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THE FLORAL ODOUR OF *PELTANDRA VIRGINICA* CONTAINS NOVEL TRIMETHYL-2,5-DIOXABICYCLO[3.2.1]NONANES

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Key Word Index—*Peltandra virginica*; Araceae; floral odour; headspace analysis; GC-MS; trimethyl-2,5-dioxabicyclo[3.2.1.]nonanes.

Abstract—The qualitative and quantitative composition of the floral odour of *Peltandra virginica* was determined by trapping odour components from freshly cut inflorescences on Tenax and Carbotrap adsorbents using a purge and trap apparatus. Analysis showed that a single novel compound, 1,3,6-trimethyl-2,5-dioxabicyclo[3.2.1.]nonane, comprised nearly 70% of the odour. Four isomers of this compound were found in much smaller amounts (1.0–7.6%) while an analogue with m_r 142 comprised 13% of the odour. Small amounts (*ca* 0.3–2.5%) of two isomers of methylundecene and three isomers of dimethyldodecenone were also detected. This is the first case of trimethyldioxabicyclo[3.2.1]nonanes reported in floral odours.

INTRODUCTION

Along with visual cues, olfactory cues are important stimuli at all or most stages of insect perception of flowers [1]. Therefore, to understand the interaction between a plant and its pollinator(s) it is necessary to identify the floral cues produced by the plant and to verify the pollinator's perception of these stimuli [2]. The purpose of the present study was to identify the floral odour compounds produced by *Peltandra virginica* Kunth as part of a more general study of the pollination biology of this species. Aroids use complex floral morphologies in tandem with floral odours to attract and manipulate a diverse range of pollinators, primarily beetles and flies [3–7]. However, information on floral odour composition is available for only a few aroid species [8].

Peltandra virginica is a common emergent aquatic found in freshwater wetlands throughout eastern North America [9]. The plant produces an odoriferous inflorescence, 6–25 cm long, which comprises a yellow spadix enclosed by a green elongated spathe.

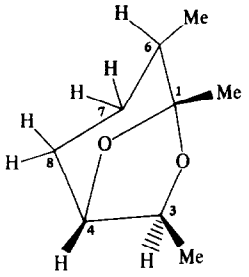
A strong mutualism exists between *P. virginica* and its pollinator, a small chloropid fly, *Elachiptera formosa* Loew. This fly species uses the inflorescence as a mating and brood site and is apparently found only in the vicinity of *P. virginica*. The female flies oviposit inside the floral chamber and the larvae feed on pollen but do not damage the developing fruit. *Peltandra virginica* can neither self-pollinate nor propagate asexually and, therefore, *E. formosa* is essential for its reproduction. Future studies will examine the biological activity of the floral odour compounds, which appears to be an important link between these two organisms.

RESULTS AND DISCUSSION

To the human nose, the odour of *Peltandra virginica* has a musty quality with resinous overtones. Because porous trap materials vary in their ability to trap volatile organic compounds, trapping of floral odour was conducted with two adsorbents to ensure that all floral volatiles were colleted [10–14]. Similar total ion chromatograms were produced from traps containing both Tenax TA and Carbotrap and from traps containing only Tenax TA.

Samples for derivitization with trimethyl silyl chloride (TMS) and diazomethane were collected using a Likens–Nickerson extractor, an apparatus which provides for continuous steam distillation with ether extraction. However, the high temperatures produced during the distillation process gave rise to an extract which contained many matrix-derived volatile artifacts that were not present in the samples collected with the adsorbent trapping method. Therefore, all subsequent samples were collected with the adsorbent trapping method.

In all samples the total ion chromatograms were dominated by a single novel component, identified as 1,3,6-trimethyl-2,5-dioxabicyclo[3.2.1]nonane (**1**), which comprised 69% of the total trapped compounds (Table 1). Four isomers of this compound (**2–5**) were present in much smaller amounts (1.0–7.6% of the total composition). An analogue with a m_r of 142 amu (**6**) comprised nearly 13% of the total adsorbed compounds. A small percentage (*ca* 0.3–2.7%) was also composed of two isomers of methylundecene (**7**, **8**) and three isomers of dimethydodecen-2-one (**9–11**).



1

In the initial study none of the EI mass spectra of the major components from the preliminary samples matched compounds from reference spectra [15] so further analyses were performed to elucidate the molecular structures of these compounds. The GC set-up used for fractionation of the sample was also used for sensory evaluation of all GC peaks because the heated exit port also functioned as a sniff port. All of the floral volative GC peaks had the characteristic odour of *P. virginica* inflorescences, especially that of **1**.

