

Supplementary Material Part I - Supplementary Tables

Supplementary Table 1. “*Harmonia*”-MPs in insects and their function (according to El-Sayed 2016). Bold: presumed function as pheromones in few insect species. 3-sec-butyl-2-methoxypyrazine (SBMP), 3-isopropyl-2-methoxy-pyrazine (IPMP), 3-isobutyl-2-methoxypyrazine (IBMP), 3,5-dimethyl-2-methoxy-pyrazine (DMMP).

order	species	MPs	function	reference
Lepidoptera	<i>Actinote pelleria</i>	IBMP	allomone	Moore et al. 1990
	<i>Amata sp</i>	SBMP, IPMP	allomones	Rothschild et al. 1984
	<i>Arctica caja</i>	IBMP, SBMP	allomones	
	<i>Athrophaneura aristolochiae</i>	IBMP, SBMP	allomones	
	<i>Athrophaneura kotzebua</i>	IBMP, SBMP	allomones	
	<i>Battus polydamas</i>	IBMP, SBMP	allomones	
	<i>Danaus plexippus</i>	IBMP, SBMP, IPMP	allomones	
	<i>Dryas iulia</i>	IBMP, SBMP, IPMP	allomones	
	<i>Euplagia quadripunctata</i>	IBMP, SBMP	allomones	Moore et al. 1990
	<i>Heliconius atthis</i>	IBMP, SBMP	allomones	
	<i>Heliconius charitonia</i>	IBMP, SBMP, IPMP	allomones	
	<i>Heliconius melpomene</i>	IBMP, SBMP, IPMP	allomones	
	<i>Papilio rumanzovia</i>	IBMP, SBMP	allomones	
	<i>Pollanisus sp</i>	SBMP	allomone	
	<i>Tyria jacobaeae</i>	SBMP	allomone	
	<i>Zerynthia polyxena</i>	IBMP	allomone	
	<i>Zygaena lonicerae</i>	IBMP, SBMP	allomones	Rothschild et al. 1984
Coleoptera	<i>Adalia bipunctata</i>	IBMP, IPMP	pheromones	Susset et al. 2013
	<i>Calopteron reticulatum</i>	IPMP	allomone	Eisner et al. 2008
	<i>Calopteron terminale</i>	IPMP	allomone	
	<i>Coccinella septempunctata</i>	IPMP (in ladybeetle treated wines also: SBMP, IBMP, DMMP)	pheromone	Petterson et al. 1999, Cudjoe et al. 2005, Botezatu & Pickering 2012
	<i>Coccinella transversalis</i>	SBMP, IPMP	allomones	Moore et al. 1990
	<i>Epilachna curcurbitae</i>	IPMP	allomone	
	<i>E. vigintisexpunctata</i>	IBMP, SBMP, IPMP	allomones	
	<i>Eumorphus tetraspilotus</i>	SBMP	allomone	
	<i>Harmonia axyridis</i>	IBMP, SBMP, IPMP, DMMP	pheromones	Pickering et al. 2004, 2005, 2008, Cudjoe et al. 2005, Cai et al. 2007
	<i>Harmonia conformis</i>	SBMP	allomone	Moore et al. 1990
	<i>Hippodamia convergens</i>	IBMP, SBMP, IPMP	pheromones	Cudjoe et al. 2005, Wheeler & Cardé 2013
	<i>Illeis sp</i>	SBMP	allomone	Moore et al. 1990
	<i>Metriorrhynchus rhipidus</i>	SBMP	allomone	
	<i>Micraspis frentanta</i>	SBMP	allomone	
	<i>Palaestra foveicollis</i>	SBMP	allomone	
	<i>Pseudolycus haemopterus</i>	SBMP	allomone	
	<i>Rhagonycha fulva</i>	SBMP	allomone	
	<i>Rodatus boucardi</i>	IPMP	allomone	
	<i>Zonitis lutea</i>	IBMP, SBMP, IPMP	allomones	
	<i>Lyzus sp</i>	IPMP	allomone	Eisner et al. 2008
Hemiptera	<i>Cercopis vulnerata</i>	SBMP	allomone	Körner 2006
	<i>Murgantia histrionica</i>	SBMP, IPMP	pheromones	Aldrich et al 1996
	<i>Oncopeltus fasciatus</i>	IBMP	allomone	
Orthoptera	<i>Poekilocerus bufonius</i>	SBMP	allomone	Moore et al. 1990

Supplementary Table 2. Described functions of MPs as pheromones (sex, communication, and aggregation) and/or allomones in coccinellid beetles. SBMP: 3-sec-butyl-2-methoxypyrazine, IPMP: 3-isopropyl-2-methoxypyrazine), IBMP: 3-isobutyl-2-methoxypyrazine.

