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Supplemental Information

Evidence for the recruitment of florivorous plant bugs as pollinators

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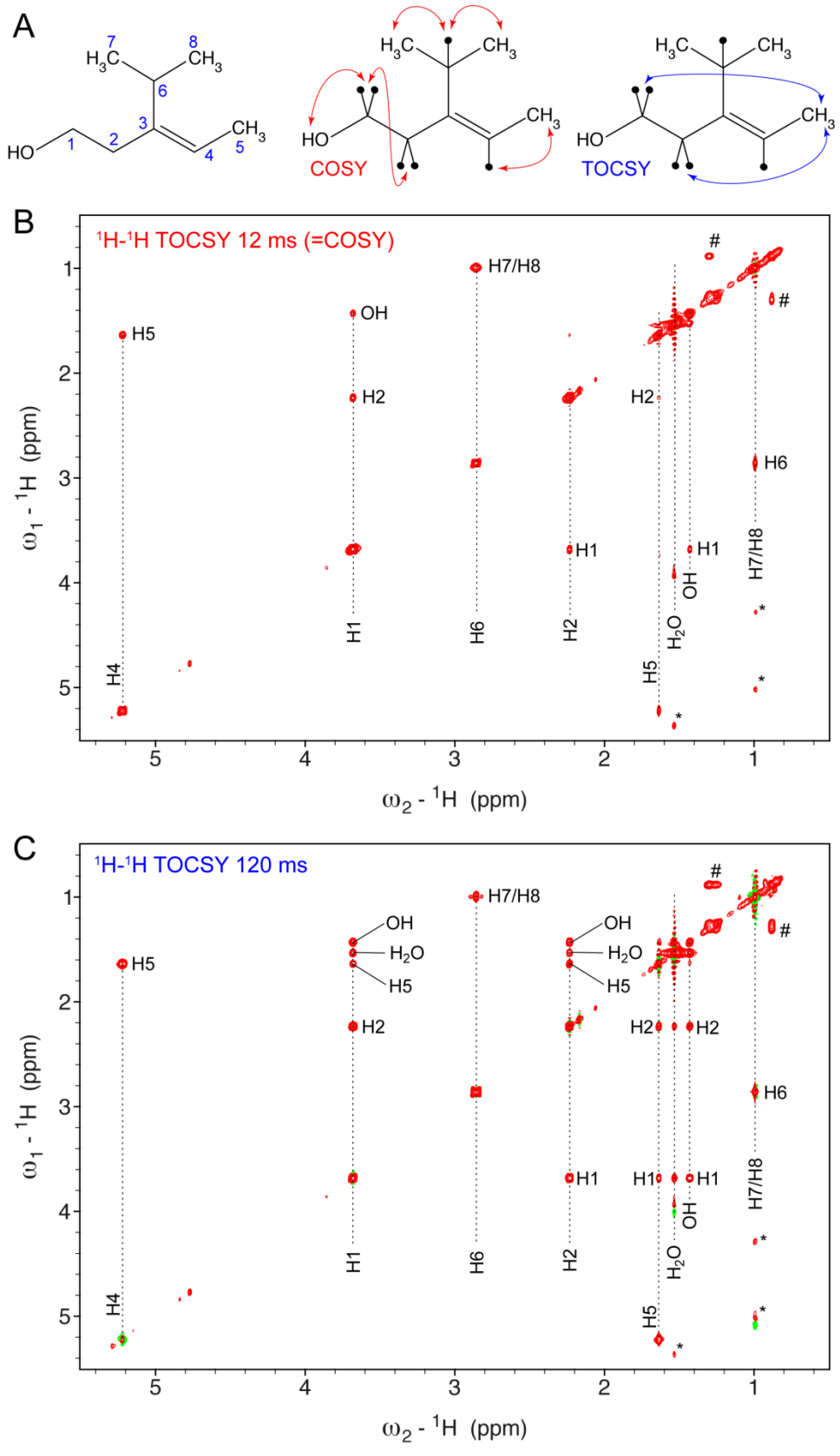
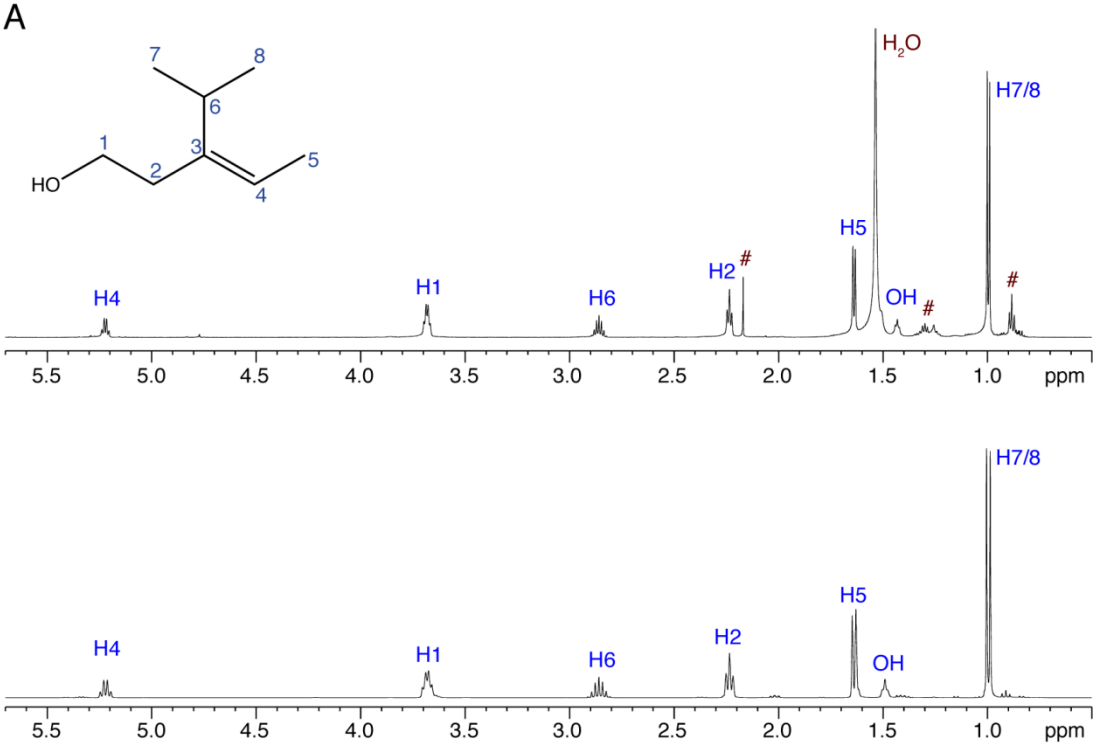

