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SHORT COMMUNICATION

Evaluation of the Presence of 1,3-Dimethylamylamine in *Pelargonium* Leaves and Essential Oils by Mass Spectrometric and Chromatographic Methods

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Abstract

1,3-Dimethylamylamine (DMAA) is known to be added to dietary supplements from synthetic sources and, presumably, from natural geranium oil. However, the natural occurrence of DMAA in geranium oil (*Pelargonium graveolens*) has been controversial as published studies report contradicting findings. It is unclear if the difference in detection of DMMA in *Pelargonium* species is a result of the loss during extraction methods, different detection capabilities of analytical methods or if the content of DMAA is dependent of the species and geographical origins. Consequently, the purpose of this study is threefold: (1) to compare the analytical performance of mass spectrometry methods for the detection of DMMA, including GC/MS, DART–MS/MS and LC–MS/MS; (2) to evaluate if DMMA is lost during the extraction of essential oils from *Pelargonium* leaves of species from Brazil testing headspace extraction, and (3) to evaluate if DMMA is naturally present in a variety of essential oils originating from six countries. This study shows that for detection of more volatile compounds, headspace GC–MS proved to be more favorable than hydrodistilled essential oil analyzed by direct injection in GC–MS. DART–MS/MS showed to be a good alternative for identification of essential oils compounds and DMAA without sample preparation; LC–MS/MS proved to be sensitive for DMMA identification. Nevertheless, even after the analysis using mentioned methods, all essential oils and for the first time, the volatile components extracted from leaves, showed to be absent of DMAA, proving that its presence is not natural in these species.

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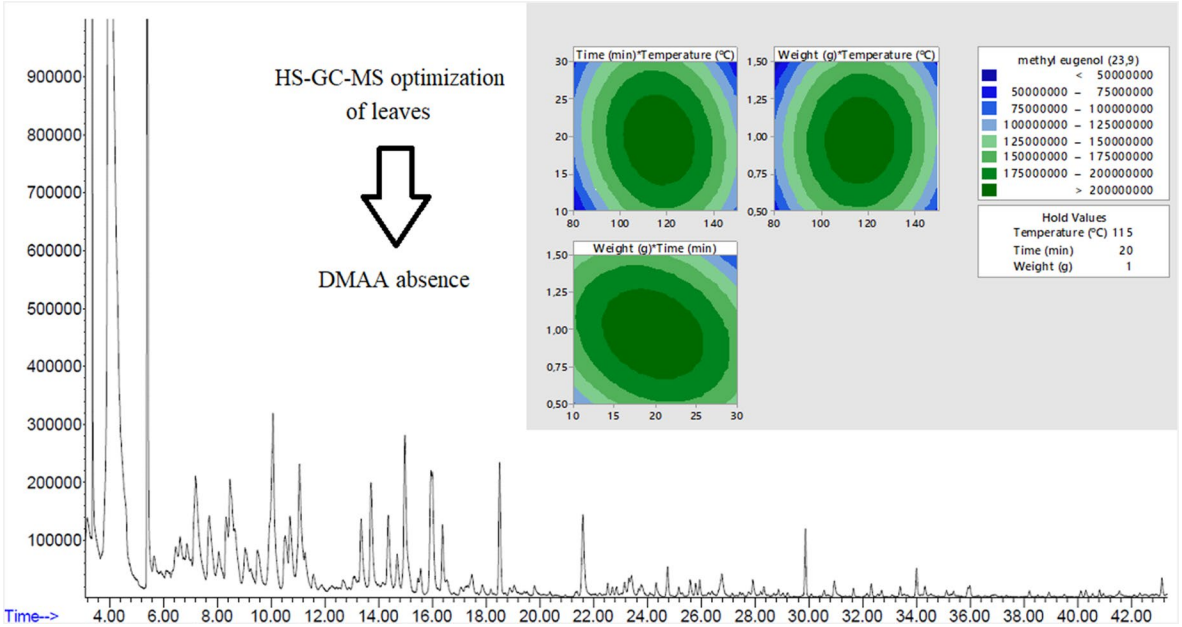
Graphical Abstract



Keywords 1,3-Dimethylamylamine · DMAA · *Pelargonium* · Headspace · Essential oil

Introduction

The frequency of 1,3-Dimethylamylamine (DMAA) abuse has increased even after its prohibition, and there is some debate regarding its origin and natural occurrence in botanic matter [1]. Despite the unreliability of the study that first reported natural occurrence of DMAA in *Pelargonium graveolens* [2], there have been conflicting reports concerning this investigation. For example, several groups have evaluated chemical composition of hydrodistilled and steam-distilled essential oils of *Pelargonium* sp., and the presence of DMAA has not been seen [3]. Also, the existence of the same diastereomeric ratios of DMAA for synthetic standards and for dietary supplements is a strong indication of its unnatural source, since diastereomeric ratios with natural origin should have distinct proportions [4].

