

1   **Table S1. Induced changes in volatile emission**

2   Plant volatiles were collected 1 - 13 h, 13 - 25 h and 25 - 37 h after having wounded one leaf  
3   with a fabric pattern wheel and treating it with either *Manduca sexta*'s oral secretions  
4   (W+OS), OS purified by ion-exchange chromatography (W+IOS), a buffer at the same pH as  
5   *M. sexta*'s OS (W+B), synthetic fatty acid amino acid conjugates (W+FACs) or with 2-  
6   hydroxyoctadecatrienoic acid (W+2-HOT). The results of six types of statistical comparisons  
7   (ANOVA on normalized log-transformed peak intensities, n = 6 biological replicates *per*  
8   treatment) are presented: A, the W+OS response, W+OS vs control (CTRL) samples to detect  
9   total changes elicited by the W+OS treatment; B, the W+B response, W+B vs CTRL and C,  
10   the OS response, W+OS vs W+B, to evaluate the relative contributions of the W and OS  
11   responses to those changes; D, the IOS response, W+IOS vs W+B; E, the FAC response,  
12   W+FACs vs W+B and F, the 2-HOT response, W+2-HOT vs W+B. Leaf volatiles detected  
13   significantly up (grey cells) or down-regulated (black cells) for at least one statistical  
14   comparison are listed by chemical classes, with their *P* values and their retention times (RT, s)  
15   on the first and second dimensions. Numbers indicate the type of identification (Id.): 1,  
16   comparison with standards; 2, putative identification. Retention indices (RI) were calculated  
17   according to Kováts (1958) and compared to literature (lit.) reports: <sup>a</sup>(Ruther, 2000), <sup>b</sup>(Adams,  
18   2004), <sup>c</sup>(Engel *et al.*, 2002), <sup>d</sup>(Triqui and Reineccius, 1995)<sup>e</sup>(Guth and Grosch, 1991),  
19   <sup>f</sup>(Jirovetz *et al.*, 2002).

Class	Compound	Id.	RT (s)	RI	1: 1 - 13 h						2: 13 - 25 h						3: 25 - 37 h									
					RT1	RT2	Calc.	Lit.	A	B	C	D	E	F	A	B	C	D	E	F	A	B	C	D	E	F
					W+OS	W+B	OS	IOS	FACs	2-HOT	W+OS	W+B	OS	IOS	FACs	2-HOT	W+OS	W+B	OS	IOS	FACs	2-HOT	W+OS	W+B	OS	IOS
Alcohol	Pentanoic acid, 3-methyl-2-pentanol, 4-methyl-2-pentanol, 3-methyl-	2	450	2.49	963	-	-	0.015	0.043	0.011	0.008	0.013	0.017	0.021	0.014	0.0039	0.004	0.0039	0.005	0.011	0.005	0.004	0.004	0.005	0.004	
	cis-3-Hevenol	2	228	2.17	837	-	-	-	-	0.021	0.017	0.016	0.015	0.027	0.015	0.016	0.02	0.021	0.017	0.016	0.015	0.027	0.015	0.016	0.015	0.016
	1-Heanol	1	246	2.57	858	849a	-	-	-	0.021	0.004	0.048	0.015	0.027	0.015	0.016	0.02	0.021	0.017	0.016	0.015	0.027	0.015	0.016	0.015	0.016
	Heptanal	1	270	2.56	872	876a	-	-	-	0.015	0.027	0.016	0.015	0.027	0.015	0.016	0.02	0.015	0.027	0.016	0.015	0.027	0.015	0.016	0.015	0.016
Aldehyde	Octanal	2	552	2.73	1004	1006ce	-	0.011	0.012	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Unknown	-	636	4.82	1049	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Unknown	-	822	2.81	1145	-	-	0.007	0.023	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Inden-2-one, octahydro	-	858	4.03	1166	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Aromatic	Benzothiazole	-	954	4.13	1215	-	-	0.032	0.012	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	cis-3-hexenylacetate	1	570	2.84	1014	1008a	0.021	0.034	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	cis-3-Hexenylpropionate	1	750	2.73	1104	1100a	0.001	0.012	0.005	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	cis-3-Hexenylisobutyrate	1	834	2.51	1151	1147b	0.002	0.031	0.023	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hexenyl ester	Hexylisobutyrate	1	840	2.32	1154	1152b	0.003	0.023	0.023	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	cis-3-hexenyl, trans-2-butenoic ester	2	882	2.71	1176	-	0.001	0.023	0.023	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	cis-3-Hexenylbutyrate	1	912	2.56	1191	1187a	0	0.042	0.042	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	trans-2-hexenylbutyrate	1	924	2.65	1197	1198a	0.002	0.021	0.021	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Methylester	cis-3-Hexenyl-2-methylbutyrate	1	984	2.51	1234	1231a	0.002	0.048	0.048	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	cis-3-hexenyl-3-methylbutyrate	1	996	2.51	1241	1245b	0.003	0.012	0.047	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	cis-3-Hexenylsuccinate	1	1140	2.85	1328	1322a	0	0.04	0.038	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
	cis-3-Hexenylmethylpentanoate	2	1170	2.51	1348	-	0.038	0.033	0.033	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Terpenoid	Pentanoic, 3-methyl-, methyl ester	2	300	2.8	888	-	0.007	0.044	0.044	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	$\alpha$ -Pinene	1	396	2.04	938	939b	0.026	0.026	0.026	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	$\beta$ -pinene	2	474	2.29	973	979c	0.002	0.002	0.002	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Limonene	1	600	2.29	1030	1029b	0.045	0.045	0.045	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Terpenoid	1,8-Cineole	1	600	2.66	1030	1031b	0.024	0.024	0.024	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Unknown	-	714	2.71	1082	-	0.039	0.045	0.045	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Unknown	-	720	2.34	1088	-	0.021	0.034	0.034	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Terpineol	1	906	3.02	1188	1189b	0.027	0.027	0.027	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Terpenoid	Unknown	-	1176	3.27	1352	-	0.039	0.032	0.032	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Unknown	-	1272	2.59	1380	-	0.037	0.037	0.037	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	trans- $\alpha$ -Bergamotene	1	1302	2.28	1435	1435b	0.021	0.039	0.039	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Unknown	-	1476	2.88	1541	-	0.027	0.027	0.027	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