A
COSY
TOCSY
B
^{1}H-^{1}H TOCSY 12 ms (=COSY)
H7/H8
OH
H5
H2
H6
H1
H4
H$_2$O
#
*
ω_1 - ^{1}H (ppm)
ω_2 - ^{1}H (ppm)
C
^{1}H-^{1}H TOCSY 120 ms

Figure S1. Identification of the major scent component by NMR spectroscopy as (*Z*)-3-isopropylpent-3-en-1-ol, Related to Figure 5. (A) Chemical structure and nomenclature of the atoms (left), observed short-range ^{1}H-^{1}H correlations shown schematically in the form of red arrows on the structure (middle), and selected long-range ^{1}H-^{1}H correlations indicated by blue arrows (right). **(B)** ^{1}H-^{1}H TOCSY spectrum with 12 ms mixing time leading to cross-peaks similar to COSY. **(C)** ^{1}H-^{1}H TOCSY spectrum with 120 ms mixing time for the observation of long-range ^{1}H-^{1}H correlations. (# stands for signals of hexane, which was an impurity, * for artefacts in t_1).

A


7
8
6
1
3
5
2
HO
4
H4
H1
H6
H2
#
H5
H2O
OH
#
#
H7/8
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
H4
H1
H6
H2
H5
OH
H7/8
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

B

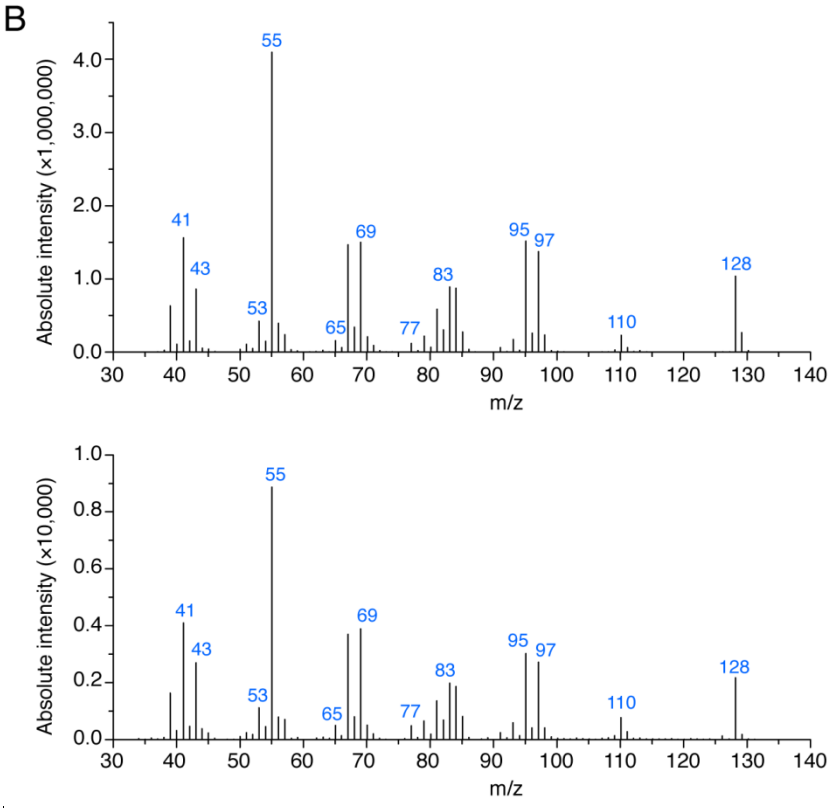

Absolute intensity (×1,000,000)
4.0
3.0
2.0
1.0
0.0
55
41
43
53
65
69
77
83
95
97
110
128
30
40
50
60
70
80
90
100
110
120
130
140
m/z
Absolute intensity (×10,000)
1.0
0.8
0.6
0.4
0.2
0.0
55
41
43
53
65
69
77
83
95
97
110
128
30
40
50
60
70
80
90
100
110
120
130
140
m/z

Figure S2. Comparison of NMR (A) and MS (B) spectra between the natural (top) and synthetic compound (bottom), Related to Figure 5. (A) 1H NMR spectra of the natural product (top) and the synthetic (bottom). The chemical structure of the compound is shown at the top left with the atom nomenclature. Impurities in the NMR spectrum are indicated by a #. **(B)** MS spectra of the natural product (top) and the synthetic (bottom).