The determination of plant constituents is commonly performed by first extracting the constituents using hydrodistillation and steam distillation. Also, because of their exhaustive capability, and ability to concentrate extracts, Soxhlet extraction and supercritical fluid extraction have also been used to characterization of components present in plants [5]. However, a drawback of the distillation methods is the potential for degradation of thermally labile compounds during high-temperature extractions [3]. Thus, it is possible that previous researches in this area may have underestimated the content of volatile and unstable compounds like the monoterpenes and DMAA, respectively, with exception of the study that reported the extraction of geranium material using cold-pressing process [3]. To avoid the loss of most volatile components, headspace could be a promising technique and still has not been employed for DMAA extraction from botanic matter.

This work reports the comparison of headspace GC–MS analysis of leaves and direct injection GC–MS analysis of essential oils extracted from three cultivars of *Pelargonium* from Brazil. The headspace extraction of volatile components was optimized using Box–Behnken design. In addition, GC–MS, DART–MS/MS and LC–MS/MS were used to contrast the effectiveness of identifying DMAA and different classes of chemicals in the commercial essential oils from Brazil, Egypt, South Africa, China, Reunion Island-Bourbon and Albania.

Experimental

Chemicals and Materials

Ethyl acetate (99.8%) was obtained from Sigma-Aldrich (St. Louis, MO, USA). HPLC optima grade solvents including methanol, formic acid, and water were purchased from Fischer Scientific (Pittsburgh, PA, USA). The reference

compound 1,3-dimethylamylamine hydrochloride (DMAA) was purchased from (LGC GmbH, Wesel, Germany) and Sigma-Aldrich. Headspace vials (10 mL) and aluminum screw caps with PTFE–silicone septa and 2-mL vials were obtained from Agilent Technologies (Agilent J&W Scientific, Folsom, CA, USA).

Plant Material and Essential Oils

Botanic arterial parts were obtained from three *Pelargonium* cultivars collected at Nova Petrópolis, RS, Brazil, in June 2016. The species were authenticated by the botanical expert Dr. Mara Ritter and deposited at the Herbarium of the Federal University of Rio Grande do Sul. The species were identified as *Pelargonium hortorum* L.H. Bailey, ICN 195251, *Pelargonium peltatum* (L.) L'Hér, ICN 195252, *Pelargonium fragrans* (*Pelargonium odoratissimum e P. extipulatum*), ICN 195294. Also, eight commercial essential oils of *P. graveolens* were obtained by donation from Laszlo Aromaterapia LTDA (originating from Egypt, South Africa, China, Reunion Island-Bourbon, Albania), Ferquima (Africa) and Verbena (Brazil and Africa).

Essential Oils (EO) Extraction

100 g of fresh leaves of *Pelargonium* species from Rio Grande do Sul, Brazil was chopped and weighed. Extraction was conducted through Clevenger apparatus by hydrodistillation for 4 h [6]. The hydrodistilled essential oils were then reconstituted in ethyl acetate and analyzed by GC–MS. Due to the relatively low yield (less than 1%), the essential oils obtained by hydrodistillation were analyzed using only GC–MS.

Analysis and Experimental Design

The experimental conditions for headspace sampling were optimized using the Box–Behnken Design (BBD) [7]. Headspace analyses were performed with fresh leaves that were chopped and weighed at three levels before extraction.

