

# 1,3-Dimethylamylamine (DMAA) in supplements and geranium products: natural or synthetic?

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1,3-Dimethylamylamine (DMAA) is a stimulant existing in various pre-workout supplements and often labelled as part of geranium plants. The safety and origin of DMAA in these supplements is the subject of intense debate. In this study, the enantiomeric and diastereomeric ratios of two different known synthetic DMAA compounds, as well as the total concentrations of DMAA and its stereoisomeric ratios in 13 different supplements, were determined by gas chromatography. The stereoisomeric ratios of DMAA in the synthetic standards and in all the commercial supplements were indistinguishable. Eight different commercial geranium extracts of different geographical origins (China and the Middle East) were examined for the presence of DMAA by high performance liquid chromatography coupled with mass spectrometry (HPLC-MS). No DMAA was detected in any of the eight geranium products with a limit of detection of 10 parts per billion (w/w). Copyright © 2012 John Wiley & Sons, Ltd.

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**Keywords:** DMAA; GC analysis; HPLC analysis; Synthetic versus natural; Geranium oil

## Introduction

1,3-Dimethylamylamine (DMAA), also known as 1,3-dimethylpentylamine, methylhexanamine and 2-amino-4-methylhexane, was first named 'Forthane' and introduced by Eli Lilly & Co., as a vasoconstrictor in the 1940s.<sup>[1–3]</sup> After decades of relative obscurity, it was trademarked as geranamine and brought to the sports market as a dietary ingredient in various pre-workout supplements.<sup>[4]</sup> This was possible because it was reported as a natural product extracted from geranium (*Pelargonium graveolens*) in a little known paper published in the *Journal of Guizhou Institute of Technology* in 1996.<sup>[5]</sup>

In 2009, DMAA was added to the 2010 prohibited list by the World Anti-Doping Agency (WADA) since it is a stimulant.<sup>[6]</sup> In 2010 and 2011, some athletes were disqualified or stripped of their awards in various sporting events when DMAA was detected in post-event drug tests.<sup>[7–9]</sup> Also, a few cases showed that DMAA might have serious side effects. In December 2010, the *Journal of the New Zealand Medical Association* reported that a 21-year-old man suffered a serious haemorrhage after taking DMAA containing pills subsequent to having an alcoholic drink.<sup>[10]</sup> In December 2011, it was reported that the deaths of two US soldiers were suspected to be related to the use of DMAA-containing supplements.<sup>[11,12]</sup> In 2011, the American Herbal Products Association (AHPA) declared that supplement manufacturers should not label the stimulant DMAA as geranium oil or as any part of the geranium plant.<sup>[4]</sup> This statement was supported by the United Natural Products Alliance (UNPA) in January 2012.<sup>[13]</sup>

The safety of DMAA in supplements is the subject of intense debate. Since DMAA was considered by some to be a naturally occurring component of the geranium plant, products/supplements containing geranium-based entities avoided regulation by the Food and Drug Administration (FDA). However papers

published in 1951<sup>[14]</sup> and 1960<sup>[15,16]</sup> as well as the National Cancer Institute (NCI) *in vivo* screening data of synthetic DMAA<sup>[17]</sup> have shown there may be potential side effects and toxicity. One question is whether the DMAA in supplements is from geranium parts and extracts, or if it is a synthetic product.<sup>[18,19]</sup> Other debated questions are whether DMAA should be regulated or even be allowed in supplements.<sup>[4,20]</sup> The paper which was used as the only reference for introducing DMAA to the sporting world has been criticized due to its interpretation errors and lack of convincing evidence<sup>[5]</sup>: (1) It mislabelled DMAA as 2-hexanamide, 4-methyl-<sup>[4,21]</sup> (2) There were three compounds listed in Table 1 of the paper as '28' = tricylene, '29' = 2-heptanamine, 5-methyl- and '30' = 2-hexanamide, 4-methyl- (mislabelled DMAA) between the two compounds 27 and 31. However, only one peak appeared between peak 27 and 31 in the gas chromatography-mass spectrometry (GC-MS) chromatogram. (3) In Table 1 of the paper, the concentrations of compound 27 and 31 were listed as 2.07% and 0.29%, respectively. The single peak that appeared between these two peaks in the GC-MS chromatogram obviously had a smaller peak area than these two peaks. However, the concentration of DMAA was reported as 0.66% which was larger than that of compound 31. (4) No standard was used to confirm the retention time and MS spectrum of DMAA. In December 2011, the National Measurement Institute of Australia published a short communication in *Drug Testing and Analysis* and asserted that geranium oils do not contain DMAA and the supplement products labelled containing geranium oil but which contain DMAA can only

