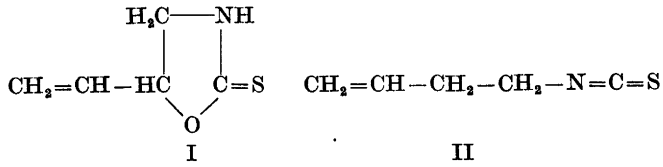
ACTA CHEMICA SCANDINAVICA 7 (1953) 1267—1270

*iso*Thiocyanates II*. Volatile *iso*Thiocyanates in Seeds and Roots of Various *Brassicae*

KAI ARNE JENSEN, JOSEF CONTI and ANDERS KJÆR

Chemical Laboratory, University of Copenhagen, Denmark

Within the family *Cruciferae* the genus *Brassica* embraces a number of plants of extensive application in human and animal nutrition. Therefore, much interest has been devoted to studies of chemical factors of possible biological importance in these plants. Foremost among those, the goitrogenic substances in vegetables and particularly various seeds of *Brassicae* (see *e. g.* Ref. [1]) have been a subject of much interest, culminating in the isolation from such sources of the antithyroid substance, L-5-vinyl-2-thioöxazolidone, (I) [2].



I

II

The structure, in conjunction with the fact that the active principle seems to be present in the intact biological material as a glycosidic precursor, raised the question as to its possible relationship to the naturally occurring *iso*thiocyanates. Not much is known with certainty regarding the *iso*thiocyanates in *Brassica* species.

The paperchromatographic technique, reported in a previous paper [3], has now been applied to a number of seeds of *Brassicae* in order to determine the chemical nature of the *iso*thiocyanates contained therein. The results, together with the spectrophotometrically estimated contents, are presented in Table 1. Similar investigations of roots and other fresh parts of some common species of the same genus, gave the results summarised in Table 2. Experimental details of the procedure employed are described in a following communication [4]. The results of a closer investigation of rape seeds, from which 3-butenyl *iso*thiocyanate (II) has been isolated, will be found in the following paper.

* The paper: *Unsaturated Five-Carbon Isothiocyanates*, which appeared in this Journal (7 (1953) 518), should be considered as number one in this series.

Table 1. Contents of volatile isothiocyanates *in seeds of various* Brassicae, *determined by paper chromatography.*

Species	% Fat	R_{Ph}	*iso*Thiocyanate(s)	mg %
Brassica nigra Koch (Black mustard)	32	0.27	Allyl	518
Brassica juncea Czern.et Coss. (Indian mustard)	37	0.27	Allyl	353
Brassica pseudojuncea	34	0.26[a] 0.59	Allyl 3-Butenyl	470
Brassica oleracea L. (Cabbage)	35	0.26[a] 0.61	Allyl 3-Butenyl	125
Br. oler.capitata var.*alba* L. (White cabbage)	37	0.27 0.73[b]	Allyl *sec*-Butyl (?)	311
Br.oler.capitata var.*rubra* L. (Red cabbage)	32	0.27 0.91[b]	Allyl Benzyl (?)	221
Br.oler.percrispa L. (Kale)	41	0.27	Allyl	8
Br.oler.botrytis L. (Cauliflower)	34	0.27[a] 0.74	Allyl *sec*-Butyl	270
Br.oler.gemmifera D.C. (Brussels sprouts)	35	0.27[a] 0.73	Allyl *sec*-Butyl	192
Br.oler.sabauda L. (Green savoy)	35	0.27 0.72[b]	Allyl *sec*-Butyl	279
Br.oler.asparagoides D. C. (Broccoli)	42	0.02 0.92[a] 1.28[b]	Methyl (?) Benzyl Unidentified	
Br.napus L. *(rapifera)esculenta* D.C. (Kohlrabi)	40	None	.	
Br.rapa rapifera Metzger (White turnip)	42	1.30	Unidentified	
Br.rapa (rapifera) communis Metzger (Turnip)	45	0.60[a] 1.03[a] 1.33[b]	3-Butenyl Unidentified Unidentified	2—3

[a] predominant; [b] traces only.

DISCUSSION

Upon consideration of the results presented in the tables, two characteristic features are evident. The predominating rôle played by allyl *iso*thiocyanate within the genus *Brassica* is easily perceptible. Second, the appearance of mixtures of two or three different *iso*thiocyanates in a certain species is the rule rather than an exception.