The designs were programmed considering the preliminary tests and the major compounds found in the essential oil after the liquid injection by GC–MS. The compounds selected as dependent variables were: fenchone, limonene and methyl-eugenol for *P. fragrans*; beta-caryophyllene, alpha-humulene and 10-epi-gamma-eudesmol, for *P. hortorum*; and beta-caryophyllene, gamma-cadinene and germacrene-B for *P. peltatum*. Three different experimental designs, one for each *Pelargonium* species, were performed for three factors at three levels: heating temperature 80 °C (−1), 115 °C (0) and 150 °C (+1); stirring time 10 min (−1), 20 min (0) and 30 min (+1) weight of leaves 0.5 g (−1), 1.0 g (0) and 1.5 g (+1). Testing of the three parameters was carried out in random order, totaling 15 runs for each design.

Experimental data were fitted following a second-order polynomial model (equation). **Yi** generically represents each response, **n** is the number of factors or variables, $\mathbf{b_0}$ is the regression coefficient of the intercept, and $\mathbf{b_i}$, $\mathbf{b_{ii}}$, and $\mathbf{b_{ij}}$ are the regression coefficients for the linear, quadratic and interaction of each factor **Ai**, respectively.

$$Yi = b_0 + \sum_{i=1}^{n} biAi + \sum_{i=1}^{n} biiA^2 i + \sum_{i \le 1 \le j}^{n} bijAij$$

The validity and predictive capacity of the mathematical model were evaluated under optimal conditions to compare the optimum responses obtained by the model with the experimental results. The model considered the results obtained for each compound (total of nine) that were carefully analyzed with the residual analysis and other statistical parameters offered by Minitab 17.0 software.

Analytical Procedure

Gas Chromatography–Mass Spectrometry (GC–MS)

Before the GC–MS liquid injections, the hydrodistilled essential oils and the commercial essential oils were diluted to 2% in ethyl acetate and analyzed in duplicates. The GC–MS analyses were performed on a 7890A gas chromatograph 5975C mass spectrometer (Agilent Technologies, CA, USA), equipped with an automatic headspace autosampler (CTC Analytics Combipal, Basel, Switzerland). A fused-silica DB-5 column (30 m × 0.25 mm × 0.25 µm) was employed for chromatographic separation. The mass detector was operated using 70-eV electron ionization (EI) with a source temperature, transfer line and injection port set at 150 °C, 300 °C and 220 °C, respectively. The oven temperature was programmed to start at 60 and ramp to 300 °C at an increase of 3 °C/min. Ultrapure helium was the carrier gas at 1 mL/min. Compounds were identified using a combination of their retention indices—using *n*-alkanes as external standards—and their mass spectral similarities to literature and NIST database entries being the same system employed for DMAA detection [8]. The limit of detection of 100 ppb was estimated for DMAA in methanol at a signal–noise ratio (S/N) ratio of three.

Direct Analysis in Real-Time Tandem Mass Spectrometry (DART–MS/MS)

For DART–MS/MS analysis, commercial essential oils were diluted to 0.1% in methanol, and 2 µL of each sample was pipetted onto a clean capillary tube and allowed

to dry before analysis. The analyses were performed using a Thermo Finnigan TSQ Quantum triple quadrupole mass spectrometer. The commercial essential oils were analyzed in duplicates using both full scan mode, from *m/z* 40–350, and selected reaction monitoring (SRM) mode. All the parameters were applied according tothe method developed and optimized previously by Santos et al. [9]. The limit of detection of 50 ppb was estimated for DMAA in methanol at a S/N ratio of three.

Liquid Chromatography–Tandem Mass Spectrometry (LC–MS/MS)

For LC–MS/MS analysis, the commercial essential oils were extracted following the methodology developed and validated by Elsohly et al. [10], and analyzed in duplicates. Analyses were performed using a Shimadzu Liquid Chromatograph LC-20AD (Columbia, MD, USA) coupled to Applied Biosystems MDS Sciex 3200 QTRAP (Foster City, CA, USA). A Luna® Omega Polar C_{18} column (50 × 2.1 mm ID, 3.0 µm), Phenomenex® (Torrance, California, USA) and a line filter KrudKatcher Phenomenex® were used for the chromatographic analysis.

For DMAA confirmation, the same precursor and product ions used in the DART–MS/MS were monitored [9]. Analyst 1.6.1 software was used for data acquisition and analysis. DMAA linearity range was established using concentrations between 25 and 1000 ppb. Limit of quantification for DMAA was 25 ppb and was estimated at an S/N ratio of ten.