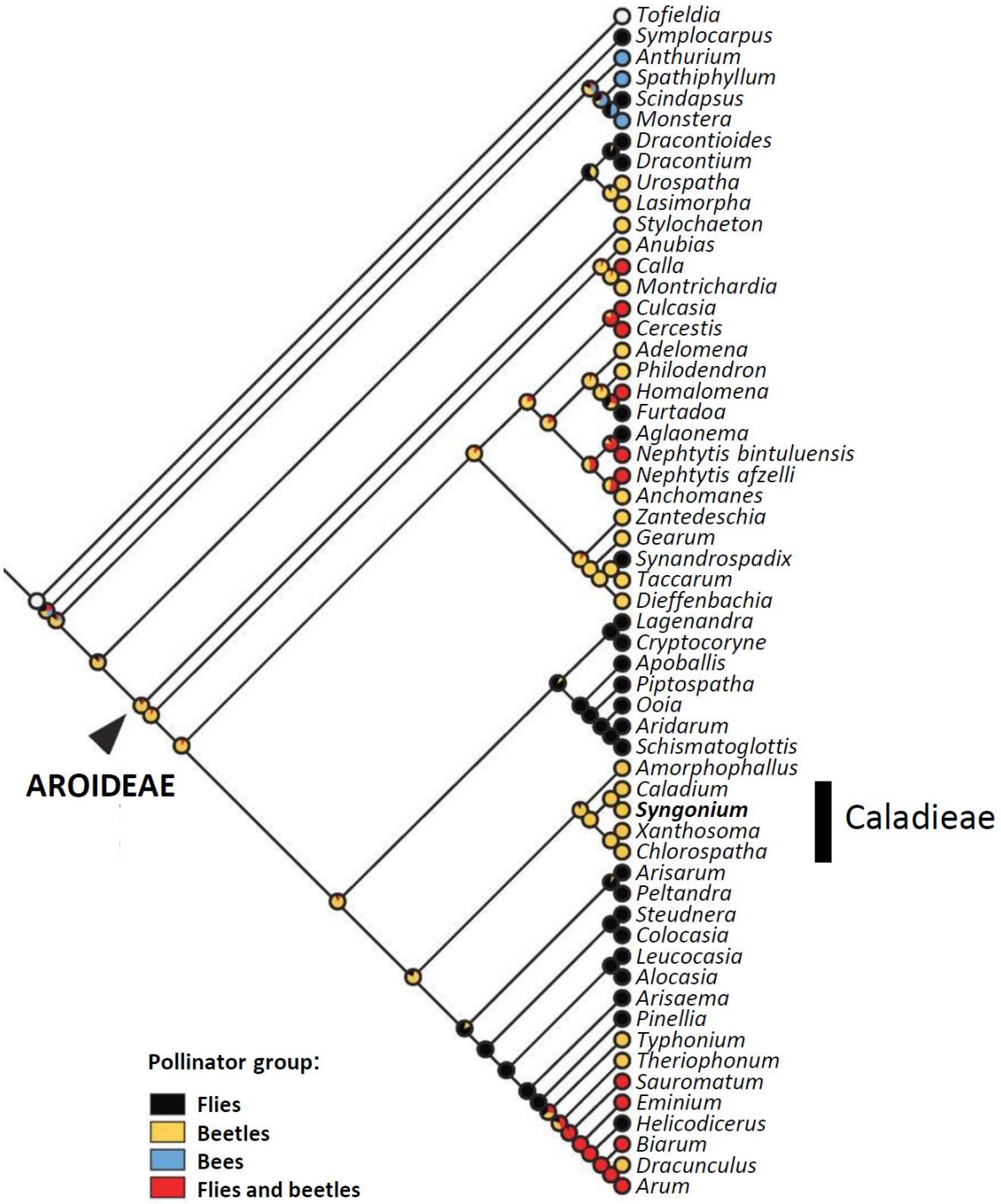


Figure S3. Beetle pollination as the ancestral state of the clade Caladieae, Related to Figure 6.

Phylogenetic relationships and known pollinators of Araceae genera, reproduced from Chartier et al. (2014), showing that the ancestral state of the clade Caladieae, where the genus *Syngonium* belongs to,

is beetle pollination and that all genera within the clade were believed to be beetle-pollinated before our study. The figure has been adapted from Chartier et al. 2014, Evolution 68-5: 1533–1543, © 2013, The Society for the Study of Evolution, with permission from the publisher.

