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Supplemental Information

A Semivolatile Floral Scent Marks the Shift to a Novel Pollination System in Bromeliads

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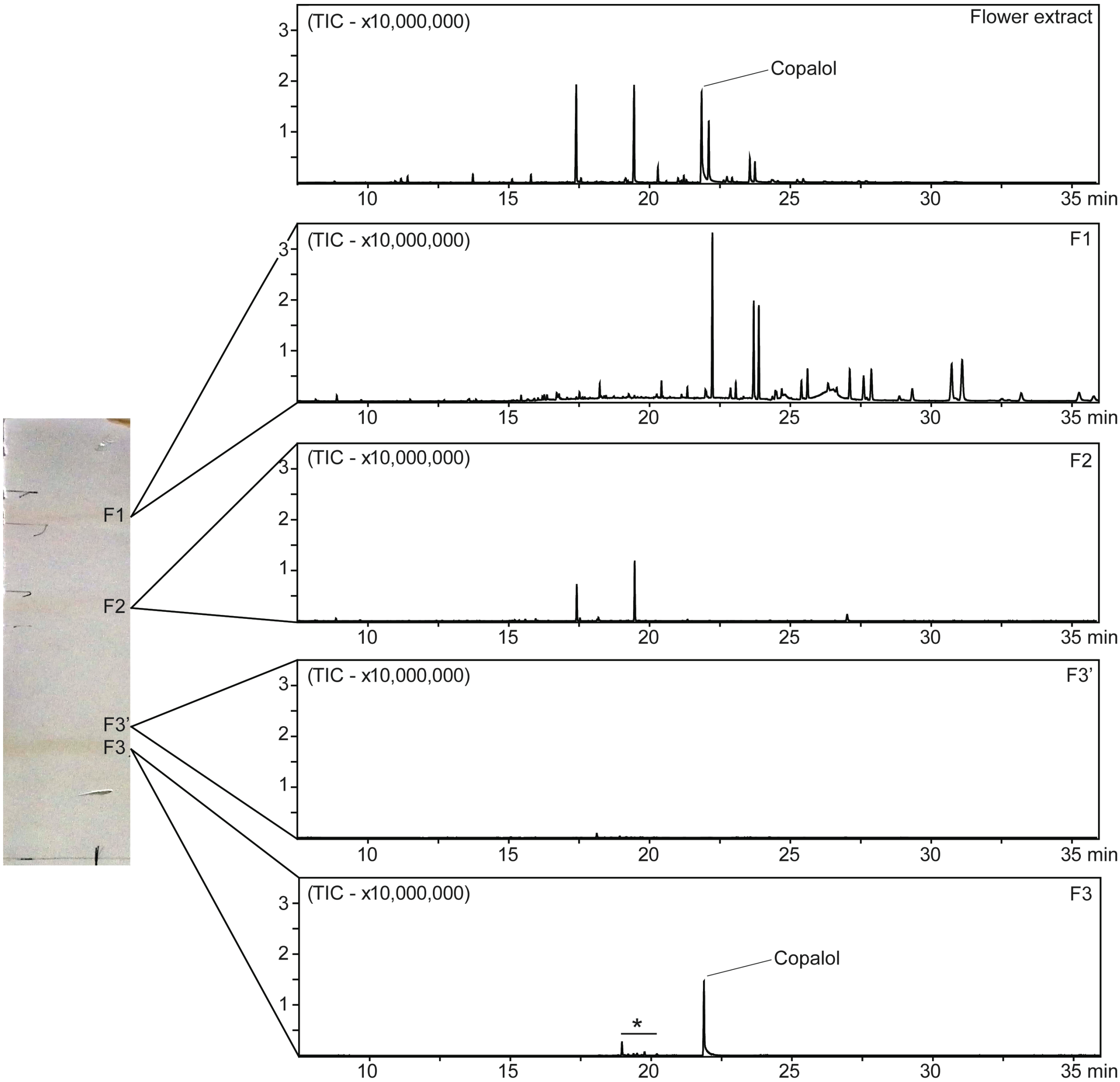

Figure S1. Photograph of the thin layer chromatrography silica plate (TLC), related to figure 4. The TLC was stained with vanillin/H_2SO_4/ethanol. Note the four fractions (F1, F2, F3' and F3), as well as their respective chromatrograms, as revealed by gas chromatography coupled to mass spectrometry. A chromatrogram of a flower extract is provided above for comparative purposes. Asterisk in the chromatogram of F3 represents products of thermal degradation of copalol while analysing it by GC/MS.