Results and Discussion

Evaluation of DMMA in *Pelargonium* Leaves and Oils

GC–MS is the main technique used in chemical characterization of essential oils because it is so well suited for volatile and semi-volatile compounds [8]. To aid comparisons, we used identical GC–MS conditions for the headspace analyses of the plant matter and the liquid injections of the essential oils. Whereas DMAA could readily be detected using both methods, it was not detected in any of the Brazilian samples. Also, the three Brazilian species showed a lower abundance of monoterpenes than expected, especially for *P. hortorum* and *P. peltatum* (Online Resource 1). Because the more volatile compounds were less abundant in the studied species, one concern was that the extraction method was biased against the more volatile components, and this bias could be a reason why some studies fail to identify DMAA.

Traditional methods like hydrodistillation, Soxhlet extraction and supercritical fluid extraction have limitations such as long extraction times (e.g., 4 h or more), the consumption of large quantities of organic solvents, or have the potential to lose the most volatile organics, especially during post-extraction concentration steps [11]. Therefore, alternative approaches involving headspace extraction directly from the leaves obtained from *P. hortorum*, *P. peltatum*, *P. fragrans* were attempted to test the hypothesis that DMAA is lost during the extraction step.

Headspace Analysis

Headspace is considered as a simple technique, which allows the extraction and pre-concentration of volatile compounds, without pretreatment and usually without using solvents. The experimental design using Box–Behnken was employed to ensure the use of best extraction conditions.

P. fragrans model generated the following optimum conditions of analysis for the three studied compounds: temperature (113 °C), stirring time (19.5 min) and weight (1.07 g). Through the predictive capacity, RSDs less than 5% were obtained, which provides reliable evaluation of the best extraction conditions (Table 1). Through analysis of variance (ANOVA) and correlation analysis, limonene and fenchone showed coefficients of correlation (R^2) greater than 0.80, and both are influenced significantly by the temperature of the extraction. The model was classified as a quadratic polynomial ($p < 0.05$) (Table 1). For methyl-eugenol, the variables of weight, temperature and extraction time significantly influenced the extraction, but independently (Online Resource 2).

P. peltatum showed adequacy of the model for beta-caryophyllene and germacrene-B compounds ($p > 0.05$). The opposite was found for gamma-cadinene, as demonstrated by the lack-of-fit of the model ($p < 0.05$). Furthermore, R^2 values of all compounds in *P. peltatum* were found to be less than 0.80. ANOVA analysis did not show any significant differences in the models (quadratic, linear and interaction), so there was minimal influence of tested variables in extraction (Table 1). The values of RSD found were all higher than 15%, so the best conditions of temperature (148 °C), stirring time (10 min) and weight (1.5 g) are not strict requirements. The results indicate that intermediate conditions of time and temperature were most desirable (Online Resource 2).

P. hortorum showed adequacy of the model for beta-caryophyllene, alpha-humulene, and 10-epi-gamma-eudesmol ($p > 0.05$) (Table 1). Using ANOVA, no significant differences were found in any model (quadratic, linear and interaction). Therefore, no influence of the variables tested was verified in the extraction (Online Resource 2). Combining all three compounds, the optimum conditions were found to be an extraction temperature of 123 °C, an extraction time of 30 min and a mass of 0.82 g.

Monoterpenes were very abundant in the leaves extracted via headspace sampling, but almost non-existent in the essential oil of *P. hortorum*, which was obtained by

Table 1 ANOVA p values from Box–Behnken design for three species of *Pelargonium*

Terms	Compounds of *P. fragrans*			Compounds of *P. hortorum*			Compounds of *P. peltatum*		
	Limonene	Fenchone	Methyl-eugenol	Beta-caryo-phyllene	Alpha-humulene	10-epi-gama-eudesmol	Beta-caryo-phyllene	Gamma-cadinene	Germacrene-B
X_1	0.037*	0.120	0.312	0.934	0.974	0.157	0.175	0.146	0.827
X_2	0.649	0.911	0.654	0.783	0.463	0.121	0.283	0.776	0.205
X_3	0.062	0.086	0.462	0.783	0.414	0.945	0.056	0.133	0.285
X_1^2	0.012*	0.005*	0.000*	0.028*	0.045*	0.570	0.395	0.462	0.091
X_2^2	0.148	0.157	0.009*	0.748	0.477	0.438	0.672	0.406	0.895
X_3^2	0.182	0.143	0.007*	0.755	0.470	0.332	0.411	0.294	0.898
$X_1 X_2$	0.713	0.751	0.216	0.946	0.917	0.070	0.822	0.941	0.920
$X_1 X_3$	0.931	0.999	0.627	0.938	0.944	0.951	0.102	0.065	0.684
$X_2 X_3$	0.568	0.203	0.086	0.136	0.539	0.745	0.917	0.874	0.508
Lack-of-fit	0.007*	0.032*	0.207	0.988	0.805	0.068	0.783	0.012*	0.738
R^2	0.868	0.878	0.953	0.719	0.656	0.737	0.763	0.748	0.637

