

Comparison of different Pyrethrum standards from the market

E. Scherbaum¹, G. Cerchia¹, P. Beiter², S. Goerlich¹, I. Sigalov¹,
D. Mack², M. Anastassiades²

¹ CVUA Stuttgart, Department for Residues of Pesticides and Contaminants, Fellbach, Germany

² EURL-SRM hosted at the CVUA Stuttgart, Fellbach, Germany

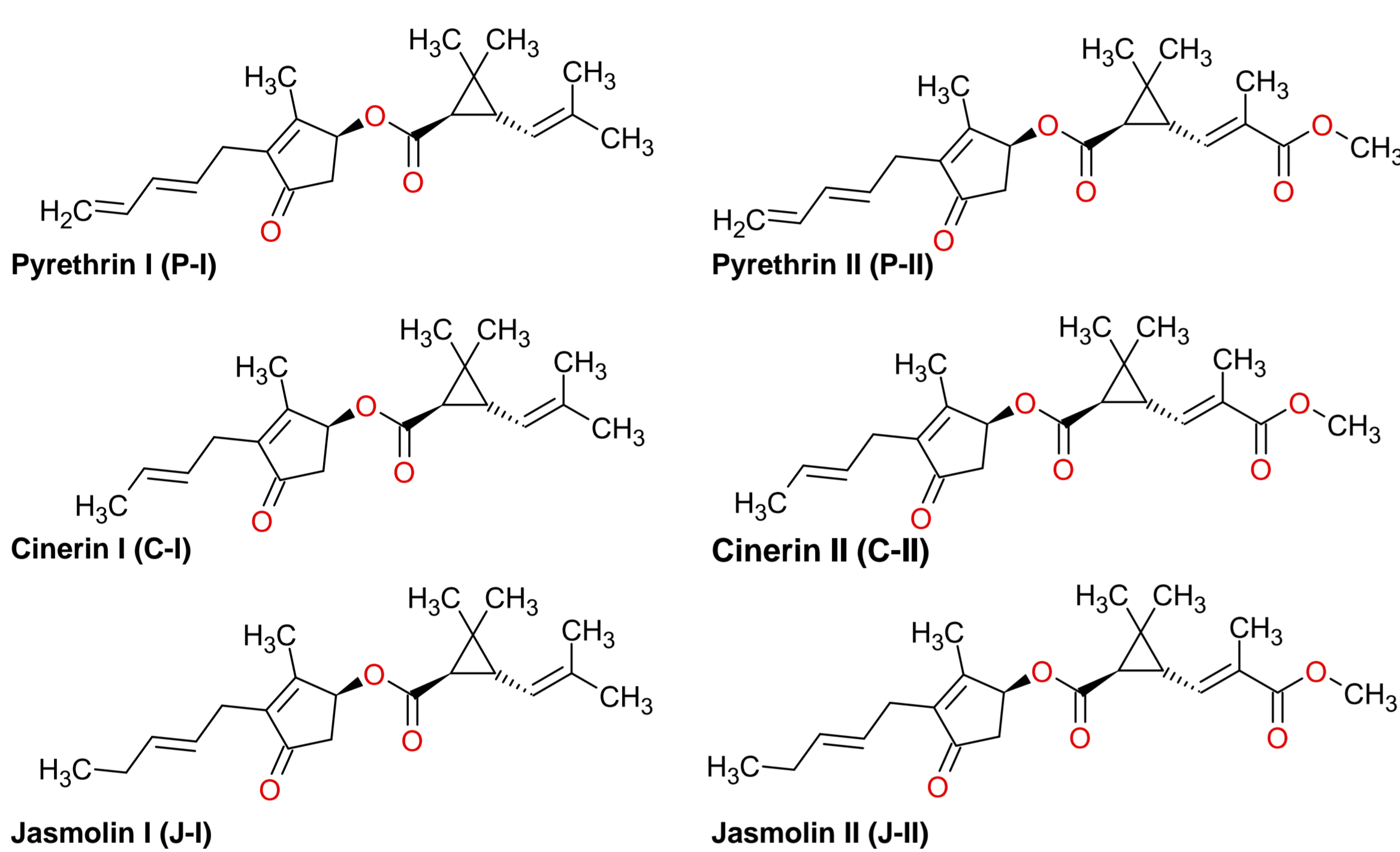
E-Mail: Ellen.Scherbaum@cvuas.bwl.de

Introduction

The ISO common name “pyrethrins” refers to a group of six chemically-related “pyrethrin esters” naturally occurring in the flowers of *Chrysanthemum cinerariifolium*. Due to their insecticidal properties, chrysanthemum extracts have been used as bio-insecticides for a very long time.

