can form 2-methylfuran and the other one can form 1-(2-furanylmethyl)-1H-pyrrole. This pathway could offer the possible grounds for the reduced amount of furans and increase of 1-furfurylpyrrole.

The total peak area ratio of volatile compounds in most of the coffee samples (11 out of 15, except SX6, SX9, A0, and AX9 samples) was decreased after pretreatment with D-xylose and D-ribose (Figure S3). The sample which has the lowest peak area ratio of total volatile was sample

pretreated with 3% ribose solution soaked without autoclave (NAR3). Comparing the sum of volatile compounds, the samples pretreated with D-ribose solution were lower than samples pretreated with D-xylose solution in both non-autoclaved and autoclaved methods. The number of volatile compounds in the total of non-autoclaved samples exhibited a noteworthy increase with the escalating concentration of pentose ($p < 0.05$). However, there is no inclination of total volatile compounds found in autoclaved samples.

Validation of the analytical method for α-DCs

The calculations of calibration curves, linearity (coefficient of determination, R^2), limit of detection (LOD), limit of quantitation (LOQ), recovery (%), and precision (relative standard deviation; RSD, %) were conducted for the validation on the analytical method for three α-DCs (Table S2-S3). Six different concentrations in water (0.1, 0.5, 1, 5, 10, and 50 μg/mL) were used for the standard calibration curve of three α-DCs (GO, MGO, DA). The regression equation and linearity of three α-DC (GO, MGO, and DA) were obtained as $y = 0.3709x - 0.1115$ ($R^2 = 0.9998$), $y = 0.3962x - 0.1061$ ($R^2 = 0.9994$), and $y = 0.3028x + 0.0241$ ($R^2 = 1.0000$), respectively (Figure S4). The LOD of glyoxal (GO), methylglyoxal (MGO), and diacetyl (DA) was 0.07, 0.06, and 0.07 μg/mL, respectively. The LOQ of GO, MGO, and DA was 0.23, 0.18, and 0.21 μg/mL, respectively. Three different concentrations (5, 10, and 50 μg/mL) in coffee matrix were used for recovery and precision test. The obtained recovery rate ranged from 90.88% (DA) to 111.75% (DA). The results of intra- and inter-day precision ranged from 0.82% (MGO) to 3.87% (DA) and from 1.35% (DA) to 3.01% (MGO), respectively.

Analysis of α-dicarbonyl compounds in coffee by GC–MS

α-Dicarbonyl compounds (α-DCs), including glyoxal (GO), methyl glyoxal (MGO), and diacetyl (DA), are known as a toxic volatile compound formed by sugar degradation and dehydration without amine catalysis and Maillard reaction during roasting [26], were analyzed in all 15 roasted coffee samples. The amount of total α-dicarbonyl compounds (α-DCs) ranged from 17.5 to 57 μg/mL, as shown in Table 3. Non-treated Robusta (NTR) coffee sample had the highest, and the coffee sample pretreated with 6% of D-xylose solution and autoclaved (AX6) had the lowest contents of total α-dicarbonyl compounds among all samples followed by the coffee sample pretreated with 9% of D-xylose solution and autoclaved (AX9). The level of methyl glyoxal (MGO) was the highest component among other α-DCs, ranging from 12.1 to 50 μg/mL. The range of glyoxal (GO) was 2.26 to 4.3 and diacetyl (DA) was 1.9 to 3.4 μg/mL each.

The concentration of the total amount of three α-DCs decreased significantly ($p < 0.05$) after pentose pretreatment compared to the control (NTR) (Figure S5). It can be explained by the loss of precursors during pentose pretreatment [15]. The sample pretreated with 0% sugar solution

Table 3 Concentrations of three α-DC and acetic acid in roasted Robusta coffee samples of non-autoclaved and autoclaved with D-xylose and D-ribose