X_1 = temperature (°C); X_2 = time (min); X_3 = weight (g)

*Significant difference at p value < 0.05

hydrodistillation (Fig. 1), supporting the hypothesis that volatiles are lost during extraction. After the optimization studies, the best conditions were selected and the presence of DMAA was evaluated. Although the headspace was more amenable to DMAA extraction compared to hydrodistillation (Fig. 1), promoting the appearance of compounds not detected during the hydrodistilled essential oils, DMAA was absent in Brazilian species.

Analytical performance of GC/MS, DART–MS/MS and LC–MS/MS

GC–MS

GC–MS identified between 97.7 and 99.8% of the known compounds present in commercial essential oils from *P. graveolens* (Online Resource 3). The results showed that none of the essential oils, including the sample from China, contained DMAA above 100 ppb, despite the fact that some exemplars from China have previously been reported to contain DMAA. The commercial essential oil from Brazil and the essential oil from Albania were also negative for DMAA and were not reported to date [12]. Factors such as variations in edafoclimatic conditions, essential oil extraction technique and method of analysis may influence the chemical profile of the oil and could explain, at least in part, the controversial results presented in the literature. However, our results provide more evidences to confirm that dietary supplements contain synthetic DMAA. Nevertheless, considering the low sensibility of the method, analyses were performed using DART–MS/MS and LC–MS/MS.

DART–MS/MS

DART–MS/MS is an analytical tool for the rapid analysis of samples at atmospheric pressure [13]. It can be used for solid or liquid materials deposited or adsorbed onto surfaces in the open atmosphere, without sample pre-treatment. The robustness and ease of use has contributed to DART's rising popularity in different fields, such as quality control, clinical and pharmaceutical applications, forensic applications, biological studies, food quality, food safety and essential oils [14].

DART–MS/MS results showed that DMAA was not detected in any of the essential oils (Fig. 2), at a level above 50 ppb, in agreement with both the previous reports [13] and the GC–MS results in this study. Despite the absence of DMAA in the essential oils, DART–MS/MS allowed their rapid analysis (less than 1 min per sample), using a minimal amount of sample (2 µL of methanol containing 0.1% essential oil), being a fast and simple alternative for the confirmation of substances in plant materials. The ability to couple tandem mass spectrometry with DART ionization provides a level of specificity that enables the detection multiple analytes in a complex sample, without any chromatographic separation [13].

LC–MS/MS

In addition to GC–MS, LC–MS/MS has also been reported for the chemical characterization of essential oils. LC–MS/MS typically provides lower limits of detection/quantification when compared to GC–MS [13]. A 25 ppb DMAA standard was used to spike the essential oil matrix to assess recovery