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**Table 1.** Geranium oils tested

No.	Oil analyzed	Manufacturer	Origin	Extraction method	Part of plant
1	Geranium essential oil	Starwest Botanicals, Inc. (Rancho Cordova, CA, USA)	China	Steam distillation	Leaves and branches
2	Geranium essential oil	Earth Solutions (Atlanta, GA, USA)	China	Steam distillation	Flowers and stems
3	Geranium essential oil	Aura Cacia (Urbana, IA, USA)	China	Steam distillation	Leaves and flowering branchlets
4	SOMA Geranium oil	Dreaming Earth Botanicals (Asheville, NC, USA)	China	Steam distillation	Leaves and stems
5	Oshadhi Geranium select	Ayus GmgH (Bühl, Baden-Württemberg, Germany)	Egypt	Steam distillation	Leaves
6	Geranium essential oil	Lotus Brands, Inc. (Twin Lakes, WI, USA)	Egypt	Steam distillation	Not labeled
7	Nature's Alchemy Geranium essential oil	Lotus Brands, Inc. (Twin Lakes, WI, USA)	Egypt	Steam distillation	Not labeled
8	Geranium essential oil	Now Foods (Bloomington, IL, USA)	Egypt	Steam distillation	Fresh plant

arise from the addition of synthetic material.<sup>[22]</sup> Also, another researcher in National Science Foundation Internationals failed to detect DMAA from several geranium essential oils available on the market.<sup>[4]</sup> Despite this criticism, USPlabs insisted that DMAA in its products, Jack3d and OxyElite, was from geranium.<sup>[23]</sup>

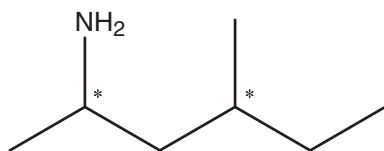
One important aspect of DMAA that has not been considered is that it is a chiral compound with two stereogenic centres (Figure 1). Hence the name DMAA does not refer to a single compound, but to a potential mixture of four stereoisomeric compounds (two pairs of enantiomers, with *S,S*- and *R,R*- configuration and *R,S*- and *S,R*- configuration, respectively). The enantiomeric pairs of synthetic DMAA must be racemic unless they result from an asymmetric process. Further, they will have a diastereomeric ratio characteristic of the synthetic process. Conversely natural plant-derived chiral compounds are usually enantiomerically enriched, often to a high degree.<sup>[24]</sup> If diastereomers are present, they also would have a distinct, characteristic ratio.

In this study we determine the enantiomeric and diastereomeric ratios of two synthetic DMAA standards from different commercial sources. Subsequently, the total concentrations of DMAA and its stereoisomeric ratios were determined in 13 different supplements. Finally, eight different geranium extracts of different geographical origins (China and the Middle East) were examined for the presence of DMAA.

## Experimental

### Materials

The supplement products were purchased from GNC (Pittsburgh, PA, USA), bodybuilding (Meridian, ID, USA), and Amazon (Seattle, WA, USA). 1,3-Dimethylpentylamine standard (free amine), pentafluoropropionic anhydride (PFPA), 2-aminopentane, dansyl chloride and trifluoroacetic acid were purchased from Sigma-Aldrich (Milwaukee, WI, USA). 1,3-Dimethylpentylamine hydrochloride was purchased from ChromaDex (Irvine, CA, USA). Sodium carbonate

**Figure 1.** The structure of 1,3-dimethylamylamine (DMAA).

and sodium hydroxide were purchased from Mallinckrodt Baker, Inc. (Phillipsburg, NJ, USA). Anhydrous magnesium sulfate was purchased from EM Science (Gibbstown, NJ, USA). High performance liquid chromatography (HPLC) grade heptane, acetone, acetonitrile, methanol, hexane, diethyl ether, ethyl acetate and dichloromethane were purchased from EMD Chemicals (Gibbstown, NJ, USA). Water was purified by a Milli-Q Water Purification System (Millipore, Billerica, MA, USA). The geranium oil extracts are listed in Table 1. A eucalyptus essential oil (Now Foods, Bloomington, IL, USA) was purchased from GNC (Pittsburgh, PA, USA).