	Day of scent release	1		2	
	Sampling time (min)	2		2	
	# of compounds	30		30	
	Sample size (individuals)	2		5	
	Total amount of scent trapped (µg/h)	9.83 (8.54-11.11)		16.9 (8.29-31.84)	
RI		Relative amount (%) of scent compounds	Occurence in samples	Relative amount (%) of scent compounds	Occurence in samples
	Aliphatic compounds				
930	3,4-dimethylpentan-1-ol	0.89 (0.78-0.98)	2	0.77 (0.2-1.3)	5
1021	(*Z*)-gambanol* **1**	**92.43 (92.06-92.71)**	2	**92.83 (91.73-93.84)**	5
1023	3-isopropylpentan-1-ol * **2**	**3.44 (2.67-4.45)**	2	**3.57 (3.1-4.7)**	5
1041	(*E*)-gambanol*	0.48 (0.41-0.57)	2	0.55 (0.33-0.88)	5
	Terpenoids				
1116	(*E*)-4,8-dimethyl-1,3,7-nonatriene*	0.04 (0.01-0.06)	2	0.01 (tr-0.01)	5
	Unknowns				
995	m/z: 84,69,55,41,95	1.19 (0.86-1.44)	2	1.21 (0.6-1.7)	5
	24 other unknowns (< 1 %) pooled	1.56 (0.01-0.33)		1.09 (0.01-0.22)	

* Identity of compounds marked with an asterisk was verified by synthetic standards.

Table S1. Floral scents of *Syngonium hastiferum*, Related to Figure 5. Total amount (µg/h) of inflorescence scents (mean, Min - Max), as well as the occurrence and relative (%) amount of scent compounds (mean, Min - Max) collected from seven inflorescences / individuals of *Syngonium hastiferum* during the morning of the first and second day of anthesis. The Kovats retention index (RI) is also given. tr = traces (< 0.01%). The sample is strongly dominated by (*Z*)-3-isopropylpent-3-en-1-ol (gambanol) **1**, followed by 3-isopropylpentan-1-ol **2**.

position	δ ^{1}H [ppm]	integral, multiplicity	coupling constant [Hz]	δ ^{13}C [ppm]	^{13}C multipli-city	HMBC correlations [ppm]
1	3.68	2H, dt	Overlapped	61.8	CH_2	–
2	2.23	2H, t	6.6	34.9	CH_2	141.2, 119.9, 61.6
3	–	–	–	141.3	C	–
4	5.22	1H, q	6.7	120.1	CH	34.5, 28.6
5	1.64	3H, d	6.7	12.8	CH_3	141.2, 119.9
6	2.86	1H, sep	7.0	28.4	CH	141.6, 120.2, 34.4, 20.9
7/8	0.99	6H, d	7.0	21.0	CH_3	141.3, 28.3, 20.9
OH	1.43	1H, t, broad	5.5	–	–	–

Table S2. NMR data of natural (*Z*)-3-isopropylpent-3-en-1-ol, Related to Figure 5. Chemical shifts of (*Z*)-3-isopropylpent-3-en-1-ol in the inflorescence headspace sample from *Syngonium hastiferum* referenced to TMS, measured in $CDCl_3$ at 298 K at a 600 MHz spectrometer.

position	δ ^{1}H [ppm]	integral, multiplicity	coupling constant [Hz]	δ ^{13}C [ppm]	^{13}C multiplicity	HMBC correlations [ppm]
1	3.68	2H, dt	6.6, 5.5	61.8	CH_2	141.2, 34.9
2	2.23	2H, t	6.7	34.9	CH_2	141.2, 119.9, 61.8, 28.4
3	–	–	–	141.2	C	–
4	5.22	1H, q	6.8	119.8	CH	34.9, 28.4, 12.9
5	1.64	3H, d	6.8	13.0	CH_3	141.2, 119.9, 61.8, 34.8, 28.4, 21.0
6	2.86	1H, sep	7.0	28.4	CH	141.2, 119.8, 34.9, 21.0
7/8	1.00	6H, d	7.0	21.0	CH_3	141.2, 28.4, 21.0
OH	1.48	1H, t	5.4	–	–	–

Table S3. NMR data of synthetic (*Z*)-3-isopropylpent-3-en-1-ol, Related to Figure 5. Chemical shifts of synthesized (*Z*)-3-isopropylpent-3-en-1-ol referenced to TMS, measured in $CDCl_3$ at 298 K at a 400 MHz spectrometer.