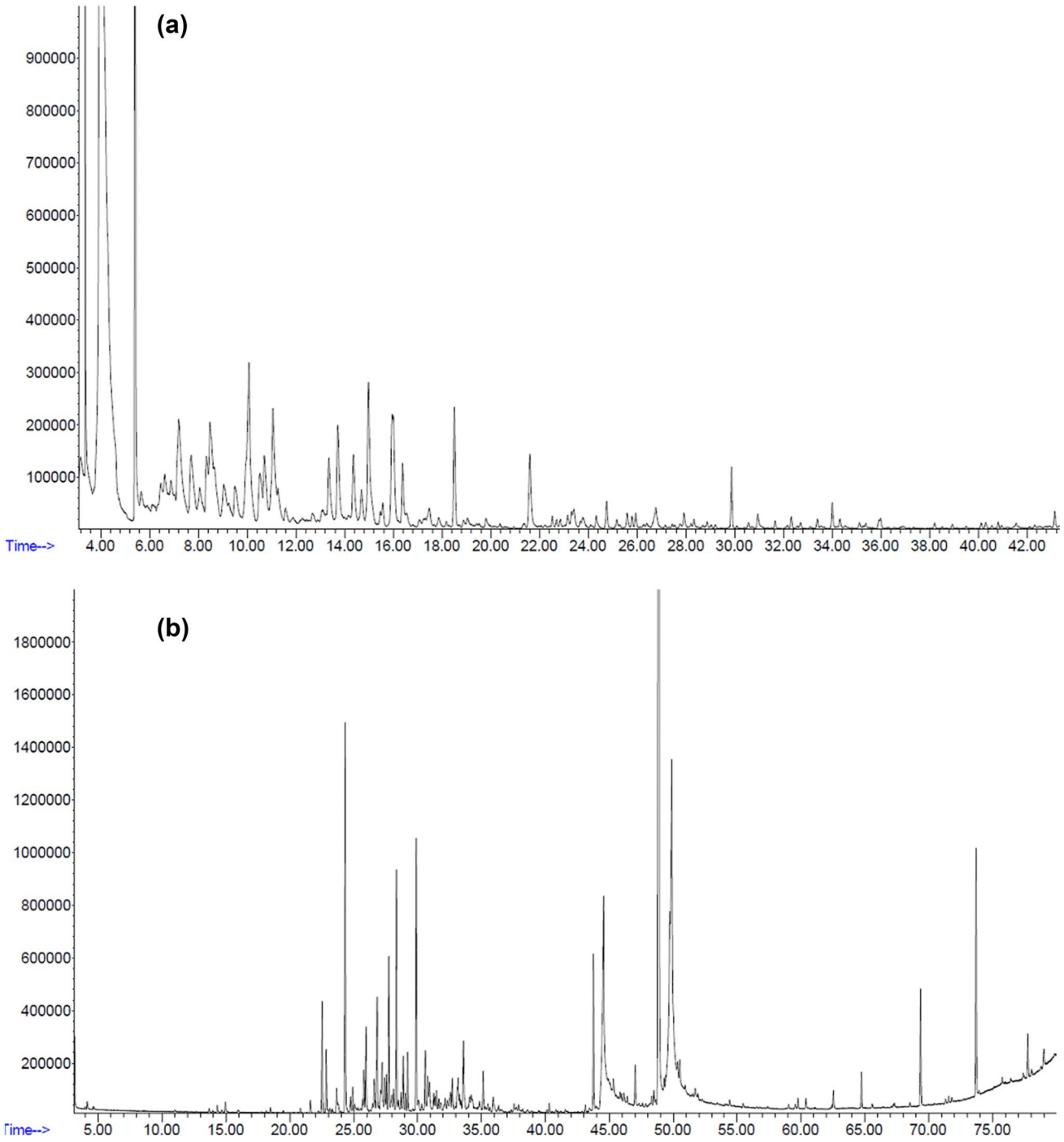


Fig. 1 Chromatograms of leaf headspace (**a**) and hydrodistilled essential oil (**b**) of the same botanic matter of *P. hortorum*

efficiency using a method described by Elsohly et al. [10]. For the spiked sample, MRM transitions for DMAA were observed at the retention time of 4.37 min (Fig. 3). Although DMAA could be recovered at 90% efficiency, it was not identified in any of the essential oils tested, above 25 ppb. These results concur with other LC–MS/MS results, [15] and with data obtained in this study using GC–MS and DART–MS/MS. Compared to GC–MS and DART–MS/MS, LC–MS/MS showed higher sensitivity for DMAA, but did not provide the extensive peak capacity of GC–MS.