### Sample preparation for GC analysis

- Standard solutions: 10 mg of DMAA standard and 10 mg of internal standard (2-aminopentane) were dissolved in 0.5 ml of dichloromethane. 0.5 ml PFPA was added to the vial and the vial was sealed with a silicone rubber insert. The solution was heated for 30 min at 50°C. Then the solvent and residual PFPA were removed at room temperature under reduced pressure. The derivatized DMAA and internal standard were transferred to a 10-ml volumetric flask and diluted to 10 ml with heptane. The stock solution was diluted to a series of solutions with concentrations of 0.8, 0.6, 0.4, 0.2 mg/ml. (The concentrations refer to DMAA.) The calibration curves of DMAA and the internal standard are available in supporting materials. The response factor of DMAA to internal standard was calculated from the calibration curves and equal to 1.02.
- Supplements: 200 mg of supplement powder was dissolved in 1 ml water. 5 mg of internal standard was spiked into the solution. The pH was adjusted to 9–10 with sodium carbonate. 1 ml dichloromethane was added to the solution and vortexed. The whole solution was filtered with a syringe filter and the organic layer was collected and dried with magnesium sulfate. The dichloromethane solution was transferred to a 3-ml screw-top vial to which 0.5 ml PFPA was added and the vial sealed by cap with silicone rubber insert. The solution was heated for 30 min at 50°C. Then the solvent and residual PFPA were removed at room temperature under reduced pressure. The sample was diluted with heptane and ready for GC injection.

### Sample preparation for HPLC analysis

- Non-spiked sample: 2 g of geranium oil were weighed into a 50 mL vial. 10 mL of de-ionized water was added and

followed by 1 mL of concentrated HCl solution. The sample was vortexed. The sample was then extracted with  $2 \times 10$  mL hexane/diethyl ether (50/50). The organic layers were discarded. 1 mL of 50% NaOH solution was added to the sample and briefly vortexed. The sample was then extracted with  $3 \times 4$  mL hexane/ethyl acetate (50/50). The organic portion was collected and evaporated to dryness.

- Spiked sample: 100 parts per billion (w/w) DMAA hydrochloride standard was spiked into each geranium oil sample and extracted by using the above procedure.
- For HPLC-electrospray ionization-linear ion trap (HPLC-ESI-LIT) analysis, the extracted residue was dissolved in 500  $\mu$ L of methanol which contained 0.1% formic acid prior to injection.
- For HPLC-electrospray ionization-triple quadrupole (HPLC-ESI-QQQ) analysis, the extracted residue was dansylated prior to analysis. In the dansylation procedure, the extracted residue was dissolved in 3 mL of 2:1 acetone:3M sodium carbonate. Then 25 mg of dansyl chloride was added and the reaction was stirred in darkness for 20 minutes at 60°C. 2 mL of dichloromethane was added and the organic layer was washed with  $2 \times 10$  mL of de-ionized water. The solvent was removed under vacuum and the residue was dissolved in 1 mL of acetonitrile prior to injection.
- Two blanks were prepared for each analysis method: 1) in one blank no essential oil was used, 2) in the other blank an equal amount of eucalyptus essential oil (Now Foods, Bloomingdale, IL, USA) was used instead of geranium oil. The blanks were prepared following the same procedures above for each analysis method.