Coffee samples	Compounds				
	GO (μg/mL)	MGO (μg/mL)	DA (μg/mL)	α-DCs (μg/mL)	Acetic acid (μg/mL)
NTR	4.30 ± 0.50^{e}	50.00 ± 5.00^{f}	2.40 ± 0.20^{b}	57.00 ± 6.00^{g}	340.00 ± 14.00^{ef}
NA0	3.10 ± 0.20^{d}	38.00 ± 1.00^{e}	2.17 ± 0.01^{ab}	43.00 ± 2.00^{f}	201.00 ± 3.00^{a}
NAX3	2.50 ± 0.10^{ab}	20.20 ± 0.50^{c}	2.80 ± 0.50^{c}	25.00 ± 1.00^{cd}	286.00 ± 2.00^{d}
NAX6	2.47 ± 0.09^{ab}	15.00 ± 1.00^{ab}	3.40 ± 0.10^{e}	21.00 ± 1.00^{ab}	263.00 ± 6.00^{cd}
NAX9	2.54 ± 0.06^{abc}	20.40 ± 0.10^{c}	3.20 ± 0.10^{de}	26.20 ± 0.20^{d}	285.00 ± 5.00^{d}
NAR3	2.70 ± 0.30^{bc}	15.90 ± 0.80^{b}	3.20 ± 0.10^{de}	21.80 ± 0.80^{bc}	243.00 ± 3.00^{bc}
NAR6	2.60 ± 0.20^{abc}	20.00 ± 1.00^{c}	2.84 ± 0.09^{cd}	26.00 ± 2.00^{d}	218.00 ± 10.00^{ab}
NAR9	2.90 ± 0.20^{cd}	30.00 ± 3.00^{d}	3.20 ± 0.40^{de}	36.00 ± 3.00^{e}	238.00 ± 1.00^{bc}
A0	2.60 ± 0.20^{abc}	28.00 ± 1.00^{d}	1.90 ± 0.20^{a}	33.00 ± 1.00^{e}	226.00 ± 6.00^{abc}
AX3	2.40 ± 0.09^{ab}	16.10 ± 0.20^{b}	3.10 ± 0.20^{cde}	21.60 ± 0.30^{bc}	327.00 ± 6.00^{e}
AX6	2.26 ± 0.07^{a}	12.10 ± 0.40^{a}	3.10 ± 0.30^{cde}	17.50 ± 0.50^{a}	337.00 ± 1.00^{e}
AX9	2.30 ± 0.05^{ab}	14.40 ± 0.90^{ab}	3.24 ± 0.02^{de}	19.90 ± 1.00^{ab}	338.00 ± 9.00^{ef}
AR3	2.30 ± 0.10^{ab}	15.00 ± 1.00^{ab}	3.10 ± 0.10^{de}	21.00 ± 2.00^{ab}	291.00 ± 5.00^{d}
AR6	2.42 ± 0.06^{ab}	18.00 ± 2.00^{bc}	3.40 ± 0.20^{e}	23.00 ± 2.00^{bcd}	349.00 ± 4.00^{ef}
AR9	2.40 ± 0.10^{ab}	14.00 ± 2.00^{ab}	3.20 ± 0.10^{de}	20.00 ± 2.00^{ab}	374.00 ± 10.00^{f}

All values are shown as mean ± S.D. (standard deviation) ($n = 3$)

Lowercase letters (series "a-g") indicate significant (Duncan's range test, $p < 0.05$) differences in the same column

(distilled water) without and with autoclave (NAC0 and AC0) had the second and third high content of total α-DCs. The autoclaved samples had lower levels of α-DCs than non-autoclaved samples. The samples soaked with D-ribose had higher levels of α-DCs and it can be explained by higher browning levels of D-ribose than D-xylose [17].

Validation of the analytical method for acetic acid

The equation of calibration curve, linearity (coefficient of determination, R^2), limit of detection (LOD), limit of quantitation (LOQ), recovery (%), and precision (relative standard deviation; RSD, %) tests were conducted for the validation of the analytical method for acetic acid (Table S4). Linearity (R^2) was evaluated with the calibration curve of 6 concentration levels (5, 10, 25, 50, 250, and 500 μg/mL) of acetic acid. Regression equation ($y = ax + b$) and linearity (R^2) of acetic acid were obtained as $y = 0.5201x + 0.1459$ and $R^2 = 1.0000$ (Figure S6). The LOD and LOQ of acetic acid were 1.05 and 3.35, respectively. The recovery rate was 110.25%, obtained by spiking 10 μL of acetic acid standard. Intra- and inter-day were obtained at 1.46% and 4.22%, respectively.