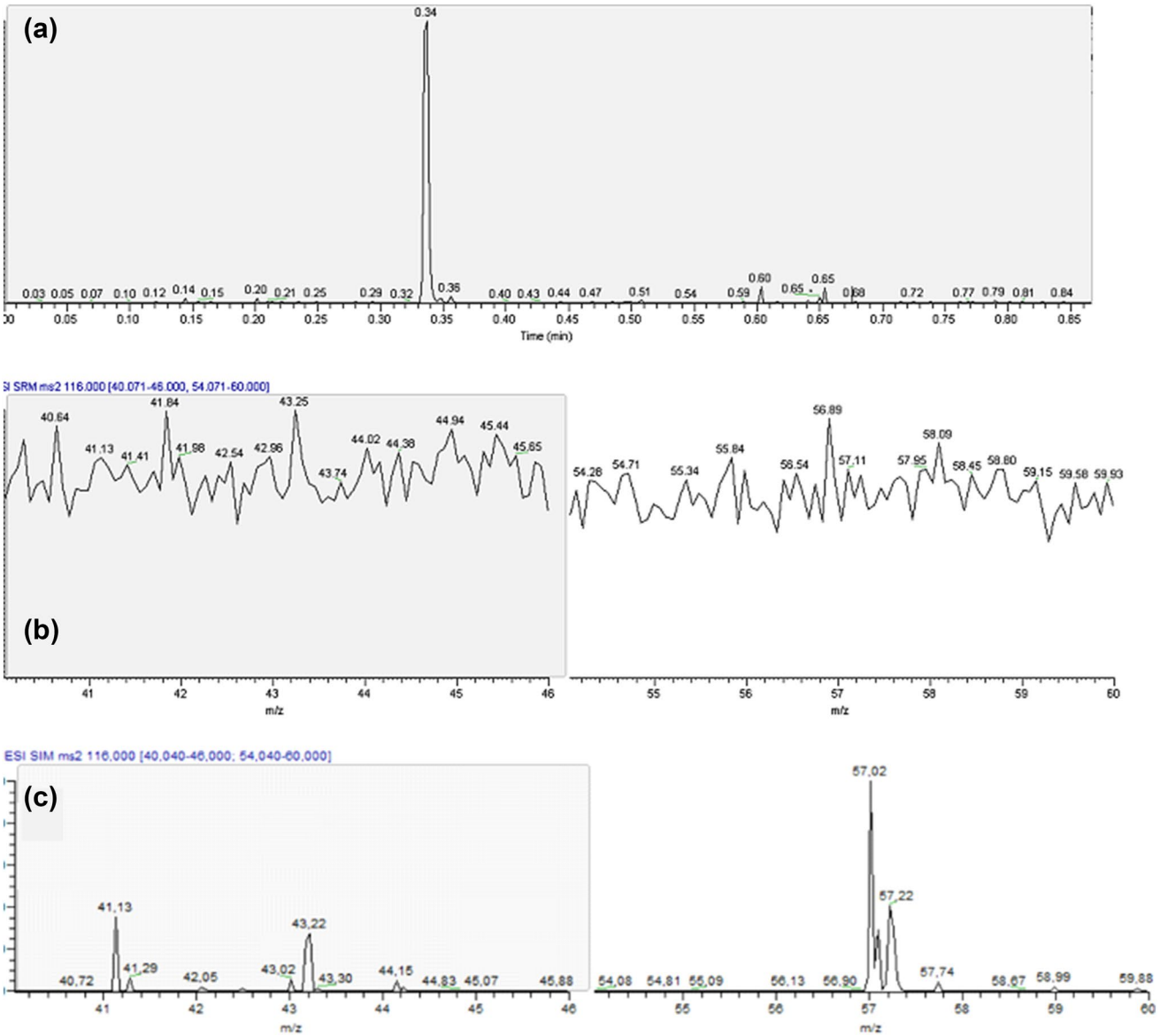
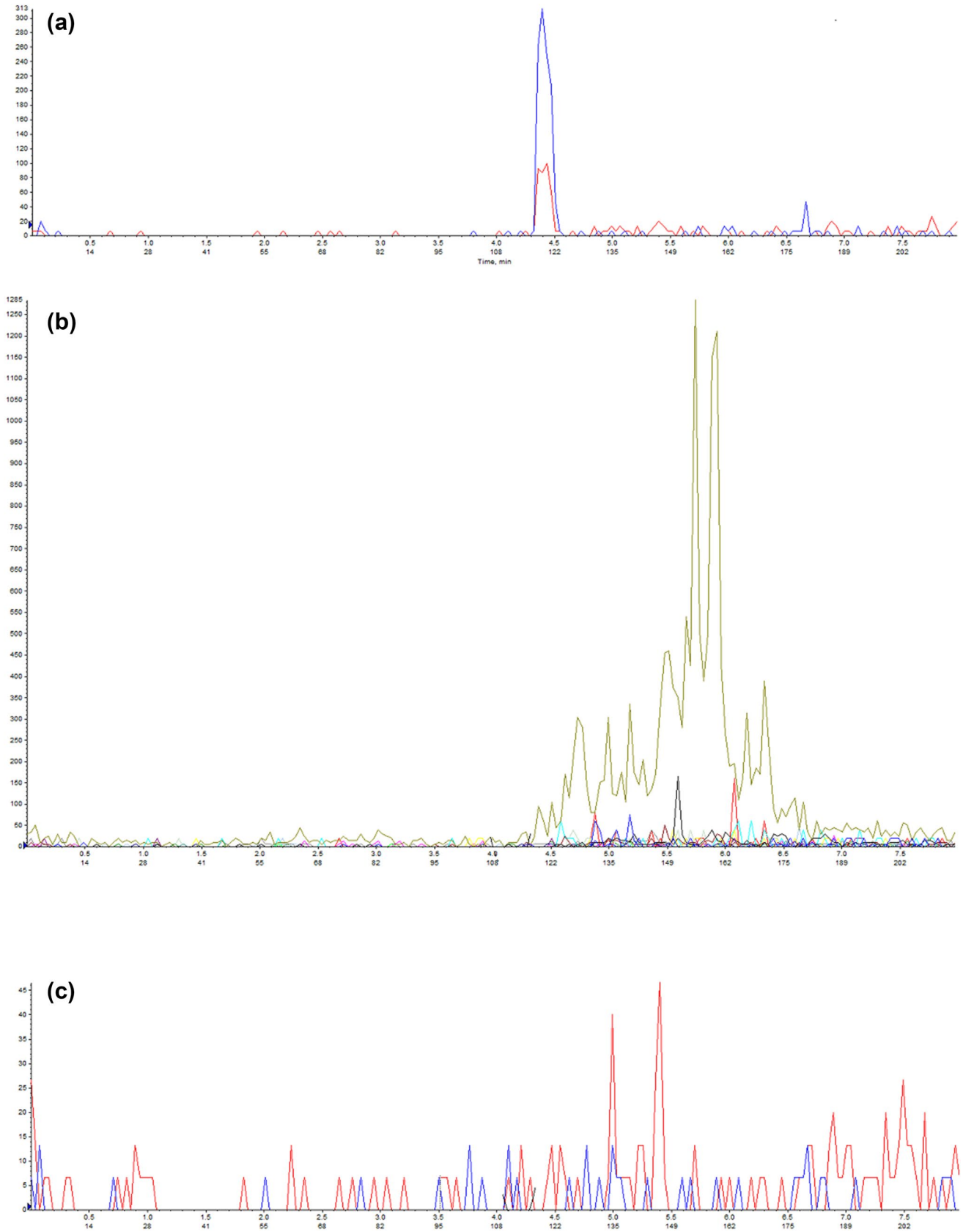