#### GC method

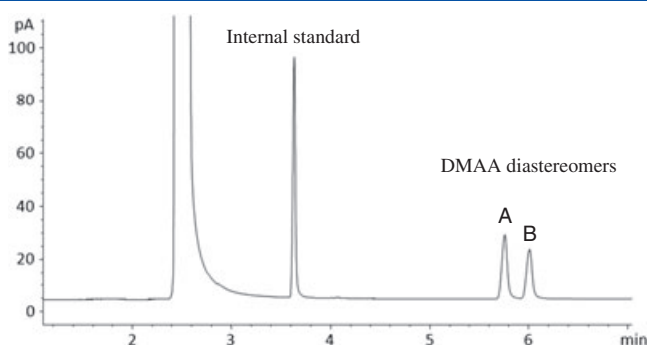
An Agilent model 6890N network gas chromatograph system was used. Helium was used as the carrier gas with a flow rate of 1 mL/min. The injection volume was 1  $\mu$ L. The split ratio was 1:100 at the injector. Detection was achieved with an FID detector. The injector and detector temperatures were 250°C. An Astec ChiralDex G-DM column (30 m  $\times$  0.25 mm i. d.  $\times$  0.20  $\mu$ m) was used for all the GC separations. Determination of DMAA diastereomeric ratios and quantification of DMAA content in supplements were operated at 90°C isothermally. 2-Aminopentane was used as internal standard in the quantification of DMAA in the supplements. The enantiomeric excess of the DMAA in the standards and the supplements were determined at 30°C isothermally.

#### HPLC-ESI-LIT method

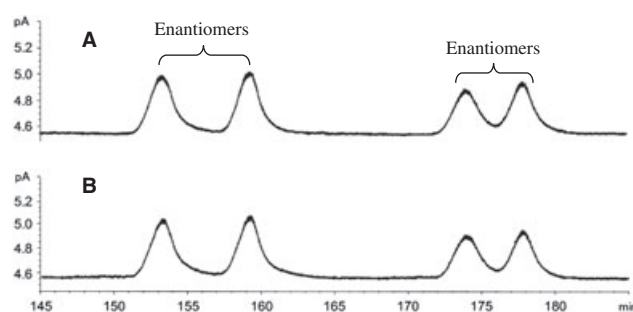
In the HPLC-ESI-LIT method, a Thermo Finnigan Surveyor autosampler, a MS pump, a Thermo LXQ linear ion trap mass spectrometer and a LARIHC CF6-P column (15cm  $\times$  2.1mm) (AZYP, Arlington, TX, USA) were used. The HPLC mobile phase consisted of 90% acetonitrile containing 0.1% formic acid and 10% methanol containing 0.1% formic acid. The total flow rate for HPLC was 0.4 mL/min. The mass spectra data were recorded in a positive mode of electrospray ionization for selected ion  $m/z$  116.2. Capillary voltage and spray voltage were set at 25 V and 5 kV, respectively. The injection volume was 5  $\mu$ L. The limit of detection (LOD) of this method was 50 parts per billion (ppb) of spiked DMAA in geranium oils.

#### HPLC-ESI-QQQ method

In the HPLC-ESI-QQQ method, a Shimadzu SIL-20AC autosampler, a LD-20AD pump, a LC/MS-8030 triple quadrupole mass spectrometer and a Kinetex 2.6u XB-C18 column (10 cm  $\times$  2.1 mm)



**Figure 2.** GC chromatogram of N-pentafluoropropionyl derivatives of DMAA standard (from Sigma-Aldrich) and internal standard at 90°C. Diastereomeric ratio = Peak Area A / Peak Area B. The retention times of the internal standard, DMAA diastereomer A and B were 3.62 min, 5.78 min, and 6.20 min, respectively.



**Figure 3.** GC chromatograms of N-pentafluoropropionyl DMAA enantiomers at 30°C. A) Synthetic DMAA, B) DMAA in the supplement manufactured by Primaforce. DMAA in all the other supplements had identical chromatograms as B). The retention times for the four enantiomers were 153.49 min, 159.18 min, 174.11 min and 177.71 min, respectively.

(Phenomenex, Torrance, CA, USA) were used. The HPLC mobile phase consisted of 70% of acetonitrile and 30% of H<sub>2</sub>O containing 0.1% trifluoroacetic acid. The total flow rate was 0.2 mL/min. The mass spectra data were recorded in the positive ion mode (multiple reaction monitoring transition of  $m/z$  349 to 171 corresponding to the primary dansyl fragment and neutral loss of sulfonyl-DMAA). The collision energy was -25 volts with argon as the collision gas. The injection volume was 5  $\mu$ L. The LOD of this method was 10 ppb.