Analysis of acetic acid in coffee by HPLC–UV

Acetic acid, which can be generated by 2,3-enolisation and sugar degradation [27], was analyzed in all 15 roasted coffee samples. The level of acetic acid ranged from 201 to 374 μg/mL as represented in Table 3. The sample soaked with 9% D-ribose solution with autoclave (AR9) exhibited the highest concentration of acetic acid, surpassing only the control (NTR) with statistical significance ($p < 0.05$). Conversely, the sample soaked with distilled water (NA0) had the lowest level of acetic acid ($p < 0.05$). The samples treated without autoclave had a lower level of acetic acid compared to the samples treated with autoclave (except the sample soaked with distilled water and autoclaved (A0)) ($p < 0.05$). In the samples treated with autoclave, the concentration of pentose increases the contents of acetic acid.

The sample soaked with 9% D-ribose solution treated with autoclave (AR9) has the second level of total α-dicarbonyl compounds and the highest level of acetic acid among all samples. This might be able to explain by β-dicarbonyl cleavage which is known as the major pathway for generating acetic acid [27]. β-Dicarbonyl is formed by the isomerization of α-dicarbonyl sugars and the β-dicarbonyl cleavage could reduce the amount of total α-dicarbonyl compounds.

Measurements of pH and color

Table 4 shows the pH and color values of non-treated and treated green and roasted Robusta coffee samples. Caramelization and Maillard reaction are affected by the pH [28]. Also, these reactions induce color formation [29].

The pH of all pretreated green bean and roasted Robusta coffee samples was lower than that of the control (NTR) ($p < 0.05$). In green bean samples, non-treated Robusta (NTR) was the highest (5.92), and the sample pretreated with 9% of ribose solution and autoclaved (AR9) was the lowest (5.37) above all samples ($p < 0.05$). In roasted samples, non-treated Robusta (NTR) was the highest (5.54), and the sample pretreated with 9% of ribose solution and autoclaved was the lowest (4.93) above all samples ($p < 0.05$).

L* values showed that pentose pretreatment produced darker colors in both green and roasted bean samples, especially in autoclaved samples. In green bean samples, all treated samples had lower L* values compared to the control (NTR) and the AR9 sample also had the lowest L* value (59.84) above all samples ($p < 0.05$). The same tendency occurred in roasted bean samples. In roasted coffee samples, all treated samples also had lower L* values compared to the control (NTR) and the sample pretreated with 9% of D-xylose solution and autoclaved (AX9) was the lowest (5.37) above all samples ($p < 0.05$). The autoclaved samples had lower L* values than non-autoclaved samples ($p < 0.05$). It can be speculated that autoclaved pretreatment soaked with pentose solution could cause a non-enzymatic browning reaction before the roasting process and autoclaved samples had more browning reaction than non-autoclaved samples after the roasting process. There is a significant increase in a* values in green beans, particularly in autoclaved samples. This increase in a* values suggests that during the roasting of green beans, the intensity of the green color decreased, while the intensity of the red color increased. This can be explained by the effect of non-enzymatic browning reaction [30].

Principal Component Analysis (PCA)

Principal Component Analysis was used to demonstrate the correlation of the level of 18 volatile compounds analyzed by GC–MS, three α-dicarbonyl compounds analyzed by GC-NPD, and acetic acid analyzed by HPLC in all coffee samples after roasting (Fig. 2). The first principal component (PC1) indicates 69.22% and the second principal component (PC2) indicates 13.17% of the variance in the whole dataset. PC1 was negatively correlated with pyrazines (3-ethyl-2,5-dimethylpyrazine, 2,5-dimethylpyrazine, 2-ethyl-5-methylpyrazine, 2,3,5-trimethylpyrazine, 2,6-dimethylpyrazine, 2-ethyl-6-methylpyrazine, mehtylpyrazine, 2-ethylpyrazine, and 2,3-dimethylpyrazine) and methylglyoxal (MGO), whereas 2-acetylfuran, 1-furfurylpyrrole, 2-methoxyphenol, pyridine, furfuryl acetate, 2-acetylpyrrole,

Table 4 pH and color values in green and roasted Robusta coffee samples non-autoclaved and autoclaved with D-xylose and D-ribose