**Supplemental Table I. Evaluation of injection, retention time and calibration precisions.**

Injection and retention time precisions were evaluated by injecting 10 times 1  $\mu\text{L}$  of a solution containing a mixture of volatile standards (*cis*-3-hexenal, *cis*-3-hexenol, *trans*-2-hexenal, *cis*-3-hexenylbutyrate, methyl salicylate and *trans*-caryophyllene) each at a concentration of 2ng/ $\mu\text{L}$ . Retention times calculated (in s) for the second dimension (column 2, C2) were stable throughout the 10 runs and showed very low relative standard deviations (RSD).

Calibration parameters and the limit of detection (LOD) and limit of quantification (LOQ) were calculated from double injections of standard mixes ranging from 20, 50, 100, 250 and 500 pg/ $\mu\text{L}$ .

Compound	C2 RSD %	Injection RSD %
<i>cis</i> -3-Hexenal	0.48	10.34
<i>cis</i> -3-Hexenol	0.14	8.15
<i>trans</i> -2-Hexenal	0.25	5.55
<i>cis</i> -3-Hexenylbutyrate	0.22	6.21
Methyl salicylate	0.24	3.61
<i>trans</i> - $\alpha$ -Caryophyllene	0.22	8.29
Tetralin (ISTD)	0.13	4.64

  

	Slope	Intercept	R <sup>2</sup>	LOD pg/ $\mu\text{L}$	LOQ pg/ $\mu\text{L}$
<i>cis</i> -3-Hexenal	0.087	-0.423	0.999	5.54	21.85
<i>cis</i> -3-Hexenol	0.27	-3.265	0.9994	16.43	61.96
<i>trans</i> -2-Hexenal	0.206	-3.152	0.999	21.69	80.41
<i>cis</i> -3-Hexenylbutyrate	0.192	-0.199	0.9999	2.84	11.36
Methyl salicylate	0.04	-0.46	0.9999	4.97	19.65
<i>trans</i> - $\alpha$ -Caryophyllene	0.04	0.089	0.9998	9.01	34.99