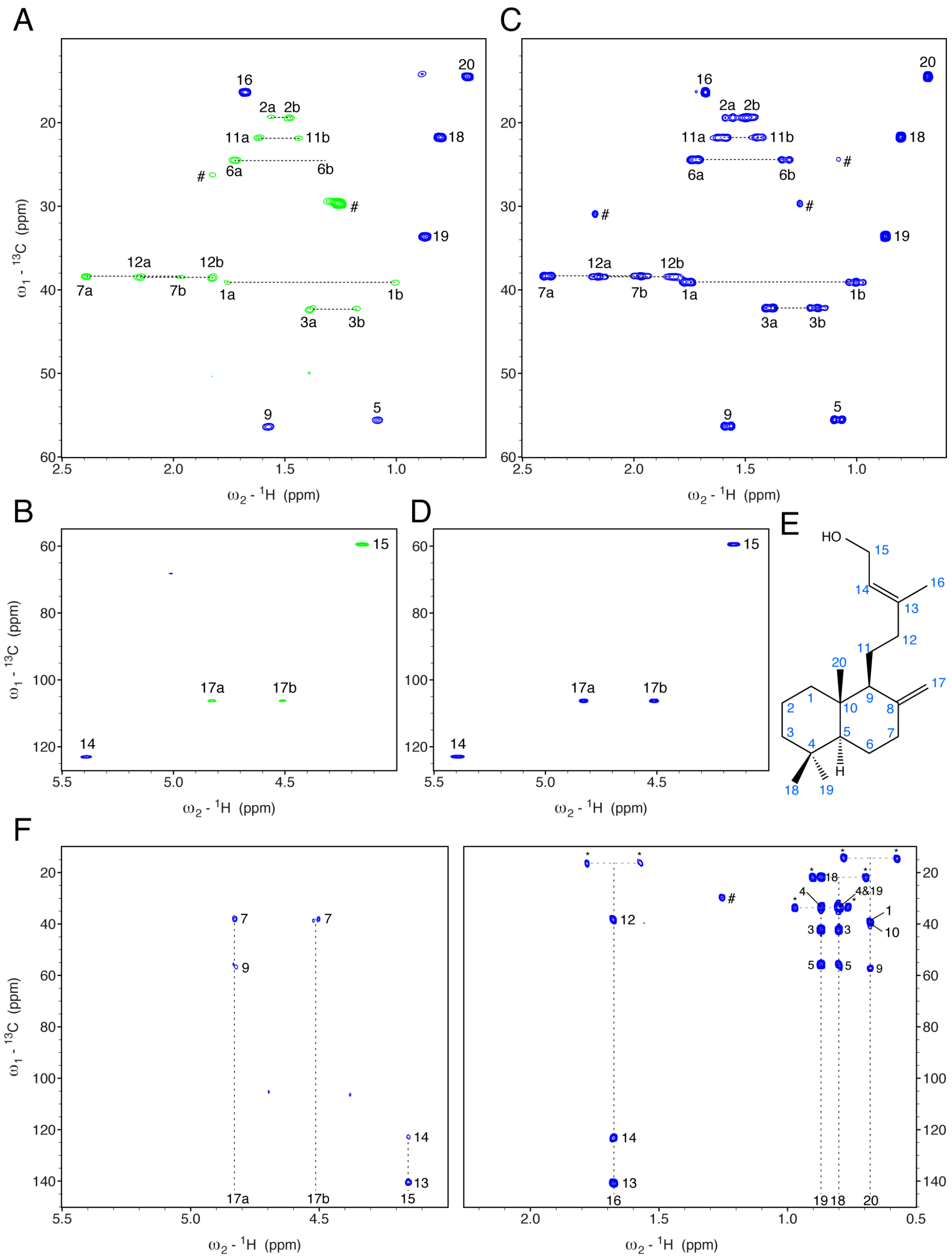

Figure S2. NMR comparison of F3 with synthetic (+)-copalol, related to figure 4. (A and B) 2D ^{1}H-^{13}C HSQC spectrum of fraction 3. The experiment included a multiplicity editing resulting in negative signs of signals of methylene groups (green). (B and C) 2D ^{1}H-^{13}C HSQC spectrum of synthetic (+)-copalol. Impurities are indicated by #. (E) Structure of (+)-copalol with atom labeling that is used in the NMR signal assignment. (F) ^{1}H-^{13}C HMBC spectrum of F3. Asterisks indicate one-bond C-H correlations that are split by $^1J_{CH}$ scalar coupling. An impurity is indicated by #.