species	pheromone: attraction (sex) and communication	aggregation pheromone	defense substance	reference
<i>Adalia bipunctata</i>		IBMP, IPMP	adaline, adalinine	Susset et al. 2013, Lognay et al. 1996, Tursch et al. 1973, 1975
<i>Coccinella septempunctata</i>	IPMP		coccinelline, precoccinelline	Tursch et al. 1975, Al Abassi et al. 1998, Cudjoe et al. 2005
<i>Harmonia axyridis</i>	IBMP, IPMP, SBMP	beta-caryophyllene	harmonine	Alam et al. 2002, Cudjoe et al. 2005, Verheggen et al. 2007
<i>Hippodamia convergens</i>	IBMP, IPMP, SBMP	IBMP	harmonine, hippodamine, convergene	Braconnier et al. 1985, Tursch et al. 1974, Cudjoe et al. 2005, Wheeler et al. 2013

Supplementary Table 3. Microbial pyrazines and the responding insects.

bacterial species	pyrazine	responding insect	reference
<i>Klebsiella pneumoniae</i>	2,5-dimethylpyrazine	<i>Anastrepha ludens</i>	Martinez et al. 1994, Lee et al. 1995, Rohbacker and Bartelt 1997, Robacker et al. 2004, Rohbacker 2007
	trimethylpyrazine		
<i>Citrobacter freundii</i>	2,5-dimethylpyrazine	<i>Anastrepha ludens</i>	DeMilo et al. 1996, Rohbacker and Bartelt 1997, Robacker et al. 2004, Robacker 2007
	trimethylpyrazine		
<i>Enterobacter agglomerans</i> isolated from mouthparts from <i>Anastrepha ludens</i> and <i>Rhagoletis pomonella</i>	2,5-dimethylpyrazine	<i>Anastrepha ludens</i> , <i>A. suspense</i> , <i>Rhagoletis mendax</i> , <i>R. pomonella</i> , <i>Schistocerca gregaria</i>	Lauzon et al. 1998, Robacker et al. 1998, Robacker und Lauzon 2002, Robacker et al. 2004, McCollum et al. 2009
	trimethylpyrazine		
unclassified bacteria on fruit surfaces	2,5-diisopropylpyrazine	<i>Carpophilus humeralis</i>	Zilowski et al. 1999
<i>Paenibacillus polymyxa</i>	tetramethylpyrazine, methylethylpyrazine, 2,5-di(propan-2-yl)pyrazine, 2,5-diisopropylpyrazine	<i>Carpophilus humeralis</i>	Beck et al. 2003, Schulz and Dickschat 2007
<i>Staphylococcus aureus</i>	2,5-dimethylpyrazine	<i>Anastrepha ludens</i>	Robacker and Moreno 1995
<i>Staphylococcus sciuri</i>	2,5-dimethylpyrazine	<i>Episyphus balteatus</i>	Leroy et al. 2011

Supplementary Table 4. GC/MS-analysis. Mean values \pm SE of MP contents (pg/mg fresh weight and pg/sample) in all performed feeding experiments. n = number of tested individuals/tissues. H = honey syrup diet, HS = honey syrup-*Sitotroga* egg diet, HSAB = honey syrup-*Sitotroga* egg-antibiotic mix diet

Figure	MP	diet	sample	n	mean	SE	mean	SE
					pg/mg fw	pg/mg fw	pg/sample	pg/sample
Fig. 1A	total MP	aphid	egg	5	8.115	\pm 0.908	16.648	\pm 1.574
			L4	6	4.192	\pm 0.571	102.403	\pm 16.753
			beetle p.h.	5	22.798	\pm 2.645	120.904	\pm 24.274
			adult	5	24.982	\pm 3.356	403.410	\pm 111.993
			beetle diapause	5	23.364	\pm 4.546	235.943	\pm 50.244
Fig. 1B	SBMP	aphid	egg	5	2.418	\pm 0.356	13.521	\pm 1.273
			L4	6	2.360	\pm 0.307	86.106	\pm 12.307
			beetle p.h.	5	4.446	\pm 0.730	118.997	\pm 22.595
			adult	5	8.978	\pm 2.509	358.312	\pm 110.153
			beetle diapause	5	5.570	\pm 1.300	224.087	\pm 49.627
Fig. 1C	IPMP	aphid	egg	5	5.163	\pm 0.754	0.052	\pm 0.006
			L4	6	1.414	\pm 0.231	0.079	\pm 0.018
			beetle p.h.	5	18.286	\pm 1.985	0.084	\pm 0.012
			adult	5	14.769	\pm 2.536	0.192	\pm 0.106
			beetle diapause	5	17.486	\pm 4.870	0.128	\pm 0.026