Table 2. Contents of volatile isothiocyanates *in fresh parts of various* Brassicae, *determined by paper chromatography.*

Species	Part	R_{Ph}	*iso*Thiocyanate(s)	mg % in fresh parts
White cabbage	Head	0.27	Allyl	1—2
Red cabbage	Head	0.27[a] 0.60	Allyl 3-Butenyl	5
Cauliflower	Head	0.27[b]	Allyl	
White turnip	Root	0.03[b] 1.01	Methyl (?) Unidentified	

[a] predominant; [b] traces only.

Allyl *iso*thiocyanate, the mustard oil *par excellence*, appears in black mustard seeds, unaccompanied by other volatile derivatives. In this connection it is pertinent to recall the remarkable isolation of β-phenylethyl *iso*thiocyanate from roots of the same species by Stahmann, Link and Walker [5]. Much controversy exists in the literature (see *e. g.* Ref. [6]) concerning the chemical nature of the *iso*thiocyanate(s) in seeds of Indian mustard (*Br. juncea*). Our finding of allyl *iso*thiocyanate as the sole volatile constituent corroborates the results of Schmalfuss and Müller [6]. The additional presence of 3-butenyl *iso*thiocyanate in a "synthetic variety", *Br. pseudojuncea*, is interesting and once again reflects the chemical specificity of even closely related species. The possible utilisation of this fact in heredity studies receives further consideration.

Except for broccoli, all species of *Brassica oleracea* investigated contain allyl *iso*thiocyanate. The minor constituents, however, differ in their chemical nature. A paper by Grimme [7] presents the results of a quantitative estimation of the volatile *iso*thiocyanates in a series of *Brassica* seeds, tacitly assuming, however, that solely the allyl derivative is implied. The only previous establishment of the identity of a mustard oil from cabbage species is furnished by Schneider and Lohmann [8], who isolated allyl *iso*thiocyanate from cauliflower seeds. The absence of this component and the unusual presence of benzyl *iso*thiocyanate plus an unidentified constituent in broccoli seeds urge a closer investigation of this material. Seeds of kohlrabi (rutabaga), known as one of the best sources of the goitrogenic factor (I) [1,2], were found to be remarkably devoid of volatile *iso*thiocyanates. On the other hand, Schultz and Gmelin [9] very recently provided paperchromatographic evidence for the presence in kohlrabi seeds of four glucosides, two of which should give rise to allyl (slight amounts only) and benzyl *iso*thiocyanate on enzymatic cleavage.

The different turnip (*Br. rapa*) species investigated possess a rather complex composition of their volatile *iso*thiocyanate fractions. The identity of the mustard oil, giving rise to the spot with an R_{Ph}-value of 1.03, is still obscure. Work is in progress to isolate this unknown *iso*thiocyanate and reveal its chemical structure.

The deviations between the *iso*thiocyanates in seeds and fresh parts of the same species, as evident upon comparison of the Tables 1 and 2, are indicative of the *iso*thiocyanate contents as a function not only ofthe species but also of the parts of a particular plant (*cf.* Ref. [5]).

Animal tests have indicated practically no antithyroid activity of the naturally occurring *iso*thiocyanates.

SUMMARY

Seeds and fresh parts of various *Brassicae* have been investigated for their contents of volatile *iso*thiocyanates by a paperchromatographic technique.

The tabulated results have been discussed in the light of previous results.

The authors wish to thank Dr. K. J. Frandsen, Øtoftegaard, for the gift of various seed samples.

The work was initiated by a grant from *Laurits Andersens Fond* and in its later phases supported by *Carlsbergfondet (The Carlsberg Foundation)*.

REFERENCES

1. Greer, M. A., Ettlinger, M. G., and Astwood, E. B. *J. Clin. Endocrinol.* **9** (1949) 1069.
2. Astwood, E. B., Greer, M. A., and Ettlinger, M. G. *J. Biol. Chem.* **181** (1949) 121.
3. Kjær, A., and Rubinstein, K. *Acta Chem. Scand.* **7** (1953) 528.
4. Kjær, A., Conti, J., and Larsen, I. *Acta Chem. Scand.* **7** (1953) 1276.
5. Stahmann, M. A., Link, K. P., and Walker, J. C. *J. Agr. Research* **67** (1943) 49.
6. Schmalfuss, H., and Müller, H.-P. *Forschungsdienst* **17** (1944) 205.
7. Grimme, C. *Pharm. Zentralhalle* **53** (1912) 733.
8. Schneider, W., and Lohmann, W. *Ber.* **45** (1912) 2955.
9. Schultz, O.-E., and Gmelin, R. *Z. Naturforsch.* **8b** (1953) 151.

Received September 8, 1953.