## Results and discussion

### GC analysis of DMAA in supplements

The diastereomeric ratios of the synthetic DMAA standards from Sigma-Aldrich and ChromaDex were  $1.22 \pm 0.06$  and  $1.42 \pm 0.09$ , respectively (Figure 2). As expected, both were racemic pairs of enantiomers (Figure 3A). The concentrations (weight %) and diastereomeric ratios of DMAA in 13 commercial supplements are given in Table 2. The total concentrations of DMAA varied widely in the supplements, from ~0.1% to ~11%. All diastereomeric ratios were in the same range as the two synthetic DMAA compounds, *vide supra*. Furthermore, the enantiomeric compositions of the DMAA in all 13 supplements were racemic (Figure 3B). Thus, the stereoisomeric compositions of DMAA in the synthetic standards and in all the commercial supplements were indistinguishable.

The concentrations of DMAA in most of the supplements were fairly high. In general, the concentrations of molecules with low

**Table 2.** The diastereomeric ratio and concentration of DMAA in supplements

	Supplements	Manufacturer	Diastereomeric Ratio	% DMAA Dry weight	DMAA per serving(mg)	Stated DMAA per serving(mg)	Labelling DMAA as
1	1,3-DIMETHYLAMYLAMINE	Primaforce	1.23	3.7 ± 0.4	17 ± 2	20	1,3-dimethylamylamine
2	Speed V2 diet pills	LG Science	1.28	0.20 ± 0.06	1.2 ± 0.4	*	geranium oil extract
3	ADRALIN dietary supplement	CTD Labs	1.31	2.1 ± 0.3	34 ± 4	*	1,3-dimethylpentylamine
4	RIPPED JUICE	BETANCOURT NUTRITION	1.34	11.2 ± 1.0	80 ± 7	*	geranamine
5	OxyELITE Pro	USPLabs	1.36	10.2 ± 1.7	31 ± 5	*	1,3-dimethylpentylamine hydrochloride
6	Jack3d	USPLabs	1.43	2.6 ± 0.5	142 ± 25	*	geranium stem
7	FlashOver	Omega Sports	1.32	2.9 ± 0.5	285 ± 51	20	1,3-dimethylamylamine
8	OVERDOSE	NRGX LABS	1.27	0.11 ± 0.01	217 ± 26	*	geranium stem
9	PWR	iSatori, LLC	1.28	0.33 ± 0.09	16 ± 4	*	1,3-dimethylpentylamine
10	1.M.R	BPI	1.31	1.1 ± 0.1	85 ± 9	*	1,3-dimethylamylamine
11	STIM-FORCE	LABRADA NUTRITION	1.31	0.72 ± 0.04	27 ± 1	*	1,3-dimethylpentylamine hydrochloride
12	HEMO RAGE	NutreX research, Inc.	1.35	1.03 ± 0.04	33 ± 1	*	1,3-dimethylpentylamine
13	HYDROXYSTIM	MuscleTech	1.25	1.9 ± 0.2	10 ± 1	177	geranium extract

\* The amount of DMAA per serving in the supplement was not stated.

molecular weight in botanicals and their extracts are not that high,<sup>[25,26]</sup> and therefore their concentrations in commercial products containing a small proportion of the botanicals/extracts would be even lower. Consequently, the level (concentration), nature (stereoisomeric composition) and existence of DMAA in geranium plants/extracts are particularly germane to the ongoing debate.

### HPLC analysis of geranium oils

To determine if geranium oil contains DMAA, a detection method with high sensitivity is preferred. In this study, two mass spectrometric methods were used for the detection of DMAA. One used an ESI-linear ion trap mass spectrometer (ESI-LIT-MS) and the other utilized an ESI-triple quadrupole mass spectrometer (ESI-QQQ-MS). When the underivatized extracted residues of geranium oils were directly injected to these mass spectrometers, the signal of DMAA was greatly suppressed by the other geranium oil components remaining in the residue. However, the LOD was significantly reduced when the components in the samples were separated via HPLC before entering the mass spectrometer.

For the underivatized samples, a LARIHC CF6-P column was used for the separation. This column provided adequate retention of primary amines when using polar organic mobile phases.<sup>[27,28]</sup> The retention time of DMAA in this column was about 8 min. (See Experimental and Supporting Information.) The LOD of this HPLC-ESI-LIT method was 50 ppb for underivatized DMAA in geranium oil. No DMAA was detected in any of the 8 geranium oil samples with this method.