Fig. 1D	IBMP	aphid	egg	5	0.534	± 0.114	3.074	± 0.723
			L4	6	0.419	± 0.231	16.218	± 10.044
			beetle p.h.	5	0.066	± 0.066	1.823	± 1.823
			adult	5	1.235	± 0.428	44.906	± 13.137
			beetle diapause	5	0.307	± 0.102	11.728	± 3.779
Fig. 2A	total MP	aphid	female gut	5	5.783	± 1.622	20.013	± 4.448
			female residual body	10	8,514	± 1.437	205.908	± 34.576
			male gut	6	11.956	± 3.424	30.640	± 9.382
			male residual body	8	22.386	± 3.552	426.478	± 70.175
Fig. 2B	total MP	grape	female gut	5	5.741	± 1.075	25.414	± 5.698
			female residual body	9	14.898	± 2.775	390.081	± 87.958
			male gut	6	7.253	± 1.411	17.888	± 2.977
			male residual body	12	11.717	± 1.641	272.109	± 40.422
Fig. 2C	total MP	H	female gut	8	21.487	± 2.692	33.604	± 4.275
			female residual body	7	16.476	± 1.695	386.058	± 55.955
			male gut	6	15.384	2.832	18.312	± 3.002
			male residual body	6	20.897	± 1.791	436.080	± 42.533
Fig. 2D	total MP	HS	female gut	7	9.735	± 2.139	31.678	± 8.965
			female residual body	7	19.251	± 2.259	643.689	± 101.086
			male gut	6	16.887	± 5.985	20.675	± 5.529
			male residual body	6	25.630	± 6.286	530.780	± 127.378
Fig. 4A, B	total MP	HS	female gut	7	9.735	± 2.139	31.678	± 8.965
			male gut	7	16.887	± 5.985	20.675	± 5.529
			female residual body	6	19.251	± 2.259	643.689	± 101.086
			male residual body	6	25.630	± 6.286	530.780	± 127.378
	HSAB		female gut ab	8	7.855	± 1.486	33.802	± 7.646
			male gut ab	8	15.181	± 2.891	21.364	± 5.961
			female residual body ab	8	17.093	± 4.576	480.853	± 140.491
			male residual body ab	7	22.879	4.957	499.091	± 110.338
Fig. 4C, D	total MP	HS	L4	5	1.928	± 0.434	29.421	± 8.745
			L4 gut	5	3.733	± 3.224	0.031	± 0.019
			L4 residual body	5	1.029	± 0.377	0.114	± 0.035
			beetle p.h.	8	33.622	± 4.134	456.172	± 136.497
			beetle p.h. gut	6	16.438	± 4.674	22.916	± 6.478
			beetle p.h. residual body	6	15.092	± 2.842	147.059	± 35.642
	HSAB		L4 ab	5	1.121	± 0.416	9.222	± 4.649
			L4 gut ab	5	0.842	± 0.314	1.084	± 0.685
			L4 residual body ab	5	0.225	± 0.101	0.538	± 0.494
			beetle p.h. ab	5	11.329	± 4.099	57.882	± 40.270
			beetle p.h. gut ab	5	6.077	± 2.219	9.193	± 1.672
			beetle p.h. residual body ab	5	4.997	± 0.872	44.926	± 11.221

References for Supplementary Tables

- Al Abassi, S., Birkett, M.A., Pettersson, J., Picket, J.A., & Woodcock, C.M. (1998). Ladybird beetle odor identified and found to be responsible for attraction between adults. *Cellular and Molecular Life Sciences* 58(8), 876-879.
- Alam, N., Choi, I.S., Song, K.-S., Hong, J., Lee, C.O., & Jung, J.H. (2002). A new alkaloid from two coccinellid beetles *Harmonia axyridis* and *Aiolocaria hexaspilota*. *Bulletin of the Korean Chemical Society* 23, 497-499.