Composition

The six pyrethrin esters result from the possible combinations of three different alcohol components (pyrethrelone, cinerolone and jasmolone) with two acid components (chrysanthemic and pyrethric acid). The most prominent components are pyrethrin I & II, which together constitute roughly 80% of pyrethrins.



Production

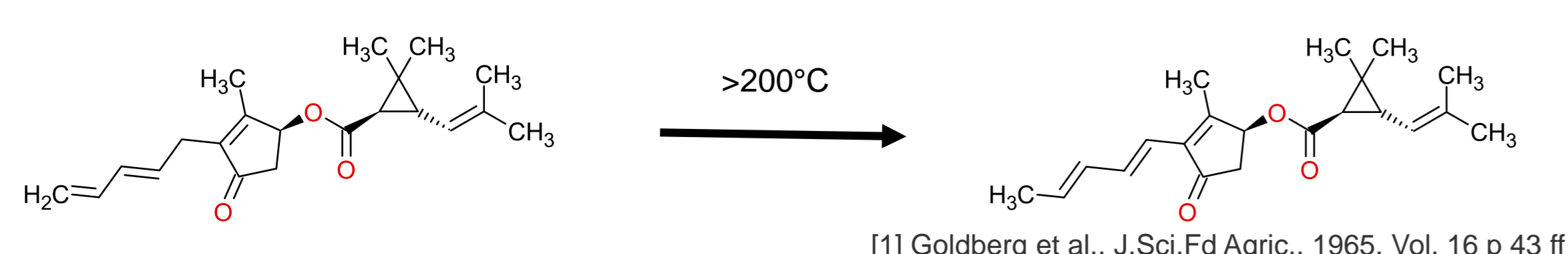
Kenya used to be the by far largest producer of pyrethrum, but nowadays Australia, China and Tanzania are the main producers. The content and composition of pyrethrum extracts depends on the location of production and the processing procedure.

EU Monitoring Program

As pyrethrins are widely used, especially in organic agriculture, they are among the parameters entailed in the SANTE WD to be considered by EU MS when establishing national monitoring programs for pesticides (SANCO/ 12745/2013). Plans to include pyrethrins in EU-coordinated monitoring regulation haven't materialized yet due to concerns about the reliability and comparability of available analytical standards and expected shifts in the component ratios in harvested crops, due to the deviating degradation patterns of the components.