The EI mass spectrum of 1 showed a weak molecular ion at *m/z* 156 which was followed by high intensity ions at *m/z* 114 and 72. In the CI mass spectral mode (isobutane), a strong $[M+H]^+$ ion appeared at *m/z* 157. High resolution mass spectrometry conducted on the GC-fractionated sample provided an empirical formula of $C_9H_{16}O_2$ for compound **1**. High resolution mass spectrometry demonstrated tht the parent ion lost a C_3H_6+fragment yielding a $[C_6H_{10}O_2]^+$ ion (corresponding to the ion at *m/z* 114) which, in turn lost a C_2H_2O+fragment to yield a $[C_4H_8O]^+$ ion (at *m/z* 72).

No derivatives were obtained after standard treatment of an ether extract of **1** with either TMS or diazomethane, indicating that **1** did not contain any active primary protons. The IR band at 1011 cm^{-1} indicated the presence of an unusual arrangement of etheral oxygen in the compound. A preponderance of methyl groups was indicated by a strong IR band at 1390 cm^{-1} while a weaker band at 1462 $^{-1}$ indicated the presence of methylene groups. Two peaks of similar intensity at 2920 cm^{-1} and 2950 cm^{-1} confirm this. The IR spectra lacked the characteristic bands associated with aromaticity, olefinic hydrogen, carbonyls, hydroxyls, and branched methyl groups such as isopropyl.

The ^1H and ^{13}C NMR data are given in Table 2, including connectivity information from decoupling and from 2D correlated spectroscopy (COSY) experiments. The ^{13}C data shows nine unique carbon signals consistent with the mass spectral empirical formula $C_9H_{16}O_2$. This indicates a structure having two double bonds/rings. The carbon multiplicities show three methyl, two methylene, three methine one quaternary carbon group; showing all 16 protons to be attached to carbon; thus excluding the presence of any labile protons. The presence of quaternary carbon (C-1) having a chemical shift of δ110 is consistent with a carbon bearing two oxygens and the shifts, δ79.4 and 75.6 (C-3 and C-4) is consistent with methine carbons bearing single oxygens. The ^1H data shows chemical shifts at δ4.11 and 4.03 consistent with the presence of methine protons attached to oxygen bearing carbons. This information establishes, the substructure, –CHOCOCH–. As there are no double bonds, the structure must contain two rings. Although there was no evidence for coupling between H-3 and H-4, saturation of the methyl attached to C-3 gave rise to a 4.5% (NOE) enhancement of H-4. This shows that H-4 is vicinal to H-3 thus establishing a dioxolane substructure. The lack of coupling between H-3 and H-4 is consistent with a dihedral angle of *ca* 90°, which was supported by constructing a Dreiding model of the structure.

A ^1H COSY experiment showed the connectivity between protons: Me-3 and Me-3, 4 and 8, 7 and 8, 6 and 7, 6 and Me-6. The cross peaks for 4, 8 coupling showed both axial and equatorial protons of 8. The water resonance at δ1.5, however, interferred with a detailed observation of H-7 protons. Decoupling of the Me- protons collapsed H-6 to a doublet of doublets with *J* vaues of 5.1 and 11.1 Hz. This suggests that H-6 is axial and coupled to the axial and equatorial protons of H-7. A small NOE (*ca* 1%) was observed for the Me-6 protons on saturation of Me-1 protons as well as the reverse. This is not surprising as methyl to methyl NOEs are generally very small. A complete stereochemical structure assignment was not possible due to a limited amount of sample.

The EI and CI mass spectra of the four trimethyl-2,5-dioxabicyclo[3.2.1]nonane isomers (**2**–**5**) were nearly identical to the mass spectra produced by **1**. The EI mass spectra of these compounds had a weak or absent signal at $[M]^+$ and moderate to strong signals at *m/z* 114 and 72. The CI mode produced a strong signal at *m/z* 157 $[M+H]^+$.

The EI mass spectrum of the 142 m_r compound (**6**) was similar to that of **1** but it had a weak signal for $[M]^+$ at *m/z* 142, a strong signal for ions at *m/z* 72 and 57, and moderate signals for ions at *m/z* 85 and 69. The CI mode mass spectra showed a strong $[M+H]^+$ signal at *m/z* 143. High resolution mass spectrometry gave an empirical formula of $C_8H_{14}O_2$ for this compound. Analysis with EI mass spectrometry demonstrated that the trimethylsilyl (TMS) derivative of **6** had a m_r of 214, indicating that an active proton, possibly from a primary alcohol, is present. This compound is higher boiling than **1** as it has a longer retention time yet its mass is 14 amu less than that of **1**. It is possible that **6** is similar in structure to **1**, except that the dioxolane ring is open and that it has only two methyl groups.

