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# *iso*Thiocyanates XX *. 4-Pentenyl *iso*Thiocyanate, a New Mustard Oil Occurring as a Glucoside (Glucobrassicanapin) in Nature

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A new volatile mustard oil has been isolated from seed cake of rape (*Brassica napus* L.) and identified as 4-pentenyl *iso*thiocyanate (III), the higher homologue of 3-butenyl mustard oil, (II), previously recognized in the same material. The structure proof of (III) rests on infra-red data for the corresponding thiourea, and degradation of its derivative with 1-naphthylamine, (V), to compounds of established structure.

A synthesis of pure 4-pentenyl *iso*thiocyanate has been accomplished, and synthetic 1-(1-naphthyl)-3-(4-pentenyl)-thiourea (V) shown to be identical with the product derivable from the natural mustard oil.

The latter occurs in the seed as a glucoside for which the name *glucobrassicanapin* is proposed. The identification of the new *iso*thiocyanate makes possible the establishment of a complete picture of the mustard oils of rape seed. Six individual glucosides are genuinely present, three of which in very small amounts only. They are: glucoiberin (or a closely allied compound, traces only), progoitrin (glucorapiferin), sinalbin (traces), gluconapin, glucobrassicanapin and gluconasturtiin (traces), yielding (−)-3-methylsulphinylpropyl mustard oil (or a related species), (−)-5-vinyl-2-oxazolidinethione, *p*-hydroxybenzyl, 3-butenyl, 4-pentenyl and 2-phenylethyl *iso*thiocyanate, respectively, on enzymic hydrolysis.

In a previous paper of this series [1] it was demonstrated that seed of rape (*Brassica napus* L.) on enzymic hydrolysis furnished three volatile *iso*thiocyanates. Of these, the chief constituent was proved to be 3-butenyl mustard oil (II), a conclusion independently attained at also by Ettlinger and Hodgkins [2]. One of the minor components has now been identified as the homologous and heretofore unknown 4-pentenyl *iso*thiocyanate (III).

$CH_2=CHCH_2NCS$ I  $CH_2=CHCH_2CH_2NCS$ II  $CH_2=CHCH_2CH_2CH_2NCS$ III

* Part XIX of this series: *Acta Chem. Scand.* 10 (1956) 1100.

The occurrence of more than one species in the volatile mustard oil fraction of rape seed has been suspected for many years. In 1899 Jørgensen [3] considered the possible existence of an "angelyl mustard oil" in admixture with the preponderant $C_5$-species ("crotyl mustard oil"), mainly on basis of nitrogen analyses of the corresponding crude thiourea-mixtures. Schmalfuss [4] subjected the volatile mustard oil mixture from a total of 50 kg of rape seed to fractional distillation and obtained, in addition to 4-pentenonitrile and what is known today as 3-butenyl *iso*thiocyanate, a higher boiling *iso*thiocyanate furnishing a thiourea with an unsharp m. p. of *ca.* 50°. No analytical data or suggestions as to composition and structure were presented. More recently, André and Delaveau [5] succeeded in obtaining an *iso*thiocyanate with comparable physical properties, again by fractionation of the volatile rape seed (colza) mustard oils. The product was devoid of optical activity, and analytical data of the corresponding crystalline thiourea indicated the composition $C_5H_9NCS$ of the mustard oil. The French authors realized the theoretical existence of 13 isomerides satisfying these conditions but did not attempt any determination of the actual structure. They did present, however, good evidence for the second minor component, which is present in trifling amounts only, being 2-phenylethyl *iso*thiocyanate, a species occasionally encountered also in other crucifer seeds.

The starting material in the present experiments was commercially produced rape seed cake which was subjected to enzymic hydrolysis by the addition of white mustard seed, functioning as a source of myrosinase. It was formerly shown [6] that the latter seed gives rise to traces only of volatile mustard oils, insignificant for the present purpose. Steam distillation furnished a yield of less than 0.1 % of volatile *iso*thiocyanates which were fractionated *in vacuo*. Subsequent to the bulk of 3-butenyl mustard oil, the new *iso*thiocyanate distilled as a colourless product, containing traces only of the 3-butenyl species as estimated by paper chromatography of the corresponding thiourea. For the purpose of structure determination and characterization, the *iso*thiocyanate was transformed into crystalline thiourea-derivatives upon reaction with ammonia and 1-naphthylamine. Analyses of both derivatives indicated the composition $C_5H_9NCS$ of the parent *iso*thiocyanate. The infra-red spectrum of the simple thiourea (IV) suggested the presence of a vinyl-grouping. The unbranched character of the five-carbon chain was demonstrated in the following way. The naphthylthiourea (V) was transformed into the corresponding naphthylurea (VI) which, on catalytic hydrogenation, afforded 1-(1-naphthyl)-3-pentylurea (VII), identified by comparison with an authentic specimen produced from *n*-pentylamine and naphthyl *iso*cyanate.