Dansylation can change the polarity and increase the retention of DMAA in the reversed phase mode HPLC. Also, the dansylation can reduce the LOD of DMAA. Thus, the extracted residues of the geranium oils were dansylated prior to the HPLC-ESI-QQQ analysis (See Experimental). The LOD of this method was 10 ppb for DMAA in geranium oil. It should be noted that the LOD of

DMAA refers to the concentration of neat DMAA in the geranium oils and not to the concentration of the derivatization product, dansyl DMAA. Again, no DMAA was detected in any of the 8 geranium oils samples.

### Conclusions

According to the GC and HPLC analyses in this study, it appears unlikely that the DMAA in supplements originates from natural sources such as geranium oils for three reasons: (1) the DMAA extracted from these supplement products had diastereomeric ratios that were indistinguishable from the synthetic DMAA standards; (2) they are all racemic; (3) no DMAA was detected at a level of ≥10 ppb in any of the 8 geranium oil samples.

### Acknowledgement

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### Supporting information

Supporting information may be found in the online version of this article.

### Conflict of interest statement

The corresponding author, D. W. A., served as an expert witness in 2011 for the case: DeRosier v. USPLabs.

### References

- [1] H.A. Shonle, E. Rohrmann. US Patent No 2350318, **1944**.
- [2] E. Rohrmann, H.A. Shonle. Amino alkanes as pressor substances. *J. Am. Chem. Soc.* **1944**, *66*, 1516.
- [3] Anonymous. New and nonofficial remedies: methylhexamine; forthane. *J. Am. Med. Assoc.* **1950**, *143*, 1156.