Two of the minor components were identified as methylundecene isomers (**7**, **8**) while the remaining minor components were identified as dimethyl dodecenone isomers (**9**–**11**) by comparison of their EI mass spectra with data of ref. [15]. In addition CI mode gave strong $[M+H]^+$ signals at *m/z* 173 for the methylundecene isomers and *m/z* 211 for the dimethyldodecene isomers.

The above-mentioned attributes make the floral odour of *P. virginica* unusual in three respects: (i) it is composed primarily of trimethyl-2,5-dioxabicyclo[3.2.1.]nonanes, a class of compounds not previously found in floral odours (ii) it has a relatively simple composition because it is composed of only 11 components, whereas many floral odours are composed of 20–30 (or more) components [2, 16, 17] and (iii) it lacks the usual monoterpenes and aromatic compounds found in many other floral odours [2, 16, 17].

The floral odour is probably a specific attractant of *E. formosa* because of the floral volatiles' unique character and the strong mutualism between the aroid and the fly. Because of their high degree of pollinator specialization

Table 1. Components of the floral odour of *Peltandra virginica*

Component		% Composition
1	1,3,6-Trimethyl-2,5-dioxabicyclo[3.2.1]nonane	69.0
2	Trimethyl-2,5-dioxabicyclo[3.2.1.]nonane Isomer	2.0
3	Trimethyl-2,5-dioxabicyclo[3.2.1.]nonane Isomer	1.0
4	Trimethyl-2,5-dioxabicyclo[3.2.1.]nonane Isomer	1.0
5	Trimethyl-2,5-dioxabicyclo[3.2.1.]nonane Isomer	7.6
6	M_r 142 Compound (unknown)	12.7
7	Methylundecene isomer	<1.0
8	Methylundecene isomer	<1.0
9	Dimethyldodecenone isomer	2.0
10	Dimethyldodecenone isomer	2.3
11	Dimethyldodecenone isomer	2.0

Table 2. ^1H and ^{13C} NMR spectral data of compound **1**.

Label	C	H	^3J Connectivities (COSY)
1	110.0 *s*	—	—
3	75.6 *d*	4.11 1, *q*	$^3J = 6.26$ Hz 3, Me
4	79.4 *d*	4.03 1, *m*	(8*a*, 8*e*)
6	38.4 *d*	1.72 1, *m*	$^3J = 6.65$ Hz (7a, 7e, 6, Me)
7	28.7 *t*	1.4–1.6 2, *m*	(6,8)
8	25.8 *t*	1.85, 1.56 2, *m*	(7)
1, Me	22.7 *q*[a]	1.42 3, *s*	—
6, Me	21.6 *q*[a]	0.86 3, *s*	$^3J = 6.65$ Hz (6)
3, Me	16.6 *q*	1.22 3, *d*	$^3J = 6.26$ Hz, (3)

[a]Chemical shifts may be interchanged.
*Observed crosspeaks in parentheses.

many aroid floral odours are likely to contain novel compounds that are also pollinator-specific attractants. Further study of the chemical composition and biological activity of the floral odours of this interesting plant family should yield many novel compounds, some representing new classes of floral volatiles.

EXPERIMENTAL

Plant material. Peltandra virginica Kunth plants were identified by J. M. Patt and J. C. French. A voucher specimen is deposited at The Chrysler Herbarium, Department of Biological Science, Nelson Biological Lab, Rutgers University, Piscataway, NJ, U.S.A. Collections were made from the Delaware and Raritan Canal State Park in East Millstone, NJ, U.S.A. and from Weston Mills Pond in North Brunswick, NJ, U.S.A. during June and July of 1989 and 1990. During all collections the cut inflorescences were placed in water and immediately transferred to the laboratory for sampling.