- Aldrich, J.R., Avery, J.W., Lee, C.-J., Graf, J.C., Harrison, D.J., & Bin, F. (1996). Semiochemistry of cabbage bugs (Heteroptera: Pentatomidae: Eurydema and Murgantia). *Journal of Entomological Science* 31, 172-182.
- Beck, H.B., Hansen, A.M., & Lauritsen, F.R. (2003). Novel pyrazine metabolites found in polymyxin biosynthesis by *Paenibacillus polymyxa*. *FEMS Microbiology Letters* 220, 67-73.
- Botezatu, A., & Pickering, G.J. (2012). Determination of ortho- and retronasal detection thresholds and odor impact of 2,5-dimethyl-3-methoxypyrazine in wine. *Journal of the Science of Food and Agriculture* 77 (11), 394-398.
- Braconnier, M.F., Braekman, J.C., Daloze, D., & Pasteels, J.M. (1985). (Z)-1, 17-diaminoctadec-9-ene, a novel aliphatic diamine from Coccinellidae. *Experientia* 41, 519-520.
- Cai, L.S., Koziel, J.A., & O'Neal, M.E. (2007). Determination of characteristic odorants from *Harmonia axyridis* beetles using in vivo solid-phase microextraction and multidimensional gas chromatography-mass spectrometry-olfactometry. *Journal of Chromatography A* 1147, 66-78.
- Cudjoe, E., Wiederkehr, T.B., & Brindle, I.D. (2005). Headspace gas chromatography-mass spectrometry: a fast approach to the identification and determination of 2-alkyl-3-methoxypyrazine pheromones in ladybugs. *Analyst* 130, 152-155.
- El-Sayed, A.M. (2016). The Pherobase: Database of pheromones and semiochemicals. <http://www.pherobase.com>
- Eisner, T., Schroeder, F.C., Snyder, N., Grant, J.B., Aneshansley, D.J., Utterback, D., Meinwald, J., & Eisner, M. (2008). Defensive chemistry of lycid beetles and of mimetic cerambycid beetles that feed on them. *Chemoecology* 18, 109-119.
- Khrimian, A., Shirali, S., Vermillion, K.E., Siegler, M.A., Guzman, F., Chauhan, K., Aldrich, J.R., & Weber, D.C. (2014). Determination of the stereochemistry of the aggregation pheromone of harlequin bug, *Murgantia histrinoica*. *Journal of Chemical Ecology* 40, 1260-1268.
- Körner, M. (2006). Zur Rolle der Hämolympf-Inhaltsstoffe bei der Feindabwehr von Zikaden (Cicadomorpha et Fulgoromorpha) unter besonderer Berücksichtigung der Blutzikade *Cercopis vulnerata* Rossi. PhD thesis, University of Bayreuth, Germany.
- Lauzon, C.R., Sjogren, R.E., Wright, S.E., & Prokopy, R.J. (1998). Attraction of *Rhagoletis pomonella* (Diptera: Tephritidae) flies to odor of bacteria: apparent confinement to specialized members of Enterobacteriaceae. *Environmental Entomology* 27, 853-857.
- Lee, C.J., DeMilo, A.B., Moreno, D.S., & Martinez, A.J. (1995). Analyses of the volatile components of a bacterial fermentation that is attractive to the Mexican fruit fly, *Anastrepha ludens*. *Journal of Agricultural and Food Chemistry* 43, 1348-1351.
- Leroy, P.D., Sabri, A., Heuskin, S., Thonart, P., Lognay, G., Verheggen, F.J., Francis, F., Brostaux, Y., Felton, G.W., & Haubrige, E. (2011). Microorganisms from aphid honeydew attract and enhance the efficiency of natural enemies. *Nature Communications*. doi: 10.1038/ncomms1347
- Lognay, G., Hemptonne, J.L., Chan, F.Y., Gaspar, C.H., Marlier, M., Braekman, J.C., Daloze, D., & Pasteels, J.M. (1996). Adalinine, a new piperidine alkaloid from the ladybird beetles *Adalia bipunctata* and *Adalia decempunctata*. *Journal of Natural Products*. 59, 510-511.
- Martinez, A.J., Robacker, D.C., Garcia, J.A., & Esau, K.L. (1994). Laboratory and field olfactory attraction of the Mexican fruit fly (Diptera: Tephritidae) to metabolites of bacterial species. *Florida Entomologist* 77, 117-126.
- Moore, B.P., Brown, W.V., & Rothschild, M. (1990). Methylalkylpyrazines in aposematic insects, their hostplants and mimics. *Chemoecology* 1, 43-51.
- Pettersson, J., Birkett, M.A., & Pickett, J.A. (1999). Pyrazines as attractants for insects of order Coleoptera. International Publication Number WO 99/37152.
- Pickering, G.J., Lin, J.Y., Riesen, R., Reynolds, A., Brindle, I., & Soleas, G. (2004). Influence of *Harmonia axyridis* on the sensory properties of white and red wine. *America Journal of Enology and Viticulture* 55, 153-159.

