

GLUCOSINOLATES AND THEIR BREAKDOWN PRODUCTS IN SEEDS OF STANDARD AND HIGH QUALITY RAPE SPECIES

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Introduction

Because of antinutritional and toxic effects of standard quality rape species found in feeding experiments there is a world wide tendency to introduce high quality rape varieties with low content of erucic acid and reduced levels of glucosinolates (RÜBBELEN, 1976). 11 glucosinolates have been found in rape seeds up to now, some of them by new developed procedures in recent time. If the seeds are crushed during harvest or industrial processing the glucosinolates undergo a breakdown by the endogenous enzyme myrosinase (EC.3:2:3:1) to isothiocyanates (NCS), oxazolidine-2-thiones (OT) and nitriles (CN). Which of the possible split products are formed depends on the structure of glucosides, the conditions of degradation, the activity of enzyme and the presence of compounds which modify the action of enzyme (FENWICK, 1983).

It is the aim of our started investigations to prove the consequences resulting by change from standard to high quality rape species for industrial processing and utilization of the products with special emphasis to human nutrition. In this study we report about alkenyl/arylglucosinolates and their autolytic formed breakdown products (Table 1) in seeds of rape species of different quality.

Table 1
Alkyl/aryl-glucosinolates and their breakdown products found in seeds of rape species
licensed in GDR

$$\begin{array}{c} \text{Glc-S} \\ \text{SO}_4\text{-N} \end{array} \text{C-R} \xrightarrow{\text{MYROSINASE, H}_2\text{O}} \text{Glc-HSO}_4 + \text{NCS or CN+S or OT}$$

No.	glucosinolate (R)	No.	breakdown product
I	Gluconapin (3-Butyryl-)	1	3-Butyryl-NCS
		2	3,4-Epithiobutyl-CN
II	Glucoerucinapin (4-Pentonyl-)	3	4-Pentonyl-NCS
		4	4,5-Epithiopentyl-CN
III	Propyltriazin (2-Hydroxy-3-Butonyl-)	5	2-Hydroxy-3-Butonyl-CN
		6	2,3-Hydroxy-3,4-Epithiobutyl-CN
		7	3,4-Hydroxy-3,4-Epithiobutyl-CN
		8	3-Vinylisoxanzolidine-2-thione (Gestrin)
IV	Propylisoxanzolidine-2-thione (Mepalsterin)	9	3-Propylisoxanzolidine-2-thione (Mepalsterin)
V	Gluconesterin (2-Phenylethyl-)	10	2-Phenylethyl-NCS
		11	2-Phenylethyl-CN

Material and methods

Samples

All rape species are cultivated in the GDR districts Rostock, Schwerin and Potsdam between 1983 and 1985 (Table 2). The seed samples of standard varieties and species with low content of erucic acid are taken before industrial processing. The seed samples of species with reduced levels of glucosinolates are purchased from Institut für Futterpflanzenzüchtung, Malchow.

Table 2
Rape species used in this study

botanical classification	type	name	number of samples
standard rapeseed			
<i>Brassica napus</i> var. <i>napus</i>	winter rape	Sollux (Se)	12
<i>Brassica napus</i> var. <i>napobrassica</i>	summer rape	Grana (Gr)	5
<i>Brassica campestris</i>	winter rape	Pluto (Pl)	7
rape species with low content of erucic acid:			
<i>Brassica napus</i> var. <i>napus</i>	winter rape	Marinus (Mr)	10
<i>Brassica napus</i> var. <i>napus</i>	winter rape	Malux (MI)	6
<i>Brassica napus</i> var. <i>napus</i>	winter rape	Belinda (Be)	5
rape species with reduced levels of glucosinolates:			
<i>Brassica napus</i> var. <i>napus</i>	summer rape	Liraol (Li)	6
<i>Brassica napus</i> var. <i>napus</i>	winter rape	Doppelqualität (Dq)	3

Analytical procedures

All seed samples are dried at 60 °C, ground in a mill to get homogeneous meals and extracted with petrolether. The autolysis of glucosinolates are performed for all meals under the same conditions (buffer pH: 7.0, T: 25 °C, t: 12 h). The glucosinolates and their breakdown products are analyzed as follows

total glucosinolates: Glucose-release method by LEIN and SCHÖN (1969); results expressed as III

individual compounds: Screening of glucosinolates as their desulfotrimethylsilyl derivatives (LANGE, 1986 a)
 Identification and determination of breakdown products in the autolysates after extraction with methylene-chloride (LANGE, 1986 b)

Results/discussion

1. In the ranks of glucosinolate rich varieties differences between the amounts of the total glucosinolates and alkenyl/aryl compounds do not exist (Fig. 1). In case of glucosinolate low varieties differences are significant. That is a hint at the change in the pool of glucosides from alkenyl/aryl compounds to indolylglucosinolates as already shown by other authors (MARQUARD, 1985).
2. The pattern of alkenyl/arylglucosinolates differ between *Brassica napus* summer species (Gr, Li), *Brassica napus* winter cultivars (So, Mr, Ml, Be, Dq) and *Brassica campestris* (Pl) as known from literature (FENWICK, 1983). Undependent from total glucosinolates within one group only little variations occur (Fig. 2).