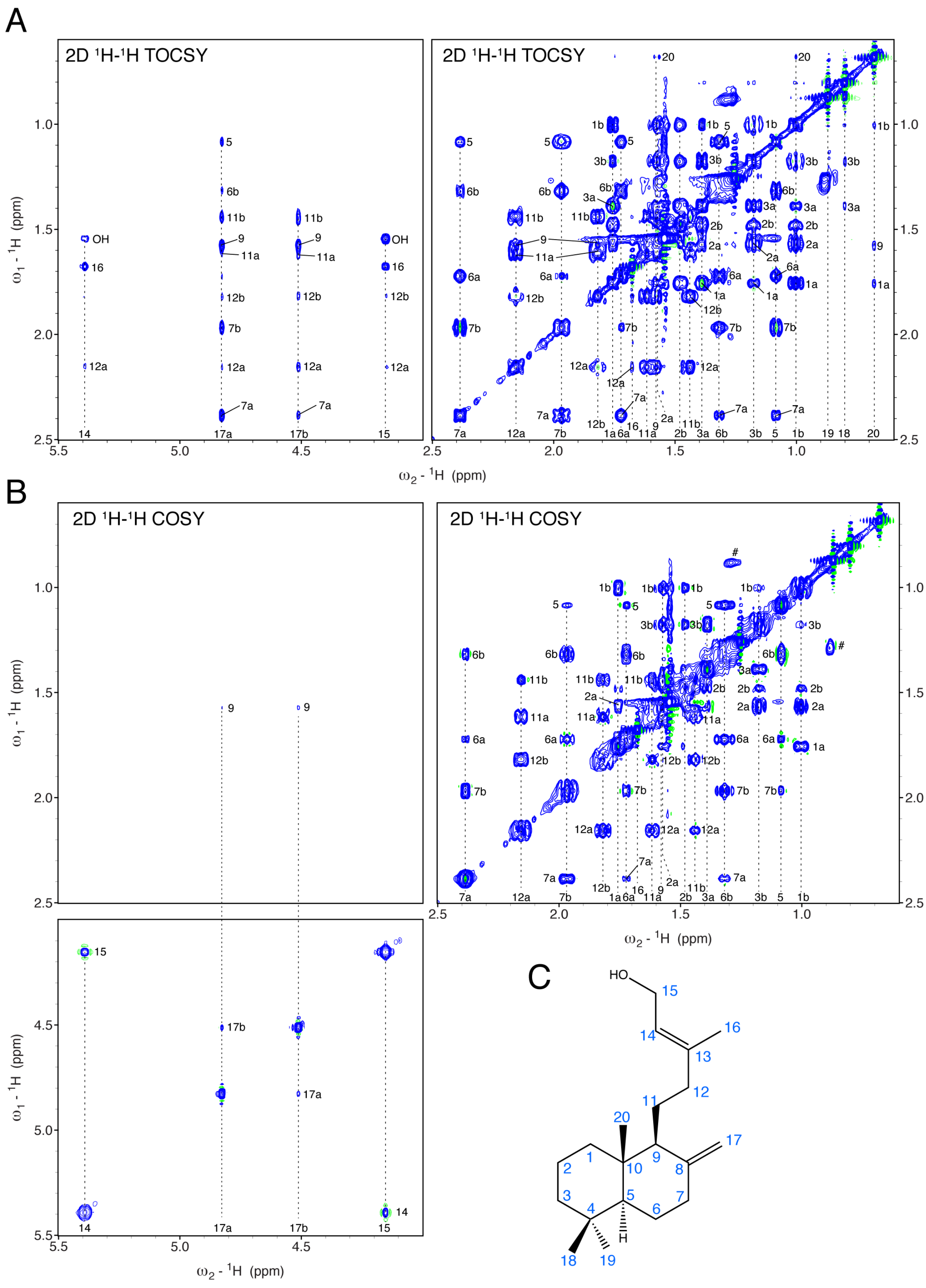

Figure S3. 2D NMR spectra F3 for connecting the chemical shifts to a spin system and assigning ^{1}H and ^{13}C chemical shifts, related to figure 4. (A) Relevant regions of a ^{1}H -^{1}H TOCSY spectrum. (B) Relevant regions of a ^{1}H -^{1}H COSY spectrum. (C) Structure of (+)-copalol with atom labeling that is used in the NMR signal assignment.

Taxon of floral visitor	Visits	(%)	Resource sought	Contact with reproductive structures		Inferred Role
				Anthers	Stigma	
Apodiformes						
Trochilidae						
Phaethornis ruber	427	27.48%	Nectar	Always	Occasionally	OP
Hymenoptera						
Apidae						
Meliponini						
Trigona spinipes	790	50.84%	Pollen/Floral tissue	Always	Never	R
Euglossini						
Euglossa sp.	12	0.77%	Perfume/ Nectar*	Always	Always	EP
Eulaema atleticana	17	1.09%	Perfume/ Nectar*	Always	Always	EP
Eulaema nigrita	281	18.08%	Perfume/ Nectar*	Always	Always	EP
Lepidoptera						
Hesperidae						
Unidentified species	27	1.74%	Nectar	Never	Never	R

*In about 10% of the visits, male euglossine bees inserted their tongues into the nectar chamber for nectaring.