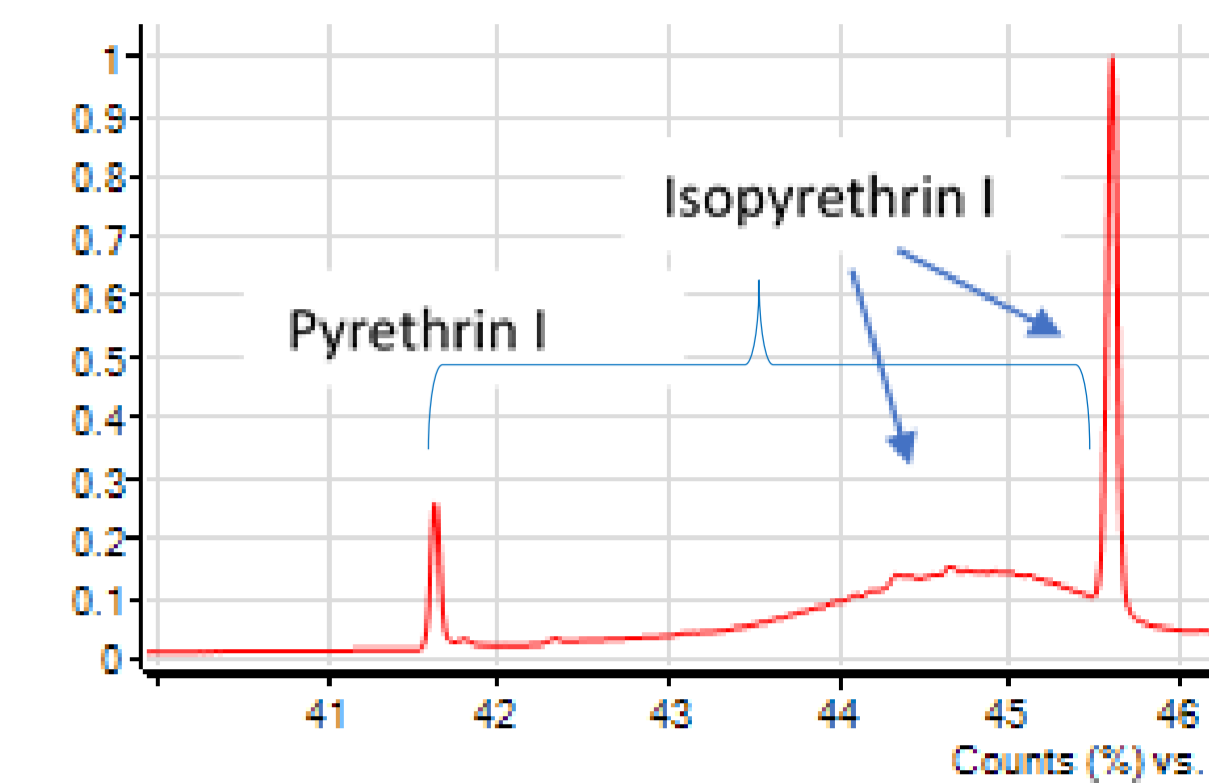
Analytical Methods

In principle, pyrethrins can be measured both by GC-MS/(MS) and LC-MS/MS. But it is also known that the two main components P-I and P-II isomerize at elevated temperatures to the corresponding isopyrethrins, with an extended system of conjugated double bonds [1]. In GC, pyrethrins elute far apart from their isomers, with the peaks being characteristically connected by a „bridge“, as the isomerization takes place both in the injector and the column. Furthermore, the mass spectra of two deviate slightly. These factors complicate GC-quantification.



In contrast, analysis of all 6 compounds is straightforward using LC-MS/MS.

Instrument parameters LC-MS/MS API QTrap 6500	
Ionization mode	ESI pos
Columns	Precolumn: C18 ODS 4mm x 2mm ID (Phenomenex AJO-4286) / Column: Zorbax 3.5 µm; Eclipse XDB-C18; 2.1x 50 mm
Column temp. (°C)	40
Eluent A / B	A: 5 mmol NH ₄ -formate in H ₂ O + 1% formic acid; B 5 mmol NH ₄ -formate in methanol (MeOH) +1% formic acid
Gradient	60%A to 0% A within 2 min (hold 5 min); back to 60%A at 7.1 min (hold 4 min) (Constant flow at 0.4 mL/min)



For comparison, 20 different standards were purchased from various providers and analyzed. It was noticed that many certificates were either incomplete or ambiguous. The term “pyrethrins” is used either for the entire mixture (of 6) or for the sum of the two main components (P-I and P-II). Only 8 of the 20 different standards indicated the content of the sum of 6 components (overall purity) and only 5 thereof the content of the individual components. All these 8 were comparable in the content of P-I and P-II (RSD 14% and 4%) but more variable in the content of minor components (RSD 20-35%) One of the standards contained only P-I and one only P-II.

The share of P-I and P-II relative to the sum of 6 was for all 20 standards quite comparable (RSDs 7% and 10%, respectively and RSD 3% for PI + PII). For the minor compounds the share was much more variable.

Three formulations from the market were shown to have a similar composition to the 8 standards mentioned above. The analysis of a cereal sample with all components at well quantifiable levels didn't show a significant shift in the relative share of components.