Coffee samples	Green beans					Roasted beans				
	pH	Color values				pH	Color values			
		L*	a*	b*	ΔE*		L*	a*	b*	ΔE*
NTR	5.92 ± 0.03^{k}	65.80 ± 0.10^{k}	2.73 ± 0.04^{a}	23.10 ± 0.08^{c}	69.79 ± 0.08^{ef}	5.54 ± 0.04^{h}	34.91 ± 0.09^{k}	12.30 ± 0.10^{k}	22.70 ± 0.40^{l}	43.40 ± 0.30^{k}
NA0	5.73 ± 0.01^{h}	62.50 ± 0.20^{b}	3.33 ± 0.04^{f}	23.19 ± 0.05^{c}	66.70 ± 0.20^{a}	5.10 ± 0.03^{cd}	33.04 ± 0.01^{j}	11.93 ± 0.02^{j}	20.66 ± 0.06^{k}	40.74 ± 0.03^{j}
NAX3	5.68 ± 0.02^{fgh}	63.10 ± 0.30^{cd}	3.19 ± 0.04	23.53 ± 0.10^{de}	67.40 ± 0.30^{b}	5.26 ± 0.01^{e}	29.33 ± 0.02^{ef}	10.06 ± 0.06^{g}	16.40 ± 0.10^{g}	35.08 ± 0.05^{f}
NAX6	5.72 ± 0.04^{hi}	63.50 ± 0.10^{de}	2.92 ± 0.02^{b}	22.48 ± 0.03^{b}	67.40 ± 0.10^{b}	5.10 ± 0.02^{cd}	30.02 ± 0.01^{g}	10.49 ± 0.06	17.18 ± 0.03^{h}	36.14 ± 0.02^{g}
NAX9	5.68 ± 0.03^{gh}	64.40 ± 0.40^{fg}	3.14 ± 0.02^{de}	23.44 ± 0.08^{de}	68.60 ± 0.30^{d}	5.06 ± 0.01^{cd}	29.38 ± 0.01^{f}	9.98 ± 0.01^{fg}	16.29 ± 0.08^{fg}	35.04 ± 0.05^{f}
NAR3	5.64 ± 0.04^{defg}	64.10 ± 0.20^{f}	3.14 ± 0.02^{de}	23.58 ± 0.05^{e}	68.30 ± 0.10^{cd}	5.00 ± 0.10^{b}	32.38 ± 0.01^{i}	11.67 ± 0.06^{i}	19.89 ± 0.02^{j}	39.76 ± 0.01^{i}
NAR6	5.62 ± 0.01^{cde}	64.2 ± 0.40^{f}	3.07 ± 0.05^{cd}	23.90 ± 0.10^{f}	68.60 ± 0.30^{d}	5.05 ± 0.02^{bc}	31.12 ± 0.02^{h}	10.99 ± 0.06^{h}	18.35 ± 0.03^{i}	37.76 ± 0.01^{h}
NAR9	5.59 ± 0.01^{cd}	65.30 ± 0.10^{ij}	3.02 ± 0.02^{c}	23.40 ± 0.02^{d}	69.48 ± 0.09^{e}	4.93 ± 0.03^{a}	29.24 ± 0.02^{ef}	9.76 ± 0.06^{ef}	16.12 ± 0.01^{f}	34.78 ± 0.02^{f}
A0	5.84 ± 0.01^{j}	64.70 ± 0.50^{gh}	3.30 ± 0.10^{ef}	21.70 ± 0.20^{a}	68.30 ± 0.40^{cd}	5.47 ± 0.03^{g}	28.90 ± 0.10^{e}	9.74 ± 0.07^{e}	15.60 ± 0.10^{e}	34.30 ± 0.20^{e}
AX3	5.75 ± 0.01^{i}	65.6 ± 0.40^{jk}	3.58 ± 0.05^{g}	23.50 ± 0.10^{de}	69.70 ± 0.20^{ef}	5.32 ± 0.03^{f}	26.20 ± 0.40^{d}	7.80 ± 0.30^{d}	12.50 ± 0.20^{d}	30.1 ± 0.50^{d}
AX6	5.67 ± 0.03^{efgh}	63.62 ± 0.04^{e}	4.37 ± 0.02^{h}	25.14 ± 0.03^{g}	68.55 ± 0.04^{d}	5.24 ± 0.02^{e}	24.30 ± 0.60^{ab}	5.70 ± 0.30^{b}	9.50 ± 0.30^{b}	26.70 ± 0.70^{b}
AX9	5.63 ± 0.02^{cdef}	64.66 ± 0.07^{gh}	5.07 ± 0.02^{i}	26.53 ± 0.02	70.08 ± 0.07^{f}	5.25 ± 0.03^{e}	23.90 ± 0.20^{a}	5.30 ± 0.10^{a}	9.00 ± 0.20^{a}	26.20 ± 0.20^{a}
AR3	5.59 ± 0.03^{c}	65.00 ± 0.20^{hi}	4.39 ± 0.03^{h}	25.32 ± 0.06^{h}	69.90 ± 0.20^{f}	5.27 ± 0.02^{ef}	25.60 ± 0.30^{c}	6.89 ± 0.07^{c}	11.10 ± 0.10^{c}	28.70 ± 0.30^{c}
AR6	5.50 ± 0.02^{b}	63.00 ± 0.10^{c}	7.00 ± 0.10^{j}	29.40 ± 0.10^{i}	69.87 ± 0.03^{f}	5.22 ± 0.03^{e}	24.62 ± 0.07^{b}	5.76 ± 0.06^{b}	9.56 ± 0.02^{b}	27.03 ± 0.08^{b}
AR9	5.37 ± 0.02^{a}	59.84 ± 0.04^{a}	8.63 ± 0.04^{k}	31.15 ± 0.09^{j}	68.00 ± 0.10^{c}	5.12 ± 0.02^{d}	24.30 ± 0.10^{ab}	5.56 ± 0.06^{b}	9.30 ± 0.10^{ab}	26.60 ± 0.20^{ab}