Trapping floral volatiles on Tenax and Carbotrap for preliminary study. Floral compounds for preliminary analysis with GC-MS- and GC-IR were entrained in the following manner. 10 inflorescences were placed in a 1.9 l glass screw top jar containing 100 ml of 3% sucrose solution. The top of the collection jar was sealed with a stainless steel lid fitted with an air inlet and outlet, a teflon gasket, and a ring cap. The odour trap consisted of a 10 cm long × 6 mm o.d. presilanized borosilicate glass tube filled with 30 mg Tenax TA 60/80 mesh and 100 mg Carbotrap (™Supelco, Inc.). The traps were conditioned in a GC oven as follows: 35° then 2° min^{-1} to 320° for 12 hr using He carrier gas at a flow rate of 40 ml min^{-1}. During sample collection the trap tube was inserted into a stainless steel union containing a graphite ferrule seal fitted into the air outlet. The jar was purged for 60 min with clean dry air at a flow rate of 80 ml min^{-1}. The trap tube was removed and the procedure repeated using a fresh trap tube. At the end of the collection period the trap tubes were purged with N_2 at 75 ml min^{-1} for 15 min to remove water vapour condesation. The trap tubes were closed with brass end caps with graphite ferrule seals and stored at −40°.

Trapping odour volatiles on Tenax for fractionation. Odours were entrained as described in the preliminary collection section. Because microgram amounts of sample were desired large glass tubes (25 cm × 12.5 mm o.d.) filled with 3 g of Tenax TA 60/80 mesh were used. Twenty-five inflorescences were used per sample. The collection jar was purged with ultra high purity grade dry air from a compressed air cylinder at a rate of 75 ml min^{-1} for 26 hr. Two 150 Watt grow-lights, set to a 16 hr light: 8 hr dark were placed 1 m on both sides of the collecting apparatus to mimic the plant's natural photoperiod.

At the end of the collection periods the Tenax was removed and eluted with 2 washes of 400 ml Et_2O for 30 min. The eluate was concd to 20 ml in a Kuderna–Danish concentrator apparatus fitted with a three-ball Snyder column. The sample was centrifuged at 2000 rpm for 10 min to remove fine particles of Tenax suspended in the Et_2O. The sample was then further concd by evapn under a stream of N_2 to a final vol of 2 ml. The percent composition of each floral component was estimated by comparing its peak area integration to the peak area produced

by the 0.70 mg of the antioxidant butylated hydroxy toluene (BHT) present in the total volume of Et_2O used to elute the sample.

Fractionation and cold trapping. The sample was fractionated into its component compounds in a GC equipped with a 2 m × 4 mm i.d. glass column packed with 3% OV-101 on 80/100 mesh Supelcoport. A 0.5 m × 0.53 mm i.d. fused silica column was attached to the end of the packed column with a stainless steel reducing union. The end of the megabore capillary column was, in turn, fitted to a fused silica universal Y-splitter (Restek Corp.). A 30:1 split of each fraction was achieved by joining a 0.5 m × 0.125 mm i.d. section of deactivated fused silica tubing to one arm of the Y-splitter and a 0.5 m × 0.53 mm id. megabore capillary column to the other arm. The split volume was determined by measuring the flow rate at the end of each column after the split assembly. The larger volume (30 ml min^{-1}) was split to a heated exit port at 260° while the smaller volume (1 ml min^{-1}) was split to an FID at 250°, allowing simultaneous monitoring and collection of each fr. The following GC parameters were used: samples size 10 μl, splitless injection at 220°, 31 ml min^{-1} He at 10 psi, and a three-step temp. program as follows: 35° (5 min), then 2° min^{-1} to 120° (0 min), 10° min^{-1} to 260° (5 min).

Each fr. was collected by cold trapping as follows: During the elution of each fraction a U-shaped 10 cm × 2 i.d. mm glass capillary tube with one end bent 90° relative to the rest of tube was fitted over a 2.5 cm long piece of heated capillary column that protruded from the exit port. A cylindrical half-hole type silicone rubber septum was used to effect a seal between the column and the U-tube. The U-tubes were conditioned by several rinses of CH_2Cl_2 and followed by drying with a hand-held hot air dryer. A separate U-tube was used for each fraction. The bottom of the U-tube was positioned in a dewar flask containing an *iso*-PrOH–dry ice slurry maintained at *ca* 80°. The fractions condensed inside of the U-tube upon cooling. Between collection times the ends of the U-tubes were covered with silicone septa and kept immersed in the isopropanol-dry ice slurry. During preliminay trials each fraction was sniffed as it eluted to insure that FID response way synchronous with elution from the collecting end of the column. At the end of fractionation the ends of the U-tubes were sealed with teflon tape and stored at -40°. It was possible to collect only the fr. with **1** in sufficient quantity to permit NMR analysis.