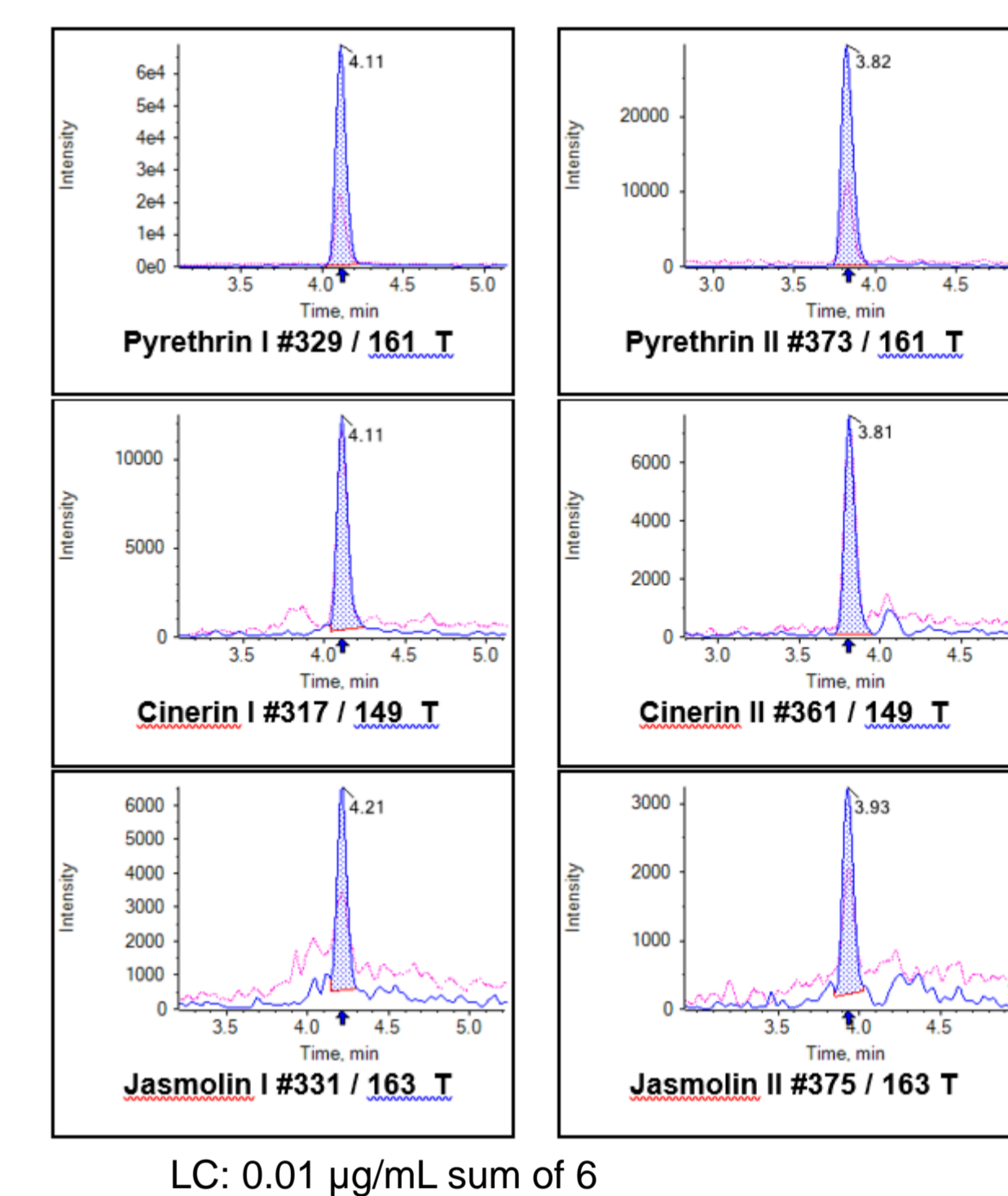
Residue levels of pyrethrins (sum) in food of plant origin were mostly <0.1 mg/kg, with the minor components being <LOQ due to their low rel. share.

Standard No.	P-I+II	P-I	P-II	C-I+II	J-I+II
Std. 1	89 %	54 %	35 %	7 %	5 %
Std. 2	87 %	55 %	32 %	7 %	6 %
Std. 3	87 %	56 %	31 %	7 %	6 %
Std. 4	87 %	57 %	30 %	7 %	6 %
Std. 5	84 %	57 %	27 %	8 %	8 %
Std. 6	84 %	57 %	27 %	8 %	8 %
Std. 7	85 %	51 %	34 %	9 %	7 %
Std. 9	89 %	55 %	34 %	7 %	5 %
Std. 10	86 %	54 %	31 %	8 %	7 %
Std. 11	87 %	59 %	29 %	7 %	6 %
Std. 12	88 %	64 %	24 %	6 %	6 %
Std. 13	80 %	49 %	31 %	11 %	9 %
Std. 14	80 %	50 %	30 %	11 %	9 %
Std. 15	100 %	100 %	0 %	0 %	0 %
Std. 16	98 %	0 %	98 %	2 %	0 %
Std. 17	84 %	57 %	27 %	8 %	8 %
Std. 18	87 %	58 %	29 %	7 %	6 %
Std. 19	86 %	51 %	35 %	8 %	6 %
Std. 20	84 %	57 %	27 %	8 %	9 %
Mean (w/o 15/16)	85 %	55 %	30 %	8 %	7 %
RSD	3 %	7 %	10 %	20 %	21 %

Relative share of the six components within the standards (Sum of 6 = 100%). Std. 15 contained only P-I and Std. 16 only P-II

Conclusion

It seems reasonable simplifying the RDs to “Sum of P-I and P-II”, which make ~85% of the sum (individ. standards are available). This would reduce the MRL* based on summed LOQs and facilitate the inclusion of pyrethrum in the EU Monitoring Program.



Compound	Parent	Daughter 1	Daughter 2
Cinerin I	317	149	107
Cinerin II	361	149	107
Jasmolin I	331	163	107
Jasmolin II	375	163	107
Pyrethrin I	329	161	133
Pyrethrin II	373	161	133



PD-64

EPRW 2024



Co-funded by the European Union



Baden-Württemberg