- [4] Anonymous. What to do about DMAA? *Nutr. Bus. J.* **2012**, *17*, 1.
- [5] P. Zang, J. Qing, Q. Lu. A study on the chemical constituents of geranium oil. *Guizhou Gongxueyuan Xuebao* **1996**, *25*, 82.
- [6] World Anti-doping Agency. WADA 2010 Prohibited List. Available at: [http://www.wada-ama.org/Documents/World\\_Anti-Doping\\_Program/WADP-Prohibited-list/WADA\\_Prohibited\\_List\\_2010\\_EN.pdf](http://www.wada-ama.org/Documents/World_Anti-Doping_Program/WADP-Prohibited-list/WADA_Prohibited_List_2010_EN.pdf) [19 September 2009].
- [7] NDTV. Now nine Aussie athletes test positive for methylhexanamine. Available at: <http://www.ndtv.com/article/commonwealth%20games/nine-aussie-athletes-test-positive-for-methylhexanamine-61768&cp> [23 October 2010].
- [8] P. Cossins. Rui Costa and his brother test positive. Available at: <http://www.cyclingnews.com/news/rui-costa-and-his-brother-test-positive> [19 October 2010].
- [9] BBC Sport. Second Nigerian tests positive at Commonwealth Games. Available at: [http://news.bbc.co.uk/sport2/hi/commonwealth\\_games/delhi\\_2010/9082481.stm](http://news.bbc.co.uk/sport2/hi/commonwealth_games/delhi_2010/9082481.stm) [12 October 2010].
- [10] P. Gee, S. Jackson, J. Easton. Another bitter pill: a case of toxicity from DMAA party pills. *N. Z. Med. J.* **2010**, *123*, 124.
- [11] T.J. Tritten. Army probing connection between body building supplement, 2 deaths. Available at: <http://www.stripes.com/news/army-probing-connection-between-body-building-supplement-2-deaths-1.163652> [15 December 2011].
- [12] P. Chiaramonte. Soldier deaths during training prompt military probe into supplement use. Available at: <http://www.foxnews.com/us/2012/02/02/soldier-deaths-during-training-sparks-military-probe-into-supplement-use/> [2 February 2012].
- [13] E. Watson. UNPA: We agree with AHPA on DMAA labeling. Available at: <http://www.nutraingredients-usa.com/Industry/UNPA-We-agree-with-AHPA-on-DMAA-labeling> [10 January 2012].
- [14] D.F. Marsh, A. Howard, D.A. Herring. The comparative pharmacology of the isomeric nitrogen-methyl-substituted heptylamines. *J. Pharmacol. Exp. Ther.* **1951**, *103*, 325.
- [15] R.B. Stoughton, G. Deoreo, W. Clendenning. Effects of intradermal injection of vasopressors in normal and diseased human skin. *Arch. Dermatol.* **1960**, *82*, 400.
- [16] D.T. Walz, T. Koppanyi, G.D. Maengwyn-Davies, M.L. Joyce. Isoproterenol vasomotor reversal by sympathomimetic amines. *J. Pharmacol. Exp. Ther.* **1960**, *129*, 200.
- [17] NCI. In vivo screening data. Available at: [http://dtp.nci.nih.gov/dtpstandard/servlet/InvivoScreen?testshortname=Tumor+LE+\(ip\)+in+06&searchlist=1106&searchtype=NSC](http://dtp.nci.nih.gov/dtpstandard/servlet/InvivoScreen?testshortname=Tumor+LE+(ip)+in+06&searchlist=1106&searchtype=NSC) [18 March 2012].
- [18] S. Daniells. Health Canada: DMAA is not from geranium. Available at: <http://www.nutraingredients-usa.com/Industry/Health-Canada-DMAA-is-not-from-geranium> [24 August 2011].
- [19] E. Adelson. Real Heat Wave Risk Posed by Fake "Geranium". Available at: <http://www.thepostgame.com/features/201108/geranium-products-might-pose-serious-risk-athletes> [15 August 2011].
- [20] S. Starling. Food? Medicine? Neither? UK agencies "trying to get to bottom" of DMAA status. Available at: [http://www.nutraingredients.com/Regulation/Food-Medicine-Neither-UK-agencies-trying-to-get-to-bottom-of-DMAA-status/?utm\\_source=newsletter\\_daily&utm\\_medium=email&utm\\_campaign=Newsletter%2BDaily&c=gaa%2FSjqPjaEIO-qUhpYc%2BX4aUxc3sFA](http://www.nutraingredients.com/Regulation/Food-Medicine-Neither-UK-agencies-trying-to-get-to-bottom-of-DMAA-status/?utm_source=newsletter_daily&utm_medium=email&utm_campaign=Newsletter%2BDaily&c=gaa%2FSjqPjaEIO-qUhpYc%2BX4aUxc3sFA) [23 February 2012].
- [21] Anonymous. Geranium oil research. **2012**. Available at: <http://dmaaresearch.com/geranium-oil-research> [18 March 2012].
- [22] A. Lisi, N. Hasick, R. Kazlauskas, C. Goebel. Studies of methylhexanamine in supplements and geranium oil. *Drug Test. Anal.* **2011**, *3*, 873.
- [23] E. Watson. USPLabs: DMAA is from geranium oil - and critics are "uninformed". Available at: <http://www.nutraingredients-usa.com/Regulation/USPLabs-DMAA-is-from-geranium-oil-and-critics-are-uninformed> [5 January 2012].
- [24] D.W. Armstrong, X. Wang, J. Lee, Y. Liu. Enantiomeric composition of nornicotine, anatabine, and anabasine in tobacco. *Chirality* **1999**, *11*, 82.
- [25] T. Mroczek, K. Glowniak, A. Wlaszczyk. Simultaneous determination of N-oxides and free bases of pyrrolizidine alkaloids by cation-exchange solid-phase extraction and ion-pair high-performance liquid chromatography. *J. Chromatogr. A* **2002**, *949*, 249.
- [26] L. Zhou, A.A. Hopkins, D.V. Huhman, L.W. Sumner. Efficient and sensitive method for quantitative analysis of alkaloids in hardinggrass (*Phalaris aquatica* L.). *J. Agric. Food Chem.* **2006**, *54*, 9287.
- [27] P. Sun, D.W. Armstrong. Effective enantiomeric separations of racemic primary amines by the isopropyl carbamate-cyclofructan6 chiral stationary phase. *J. Chromatogr. A* **2010**, *1217*, 4904.
- [28] P. Sun, C. Wang, Z.S. Breitbach, Y. Zhang, D.W. Armstrong. Development of new HPLC chiral stationary phases based on native and derivatized cyclofructans. *Anal. Chem.* **2009**, *81*, 10215.