Table S1. Floral visitors of *Cryptanthus burle-marxii* (Bromeliaceae), related to Figures 1 and 2. Frequency and behavior of floral visitors of *C. burle-marxii* in an Atlantic Rain Forest fragment in Northeastern Brazil (240 hours of observation). Abbreviations: effective pollinator (EP), occasional pollinator (OP) and robber (R).

	F3 in $CDCl_3$ (this work)	Synthetic (+)-copalol in $CDCl_3$ (this work)	Synthetic (+)-copalol in $CDCl_3$ [1]	Natural copalol in $CDCl_3$ [2]	Natural (+)-copalol in $CDCl_3$ [3]	Synthetic syn-copalol in $CDCl_3$ [1]
C1	39.11	39.09	39.19	39.19	39.1	36.76
C2	19.41	19.40	21.89[a]	21.75[a]	19.4	19.15
C3	42.18	42.17	42.27	42.39	42.2	42.68
C4	33.63	33.58	33.71	33.68	33.6	33.21
C5	55.55	55.54	55.63	55.67	56.3	45.78
C6	24.46	24.45	24.56	24.55	24.4	23.64
C7	38.37	38.36	38.47	38.45	38.2	31.56
C8	148.66	148.64	148.74	148.67	148.6	149.20
C9	56.33	56.31	56.40	56.34	55.5	57.90
C10	39.67	39.66	39.77	39.74	39.7	38.00
C11	21.80	21.78	19.52[a]	19.49[a]	21.7	24.46
C12	38.44	38.43	38.55	38.49	29.7[c]	38.15
C13	140.71	140.70	140.78	140.82	140.7	140.58
C14	122.98	123.00	123.05	124.00	123.0	122.94
C15	59.47	59.45	59.54	59.55	59.9	59.44
C16	16.36	16.35	16.49	16.48	16.3	16.52
C17	106.25	106.24	106.38	106.34	106.3	109.44
C18	21.74	21.73	21.86	21.80	21.80[e]	22.15
C19	33.60	33.61	33.75	33.71[d]	33.60	33.49
C20	14.51	14.50	14.62	14.60[d]	14.50[e]	22.35
H1a	1.756	1.760	1.72			1.57
H1b	1.003	1.010	0.99			1.05
H2a	1.564	1.572	1.57			1.61
H2b	1.482	1.494	1.39[b]			1.45
H3a	1.389	1.389	1.37			1.38
H3b	1.176	1.176	1.16			1.17
H5	1.085	1.085	1.07			1.26
H6a	1.723	1.727	1.70			1.59
H6b	1.312	1.318	1.30			1.30
H7a	2.390	2.388	2.38			2.17
H7b	1.967	1.970	1.96			2.06
H9	1.574	1.576	1.54[b]			1.50
H11a	1.618	1.609	1.60			1.62
H11b	1.440	1.444	1.45			1.47
H12a	2.155	2.155	2.15			1.90
H12b	1.819	1.817	1.79			1.74
H14	5.392	5.393	5.38			5.41
H15	4.142	4.155	4.15			4.15
H16	1.677	1.680	1.65			1.67
H17a	4.827	4.833	4.82			4.69
H17b	4.511	4.518	4.50			4.51
H18	0.801	0.802	0.79			0.80
H19	0.870	0.871	0.86			0.87
H20	0.680	0.680	0.67			0.91
OH	1.544					

[a] assignment of C1 and C11 likely swapped
[b] assignment of H2 and H9 likely swapped
[c] probably incorrect
[d] assignment of C19 and C20 was swapped
[d] assignment of C18 and C20 was swapped

Table S3, related to figure 4. ^1H and ^{13}C chemical shifts of natural and synthetic copalol at 298 K.

Supplemental references

S1. Yee, N.K.N., and Coates, R.M. (1992). Total synthesis of (+)-9,10-syn- and (+)-9,10-anti-copalol via epoxy trienylsilane cyclizations. The Journal of Organic Chemistry *57*, 4598-4608.

S2. Monti, H., Tiliacos, N., and Faure, R. (1999). Copaiba oil: isolation and characterization of a new diterpenoid with the dinorlabdane skeleton. Phytochemistry *51*, 1013-1015.

S3. Trusheva, B., Popova, M., Bankova, V., Tsvetkova, I., Naydenski, C., and Sabatini, A. (2003). A new type of European propolis, containing bioactive labdanes. Rivista Italiana EPPOS *13*, 3-8.