- Pickering, G.J., Lin, Y., Reynolds, A., Soleas, G., Riesen, R., & Brindle, I. (2005). The influence of *Harmonia axyridis* on wine composition and aging. *Journal of Food Science* 70(2), 128-135.
- Pickering, G.J., Spink, M., Kotseridis, Y., Brindle, I.D., Sears, M., & Inglis, D. (2008). The influence of *Harmonia axyridis* morbidity on 2-Isopropyl-3-methoxy-pyrazine in 'Cabernet Sauvignon' wine. *Vitis* 47(4), 227-230.
- Robacker, D.C. (2007). Chemical ecology of bacterial relationships with fruit flies. *IOBC/WPRS Bulletin* 30(9), 9-22.
- Robacker, D.C., & Moreno, D.S. (1995). Protein feeding attenuates attraction of Mexican fruit flies (Diptera: Tephritidae) to volatile bacterial metabolites. *Florida Entomologist* 78, 497-508.
- Robacker, D.C., & Bartelt, R.J. (1997). Chemicals attractive to Mexican fruit fly from *Klebsiella pneumoniae* and *Citrobacter freundii* cultures sampled by solid-phase microextraction. *Journal of Chemical Ecology* 23, 2897-2915.
- Robacker, D.C., & Lauzon, C.R. (2002). Purine metabolizing capability of *Enterobacter agglomerans* affects volatiles production and attractiveness to Mexican fruit fly. *Journal of Chemical Ecology* 28, 1549-1563.
- Robacker, D.C., & Lauzon, C.R., & He, X. (2004). Volatiles production and attractiveness to the Mexican fruit fly of *Enterobacter agglomerans* isolated from apple maggot and Mexican fruit flies. *Journal of Chemical Ecology* 30, 1329-1347.
- Robacker, D.C., Martinez, A.J., Garcia, J.A., & Bartelt, R.J. (1998). Volatiles attractive to the Mexican fruit fly (Diptera: Tephritidae) from eleven bacteria taxa. *Florida Entomologist* 81, 497-508.
- Rothschild, M., Moore, B.P., & Brown, W.V. (1984). Pyrazines as warning odor components in the monarch butterfly, *Danaus plexippus*, and in moths of the genera Zygaena and Amata (Lepidoptera). *Biological Journal of Linnean Society* 23, 375-380.
- Schulz, S., & Dickschat, J.S. (2007). Bacterial volatiles: The smell of small organisms. *Natural Product Reports* 24, 814-842.
- Susset, E.C., Ramon-Portugal, F., Hemptinne, J.L., Dewhurst, S.Y., Birkett, M.A., & Magro, A. (2013). The role of semiochemicals in short-range location of aggregation sites in *Adalia bipunctata* (Coleoptera, Coccinellidae). *Journal of Chemical Ecology* 39, 591-601.
- Tursch, B., Braekman, J.C., Daloze, D., Hootele, C., Losman, D., Karlsson, R., & Pasteels, J.M. (1973). Chemical ecology of arthropods. VI. Adaline, a novel alkaloid from *Adalia bipunctata* L. (Coleoptera, Coccinellidae). *Tetrahedron Letters* 14, 201-202.
- Tursch, B., Daloze, D., Braekman, J.C., Hootele, C., Cravador, A., Losman, D., & Karlsson, R. (1974). Chemical ecology of arthropods. IX. Structure and absolute configuration of hippodamine and convergine, two novel alkaloids from the American ladybug *Hippodamia convergens* (Coleoptera - Coccinellidae). *Tetrahedron Letters* 15, 409-412.
- Tursch, B., Daloze, D., Braekman, J.C., Hootele, C., & Pasteels, J.M. (1975). Chemical ecology of arthropods. X. The structure of myrrhine and the biosynthesis of coccinelline. *Tetrahedron Letters* 31, 1541-1543.
- Verheggen, F.J., Fagel, Q., Heuskin, S., Lognay, G., Francis, F., & Haubrige, E. (2007). Elektrophysiological and behavioral responses of the multicoloured Asian lady beetle, *Harmonia axyridis* Pallas, to sesquiterpene semiochemicals. *Journal of Chemical Ecology* 33, 2148-2155.
- Wheeler, C.A., & Cardé, R.T. (2013). Defensive allomones function as aggregation pheromones in diapausing ladybird beetles, *Hippodamia convergens*. *Journal of Chemical Ecology* 39, 723-732.
- Zahn, D.K., Moreira, J.A., & Millar, J.G. (2008). Identification, synthesis, and bioassay of male-specific aggregation pheromone from the harlequin bug, *Murgantia histrionica*. *Journal of Chemical Ecology* 34, 238-251.