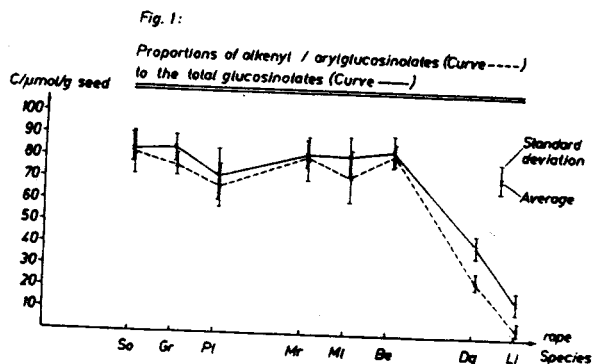
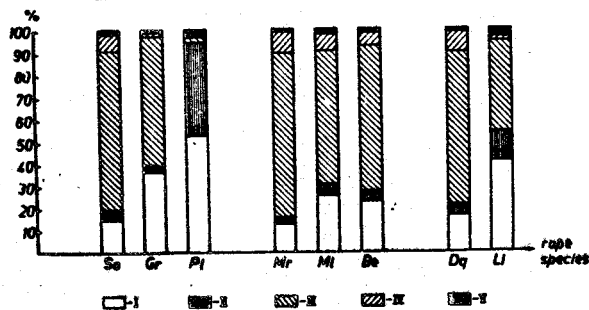


Fig. 2:
Pattern of alkenyl / arylglucosinolates



3. Nature and quantity of the autolytic formed breakdown products of glucosinolates vary in a wide range for all rape seeds (Table 3). There are seeds for which high levels of NCS and OT (So, Mr, Pl), similar proportions of CN and OT (Ml, Dq) and high levels of CN (Gr, Be, Li) are characteristic in the pool of breakdown products.

Tab. 3: Autolytic formed breakdown products of glucosinolates ($\mu\text{mol/g seed}$)

Rape species	Isothiocyanates			Nitriles							Oxazolinone-2-thiones	
	1	3	10	2	4	5	6	7	11	8	9	
So	12.3	3.6	0.8	0.1	n.d.	2.4	0.1	0.4	n.d.	55.7	7.1	
Gr	13.1	1.0	0.4	14.7	1.3	24.5	4.2	3.8	0.4	12.0	2.0	
Pl	31.8	36.7	2.6	5.0	1.7	0.8	n.d.	n.d.	n.d.	0.1	n.d.	
Mr	10.4	2.3	0.5	n.d.	0.2	2.4	n.d.	n.d.	n.d.	59.3	0.4	
Ml	18.1	3.3	1.0	2.8	0.9	6.1	1.2	1.1	n.d.	35.4	5.7	
Be	7.7	2.4	0.8	11.4	2.3	19.9	5.9	4.4	0.3	24.8	4.8	
Dq	4.2	0.9	0.3	0.3	0.2	2.4	0.5	0.5	n.d.	14.5	2.3	
Li	1.2	0.3	0.2	1.7	0.4	1.0	0.4	0.3	n.d.	0.7	0.1	

n.d. not detected

Conclusions

In this study correlations between glucosinolates, pattern of their breakdown products and seeds of rape species of different quality could not be found. In addition to the estimation of the total and the individual glucosinolates it is necessary to give more attention to the specific pathways of autolysis of the native compounds both for

breeding of high quality rape species and for processing of the seeds to get harmless products.

References

- FENWICK, G.R., R.K. HEANEY and W.J. MULLIN, 1983
Glucosinolates and their breakdown products in food and food plants
CRC Critical Review Food Science Nutrition 18, 123
- LANGE, R., M. PETRZIKA und F. LINOW, 1986 a
1. Mitt. Extraktion, Reinigung und gaschromatographisch-massenspektrometrische Erfassung der Glucosinolate
Nahrung 30, 1035
- LANGE, R., M. PETRZIKA und F. LINOW, 1986 b
2. Mitt. Enzymatische Spaltung von Glucosinolaten, Isolierung und gaschromatographisch-massenspektrometrische Identifizierung der entstehenden Aglucone
Nahrung 30, 1039
- LEIN, K.-A., und W.J. SCHÖN, 1969
Quantitative Glucosinolatbestimmung aus Halbkörnern von Brassica-Arten
Angewandte Botanik XLIII, 87
- MARQUARD, R., und V. SCHLESINGER, 1985
Methodische Untersuchungen zur Glucosinolatbestimmung bei Raps
Fette, Seifen, Anstrichmittel 87, 471
- RÜBBELEN, G., 1976
Züchtung und Erzeugung von Qualitätsraps in Europa
Fette, Seifen, Anstrichmittel 78, 10