Solvent extraction for TMS and diazomethane derivatization. Floral volatiles were extracted in Et_2O from whole inflorescences in a Likens–Nickerson extractor. Three extractions were made from a total of 155 inflorescences (15 kg fr.wt). The extracts were combined to a total vol. of 375 ml which was condensed to 3 ml in a Kudurna–Danish concentrator apparatus. The extract was analysed by GC-MS using the parameters described below. Mass chromatorgrams were used to locate the floral odour volatile peaks in the total ion current. The extract was fractionated into the major floral odour components as described above.

Desorption and GC-MS analysis. The floral volatiles were desorbed from the trap tubes using a short path thermal desorption system prototype (Scientific Instrument Services, Ringoes, NJ, U.S.A.) interfaced to the GC injection port. The thermal desorption parameters were as follows: desorber temp. at 250°, He carrier flow rate at 20 cm sec^{-1}, desorption time of 10 min. The floral odour volatiles were cryogenically trapped in the column which had been cooled to -40° by the additon of *ca* 2 kg crushed dry ice to the GC oven. A 60 m × 0.32 mm i.d. DB-1 fused silica capillary column with a 1.0 μm film thickness was used with the following conditions: injector temp. at 250°, 10:1 split ratio, 20 cm sec^{-1} He carrier at 10 psi, and a three-step temp program as follows: initial oven temp at −40° (10 min cryotrap stage) then 10° min^{-1} to 40° (0 min) then 4° min^{-1} to 280° (5 min). Mass spectra were obtained using both EI and CI mode. The EI/CI-MS parameters were as follows: scan speed 1 sec/decade, interscan time 0.8 sec, filament emission current 1 mA, ionization voltage 70 eV, CI mode source pressure at *ca* 0.8 Torr, reagent gas was isobutane, unit mass resolution set at 1000 mu, mass range scanned 35–350 amu in EI and 60–350 amu in the CI mode, source temp 2. 250°, direct interface temp. 240°. High resolution accurate mass measurements were obtained by manual peak matching versus perfluorokerosene reference standards using an instrument resolution of 10000.

IR analysis was performed on samples in $CDCl_3$ sol. Compound **1** was analysed in $CDCl_3$ with TMS as an int. referene. The measurement frequency for ^1H was 300.068 MHz and 75.45 MHz for ^{13}C. The Attached Proton Test (APT) was used to provide carbon multiplicities. All NOE data was generated using the NOED method with interleaving on a nonspun sample. The 2D COSY data was generated with a F1 and F2 of 2000 Hz and gave a final matrix of 512 × 512.

1,3,6-*Trimethyl*-2,5-*dioxabicyclo*[3.2.1.]*nonane*:*primary isomer* (**I**). IR ν_{max} cm^{-1}:1011, 1175, 1350, 1460, 1602, 2350, 2390, 2920, 2950. HRMS: Found; $[M]^+$ 156.1160; $C_9H_{16}O_2$ requires 156.1150. EIMS *m/z* (rel. int): 156 $[M]^+$ (10), 114 $[C_6H_{10}O_2]^+$ (42), 112 (8), 97 (12), 96 (9), 95 (5), 85 (5), 81 (15), 72 $[C_4H_8O]^+$ (40), 71 (28), 69 (6), 59 (4), 57 (7), 55 (26), 54 (13), 53 (4), 43 (100), 41 (11), 39 (6); CIMS (isobutane): 199 (2), 159 (2), 158 (13), 157 $[M+H]^+$ (100), 156 (6), 141 (4), 139 (2).

Trimethyl-2,5-*dioxabicyclo* [3.2.1.]*nonane isomer* (**2**). EIMS *m/z* (rel. int.): 115 (5), 114 (34), 112 (12), 97 (4), 85 (14), 81 (4), 69 (15), 68 (32), 58 (7), 45 (12), 43 (100). CIMS (isobutane): 199 (2), 159 (2), 158 (10), 157 $[M+H]^+$ (100), 123 (2), 114 (4), 99 (3), 87 (2), 81 (4), 68 (3).

Trimethyl-2,5-*dioxabicyclo*[3.2.1.]*nonane isomer* (**3**). EIMS *m/z* (rel. int.): 114 (6), 113 (14), 85 (23), 84 (4), 72 (5), 71 (100), 70 (32), 69 (4), 57 (76), 56 (16), 44 (8), 43 (82).

Trimethyl-2,5-*dioxabicyclol*[3.2.1.]*nonane isomer* (**4**). CIMS (isobutane): 158 (10), 157 $[M+H]^+$ (100), 155 (18), 141 (10),139 (2), 127 (4), 113 (4), 96 (4), 79 (4), 69 (6).