All values are shown as mean ± S.D. (standard deviation) ($n = 3$)

Lowercase letters (series "a-l") indicate significant (Duncan's range test, $p < 0.05$) differences in the same column

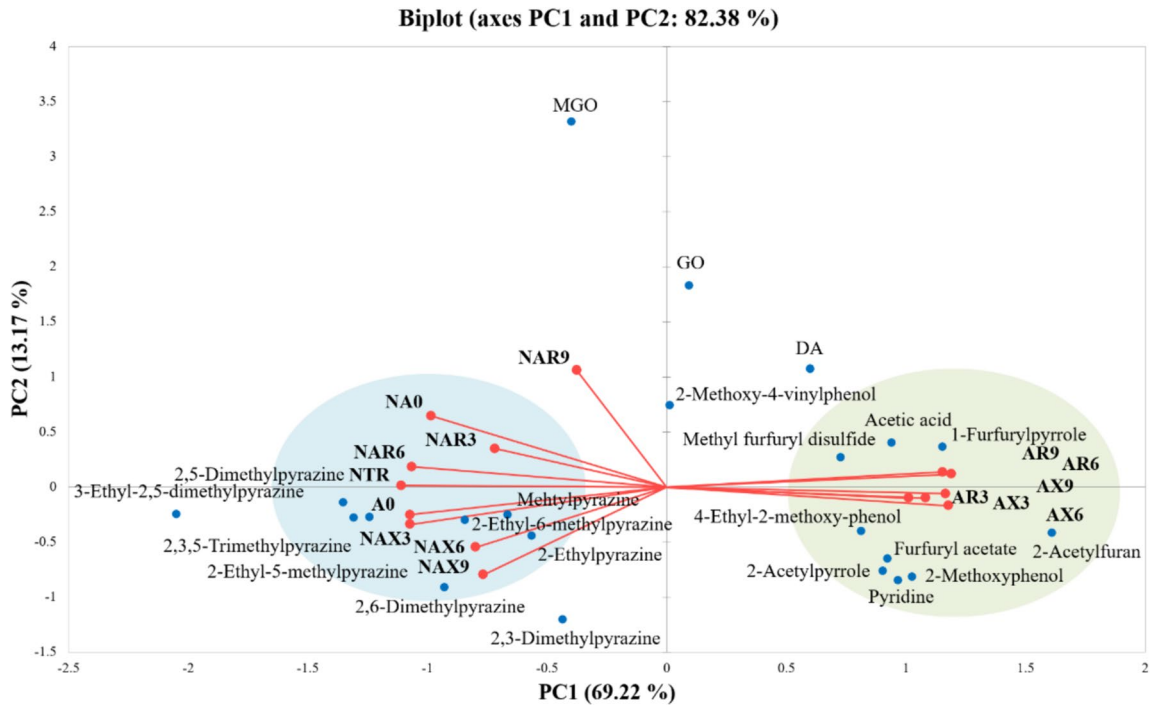

Fig. 2 Principle component analysis (bi-plot) of eighteen volatile compounds, three α-dicarbonyl compounds and acetic acid in roasted Robusta coffee samples non-autoclaved and autoclaved with D-xylose and D-ribose. 1) Non-treated Robusta coffee (NTR); Robusta coffee treated with distilled water (0% of pentose solution) and non-autoclave (NA0); Robusta coffee treated with D-xylose and non-autoclaved with three concentrations (3%, 6%, and 9%) (NAX3, NAX6, and NAX9); Robusta coffee treated with D-xylose and autoclaved with three concentrations (3%, 6%, and 9%) (AX3, AX6, and AX9); Robusta coffee treated with D-ribose and non-autoclaved with three concentrations (3%, 6%, and 9%) (NRX3, NRX6, and NRX9); Robusta coffee treated with D-ribose and autoclaved with three concentrations (3%, 6%, and 9%) (AR3, AR6, and AR9)

acetic acid, 4-ethyl-2-methoxy-phenol, methyl furfuryl disulfide, diacetyl (DA), glyoxal (GO), and 2-methoxy-4-vinylphenol were positively correlated. PC2 exhibited a negative correlation with pyrazines, 4-ethyl-2-methoxy-phenol, 2-methoxyphenol, furfuryl acetate, 2-acetylpyrrole, 2-acetylfuran, and pyridine. In contrast, it showed a positive correlation with α-dicarbonyl compounds (MGO, GO, and DA), 2-methoxy-4-vinylphenol, acetic acid, methyl furfuryl disulfide, and 1-furfurylpyrrole.

The non-treated Robusta coffee sample (NTR) was strongly correlated with 2,5-dimethylpyrazine, 2-ethyl-5-methylpyrazine, and 2,3,5-trimethylpyrazine in the negative area of PC1 along with the non-autoclaved Robusta coffees. The autoclaved Robusta coffees (AX3, AX6, AX9, AR3, AR6, and AR9) were in the positive area of PC1 except for the sample soaked with distilled water and autoclaved (A0).

The PCA showed that there are distinctive differences between samples with soaking methods (non-autoclave and autoclave). Autoclave treatment moved volatile compounds from pyrazines to 1-furfurylpyrrole, 2-acetylpyrrole, 4-ethyl-2-methoxy-phenol, 2-methoxyphenol, furfuryl acetate, methyl furfuryl disulfide, and pyridine. This treatment also made more acetic acid than the control and non-autoclaved Robusta coffee samples. In other words, treatment using autoclave increases cocoa, smoky, burnt, and fruity flavor, and acetic acid while decreasing nutty, roasted, and sweet flavors from pyrazines.

