

Supplementary Materials: Spread of *Jacobaea vulgaris* and Occurrence of Pyrrolizidine Alkaloids in Regionally Produced Honeys from Northern Germany: Inter- and Intra-Site Variations and Risk Assessment for Special Consumer Groups

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Table S2. Recovery rates and analytical limits of the LC–MS/MS method for the determination of 25 pyrrolizidine alkaloids (PA) and PA *N*-oxides (PANO) in honey.

Analyte	mean recovery (%) (n=9)	RSD _r (%)	LOD (µg/kg)	LOQ (µg/kg)
Echimidine	102.9	6.7	0.14	0.46
Echimidine <i>N</i> -oxide	110.6	16.2	0.02	0.05
Erucifoline	101.8	2.9	0.06	0.19
Erucifoline <i>N</i> -oxide	81.8	14.1	0.19	0.59
Europine	92.9	16.1	0.01	0.04
Europine <i>N</i> -oxide	102.5	13.0	0.02	0.07
Heliotrine	89.5	11.5	0.08	0.25
Heliotrine <i>N</i> -oxide	107.4	3.7	0.01	0.04
Intermedine	88.4	9.2	0.09	0.28
Intermedine <i>N</i> -oxide	98.7	7.8	0.10	0.32
Jacobine	94.0	8.8	0.07	0.24
Jacobine <i>N</i> -oxide	86.0	13.2	0.01	0.04
Lasiocarpine	98.8	15.5	0.01	0.03
Lasiocarpine <i>N</i> -oxide	110.7	17.4	0.02	0.07
Lycopsamine	86.4	6.9	0.02	0.06
Lycopsamine <i>N</i> -oxide	100.2	5.0	0.03	0.07
Monocrotaline	96.1	7.1	0.07	0.24
Monocrotaline <i>N</i> -oxide	98.4	15.9	0.17	0.54
Retrorsine	106.8	7.8	0.04	0.13
Retrorsine <i>N</i> -oxide	120.8	8.0	0.07	0.23
Senecionine	83.0	15.0	0.13	0.40
Senecionine <i>N</i> -oxide	106.2	7.8	0.02	0.06
Seneciphylline	111.2	11.5	0.15	0.47
Seneciphylline <i>N</i> -oxide	92.8	22.6	0.02	0.05
Senkirkine	102.4	5.1	0.01	0.04

RSD_r intra-day repeatability expressed as relative standard deviation; LOD, limit of detection; LOQ, limit of quantification.

Table S4. Substance specific parameters of the LC–MS/MS method for 25 pyrrolizidine alkaloids (PA) and PA *N*-oxides (PANO) ordered by retention time.

Analyte	Formula	Precursor ion (m/z)	Product ions (m/z)	DP (V)	EP (V)	CE (eV)	CXP (V)	Retention time (min)
Mc	C ₁₆ H ₂₃ NO ₆	326.1	121.1	116	10	41	20	5.2
			120.2	116	10	49	20	
Im	C ₁₅ H ₂₅ NO ₅	300.2	138.0	96	10	29	24	6.4
			120.1	96	10	37	20	
Ly	C ₁₅ H ₂₅ NO ₅	300.2	138.0	96	10	29	24	6.9
			120.1	96	10	37	20	
Eu	C ₁₆ H ₂₇ NO ₆	330.1	138.0	86	10	41	6	8.8
			156.1	86	10	41	8	
McN	C ₁₆ H ₂₃ NO ₇	342.1	137.1	116	10	41	24	9.9
			120.1	116	10	51	20	
ImN	C ₁₅ H ₂₅ NO ₆	316.2	172.1	61	10	41	30	9.9
			138.1	61	10	41	24	
EuN	C ₁₆ H ₂₇ NO ₇	346.2	172.1	106	10	45	30	9.8
			270.1	106	10	35	16	
LyN	C ₁₅ H ₂₅ NO ₆	316.2	172.1	106	10	41	30	10.0
			138.0	106	10	41	24	
Ec	C ₁₈ H ₂₃ NO ₆	350.2	120.1	111	10	43	20	10.7
			138.1	111	10	49	20	
Jb	C ₁₈ H ₂₅ NO ₆	352.1	120.1	111	10	43	20	11.2
			280.2	111	10	33	16	
Ht	C ₁₆ H ₂₇ NO ₅	314.2	138.2	86	10	41	36	12.7
			94.0	86	10	41	16	
JbN	C ₁₈ H ₂₅ NO ₇	368.2	296.2	111	10	35	16	12.7
			120.1	111	10	53	20	
EcN	C ₁₈ H ₂₃ NO ₇	366.2	118.0	111	10	49	20	12.7
			120.1	111	10	45	22	
Rs	C ₁₈ H ₂₅ NO ₆	352.1	138.1	121	10	43	24	12.9
			324.3	121	10	39	18	
HtN	C ₁₆ H ₂₇ NO ₆	330.2	172.1	106	10	41	30	13.6
			93.7	106	10	63	16	
Sp	C ₁₈ H ₂₃ NO ₅	334.1	120.1	111	10	41	20	14.1
			94.1	111	10	51	16	
RsN	C ₁₈ H ₂₅ NO ₇	368.2	118.1	111	10	47	20	14.1
			136.0	111	10	51	22	
Sc	C ₁₈ H ₂₅ NO ₅	336.2	120.1	116	10	41	20	16.9
			138.1	116	10	41	24	
SpN	C ₁₈ H ₂₃ NO ₆	350.2	118.2	116	10	51	20	16.9
			136.0	116	10	45	24	
Em	C ₂₀ H ₃₁ NO ₇	398.3	120.1	96	10	35	20	18.1
			119.5	96	10	37	42	
ScN	C ₁₈ H ₂₅ NO ₆	352.1	118.1	116	10	41	20	18.3
			136.0	116	10	53	24	
Sk	C ₁₉ H ₂₇ NO ₆	366.2	122.1	121	10	49	20	18.4
			153.0	121	10	37	26	
EmN	C ₂₀ H ₃₁ NO ₈	414.2	254.2	106	10	43	14	18.4
			352.2	106	10	35	20	
Lc	C ₂₁ H ₃₃ NO ₇	412.2	120.1	101	10	45	22	19.5
			220.1	101	10	27	12	
LcN	C ₂₁ H ₃₃ NO ₈	428.2	137.1	111	10	47	24	20.1
			138.1	111	10	45	24	

Ec, erucifoline; EcN, erucifoline *N*-oxide; Em, echimidine; EmN, echimidine *N*-oxide; Eu, europine; EuN, europine *N*-oxide; Ht, heliotrine; HtN, heliotrine *N*-oxide; Im, intermedine; ImN, intermedine *N*-oxide; Jb, jacobine; JbN, jacobine *N*-oxide; Lc, lasiocarpine; LcN, lasiocarpine *N*-oxide; Ly, lycopsamine; LyN, lycopsamine *N*-oxide; Mc, monocrotaline; McN, monocrotaline *N*-oxide; Rs, retrorsine; RsN, retrorsine *N*-oxide; Sc, senecionine; ScN, senecionine *N*-oxide; Sp, seneciphylline; SpN, seneciphylline *N*-oxide; Sk, senkirkine.