Fig. 2 DART–MS/MS analysis of essential oils of *P. graveolens* from China. Chromatogram of the TIC showing the essential oil introduction at 0.34 min (**a**); background product ion scan of DMAA *m/z* 116 at 0 min (**b**); product ion scan of a DMAA standard *m/z* 116 at 0.34 min showing DMAA-specific product ions at *m/z* 57 and *m/z* 41 and *m/z* 43 (**c**)

Conclusions

The significant contribution of this study was to assess the presence of DMAA in essential oils of *Pelargonium* sp. from Brazil and to facilitate the search of DMAA in leaves of *Pelargonium* sp. Also, using three different mass spectrometric techniques, DMAA could not be detected in essential oils above the detection limits of 25–100 ppb. GC–MS analysis was used on either the essential oils of each plant sample obtained by hydrodistillation or from direct headspace analysis of plant matter, which suggests


(a)
(b)
(c)
Time, min

◂**Fig. 3** LC–MS/MS analysis of essential oils showing the absence of DMAA in *P. graveolens*. DMAA-selective MRM transitions for a standard of DMAA (**a**); chromatogram of essential oil from China indicating the lack of DMAA (**b**); the absence of DMAA transitions for the same essential oil from China (**c**)

that DMAA is not natural in these species. Despite the absence of DMAA, DART–MS/MS and headspace GC–MS can be considered as valid alternatives to the traditional methods of plants extraction—like hydrodistillation—when the identification of the chemical composition and the determination of chemical profile of volatile components in plants are the primary objective.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no competing interests.

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