Conclusions

This study aimed to assess the impact of pentose pretreatment using D-xylose and D-ribose with two methods (non-autoclaved and autoclaved) on Robusta coffee. The analysis focused on compounds related to caramelization and the Maillard reaction, including the volatile compounds, α-dicarbonyl compounds (α-DCs), and acetic acid. Principal Component Analysis (PCA) revealed that the autoclaved method of pentose pretreatment resulted in a decrease in pyrazines and an increase in 1-furfurylpyrrole, 2-acetylpyrrole, methyl furfuryl disulfide, 4-ethyl-2-methoxy-phenol, 2-methoxyphenol, furfuryl acetate, pyridine, and acetic acid. In other words, pentose pretreatment using autoclave increased cocoa, smoky, burnt, and fruity flavor, and acetic acid while decreasing nutty, roasted, and sweet flavors from pyrazines. This study provides valuable insights into the changes in volatiles, α-DCs, and acetic acid in Robusta coffee soaked

with D-xylose and D-ribose, suggesting potential applications in the coffee industry to modulate flavor profiles. The observed shifts in volatile compound profiles, supported by the PCA analysis, highlight the potential of pentose pretreatment, particularly with autoclaving, to create distinct flavor experiences in coffee. Future research could focus on sensory evaluation of the treated coffee to further understand the impact of pentose pretreatment on consumer perception and acceptance.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40538-024-00665-y.

Supplementary Material 1

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Author contributions
J Park: Formal analysis, Investigation; E Choi: Methodology; K.-G. Lee: Supervision; Validation; Investigation; Project administration.

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Data availability
No datasets were generated or analysed during the current study.

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
The authors declare no competing interests.

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