Trimethyl-2,5-*dioxabicyclo*3.2.1.]*nonane isomer* (**5**),EIMS *m/z* (rel. int.) 156 $[M]^+$ (8), 115 (2), 114 (12), 112 (10), 99 (4), 97 (20), 96 (16), 95 (4), 85 (8), 81 (14), 73 (7), 72 (50), 71 (18), 69 (8), 68 (5), 55 (18), 53 (2), 43 (100). CIMS (isobutane): 158 (12), 157 $[M+H]^+$ (100), 143 (18), 141 (6), 135 (2), 123 (2), 95 (2), 80 (2), 73 (3).

M_r 142 *compound* (**6**). HRMS: Found; $[M]^+$ 142.0988; $C_8H_{14}O_2$ requires 142.0993. EIMS *m/z* (rel. int.): 142 $[M]^+$ (5), 99 (4),86 (2), 85 (10), 73 (6), 72 (100), 69 (5), 58 (4), 57 (54), 55 (8), 53 (2), 44 (2), 43 (98), 39 (10). CIMS (isobutane): 144 (12), 143 $[M+H]^+$ (100), 72 (2).

Methylundecene isomer (**7**). EIMS: *m/z* (rel. int.): 125 (12), 112 (14), 111 (52), 98 (4), 85 (12), 84 (38), 83 (43), 72 (14), 71 (92), 69 (82), 68 (8), 57 (56), 55 (57), 53 (10), 43 (100). CIMS (isobutane): 170 (14), 169 $[M+H]^+$ (100), 168 (10), 157 (8), 155 (12), 142 (8), 141 (42), 137 (6), 127 (8), 115 (8), 112 (20), 111 (14), 112 (20), 111 (14), 99 (32) 97 (14), 85 (40), 83 (20), 71 (14), 70 (14), 68 (10).

Methylundecene isomer (**8**). EIMS *m/z* (rel. int.): 112 (20), 111 (16), 85 (10), 84 (22), 83 (23), 71 (50), 70 (100), 69 (6), 68 (10), 57 (84), 55 (70), 51 (6), 45 (15), 43 (93). CIMS (isobutane): 179 (10), 170 (19), 169 $[M+H]^+$ (100), 168 (22), 165 (10), 155 (18), 141 (38), 140 (12),127 (54),109 (25), 100 (6), 99 (19), 97 (32), 96 (18), 85 (14), 77 (8), 71 (18), 67 (20).

Dimethyldodecenone isomer (**9**). EIMS *m/z* (rel. int.): 153 (12), 126 (11), 125 (20), 112 (4), 111 (44), 85 (60), 83 (66), 82 (5), 71 (18), 70 (60), 69 (100), 67 (6), 57 (2), 55 (56), 44 (7), 43 (72). CIMS (isobutane): 219 (12), 211 $[M+H]^+$ (100), 187 (14), 183 (20), 168 (10), 167 (16), 156 (8), 155 (20), 142 (10), 141 (30), 133 (10), 127 (30),

112 (46), 111 (32), 109 (14), 106 (8), 99 (26), 97 (29), 96 (18), 93 (11), 85 (42), 77 (6), 76 (10), 71 (27), 68 (15).

Dimethyldodecenone isomer (**10**). EIMS *m/z* (rel int.): 154 (6), 125 (8), 111 (30), 110 (6), 97 (10), 85 (39), 84 (38), 83 (32), 71 (44), 69 (92), 67 (7), 57 (74), 55 (60), 44 (10), 43 (100). CIMS (isobutane): 212 (10), 211 $[M+H]^+$ (100), 197 (24), 183 (30), 169 (20), 156 (8), 155 (32), 141 (38), 139 (10), 127 (56), 125 (28), 113 (50), 111 (22), 99 (42), 95 (22), 85 (63), 81 (20), 80 (9), 71 (51), 68 (12).

Dimethyldodecenone isomer (**11**) EIMS *m/z* (rel int.): 126 (10),125 (8), 111 (30), 97 (14), 85 (40), 84 (64), 83 (36), 81 (10), 71 (60), 69 (85), 57 (83), 55 (28), 54 (8), 53 (4), 43 (100). CIMS (isobutane): 212 (8), 211 $[M+H]^+$ (100), 183 (20), 169 (18), 155 (21), 141 (43),127 (38), 113 (49), 111 (18), 95 (14), 85 (51), 71 (82).

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