$$CH_2=CHCH_2CH_2CH_2NHCSNHR \xrightarrow{AgNO_3} CH_2=CHCH_2CH_2CH_2NHCONHR$$

IV: R = H
V: R = 1-naphthyl

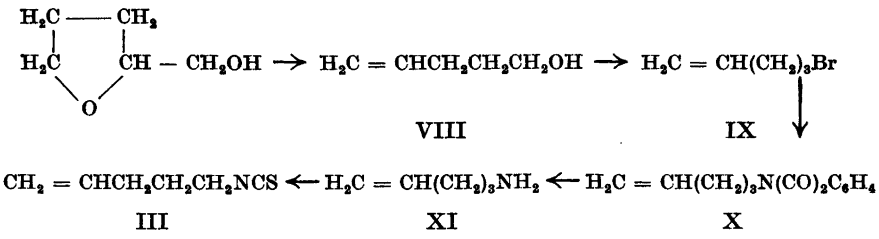
VI

$H_2$ | Pt

$$CH_3CH_2CH_2CH_2CH_2NH_2 + RNCO \longrightarrow CH_3CH_2CH_2CH_2CH_2NHCONHR$$

VII

As further corroboration the new natural *iso*thiocyanate (III) has been synthesized along conventional lines as shown in the following scheme.




4-Penten-1-ol (VIII), prepared from tetrahydrofurfuryl alcohol [7], was transformed into 5-bromo-1-pentene (IX) as described by La Forge *et al.*[8] N-(4-Pentenyl)-phthalimide (X), obtained according to the described direction [9] as a solid, m. p. 34°, with correct analysis (Ref.[9] m. p. 40°), afforded the requisite 4-pentenylamine (XI), b. p. 98°, on hydrazinolysis. The amine was characterized as an acid oxalate hemihydrate, m. p. 139°. These data deviate somewhat from those previously recorded. v. Braun [10] prepared the amine, b. p. 91—94°, by thermal decomposition of 5-aminopentyltrimethylammonium hydroxide, whereas Paul and Cottin [11] reported the b. p. 105—106° for the anhydrous amine which was also characterized as an acid oxalate, m. p. 129—130°. They apparently ignored the water of crystallization in this salt. Pure 4-pentenyl *iso*thiocyanate (III) was prepared from (XI) by a modification [12] of Dyson's thiophosgene method [13] and converted into 1-(1-naphthyl)-3-(4-pentenyl)-thiourea (V) in the usual way. Analyses, mixed melting point determination and infra-red spectra served to establish the identity of the naphthylthioureas derived from the natural and the synthetic mustard oil.

Three homologous, straight-chain *iso*thiocyanates possessing a terminal double bond, (I), (II) and (III), have thus been recognized in Nature, the first as the aglucone of the classical and widely distributed glucoside sinigrin. It is interesting that the analogous $\omega$-methylthio compounds, *viz.* 3-methylthiopropyl [14], 4-methylthiobutyl [15] and 5-methylthiopentyl [16] *iso*thiocyanate as well as various higher oxidation states of these, have been encountered also as naturally occurring aglucones. This fact suggests a common biogenetic origin, a possibility which is being further considered in this laboratory. As pointed out in a previous paper [21], 4-pentenyl *iso*thiocyanate seems to occur also in various species of the genus *Alyssum*.

Paper chromatography of the *iso*thiocyanate glucosides in rape seed extracts, essentially following the directions given by Schultz and Gmelin [17], indicates the presence of six individual components, three of which appear in very small amounts only (Fig. 1) *. The same pattern has been obtained for several seed samples of different provenance and is therefore regarded as

* In paperchromatographic survey work Gmelin [18] noticed the occurrence of five glucoside spots in a seed extract of *B. napus*. More recent data from the same laboratory [19], however, indicate the presence of only two glucosides in the same material. According to the paperchromatographic values, these may be interpreted as the chief constituents, *viz.* progoitrin [22] (glukorapiferin [23]) and gluconapin [1, 2, 26], respectively.

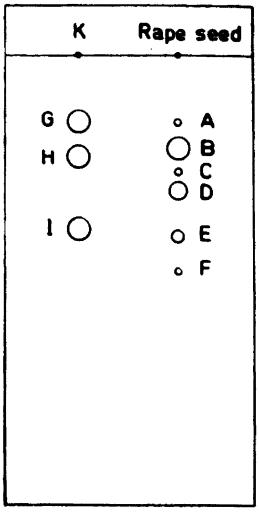



*Fig. 1. Schematic, descending paper chromatogram of rape seed* iso*thiocyanate glucosides in* n*-butanol : ethanol : water (4 : 1 : 4) (upper phase). A—F: see text. K: reference solution, containing G : glucoiberin [20], H : sinigrin and I : glucotropaeolin (from seeds of* Tropaeolum majus).

characteristic for the species *Brassica napus* L., including several varieties. The component of lowest $R_F$-value, (A), appears in traces only and may be identical with, or closely related to, glucoiberin, the glucoside previously isolated from *Iberis amara* L.[20] and containing (—)-3-methylsulphinylpropyl *iso*thiocyanate as the aglucone (*cf.* also Ref.[21]). Then follows a spot, (B), attributable to the 2-hydroxy-3-butenyl *iso*thiocyanate glucoside, recently isolated by Greer [22] in crystalline form under the name progoitrin, and almost certainly identical with the glukorapiferin of Schultz and Wagner [23], isolated from seed of a *B. napus* variety and characterized by analysis and melting point of a crystalline pentaacetate.* Enzymic hydrolysis of this glucoside is responsible [22,24,30] for the production of the goitrogenic (—)-5-vinyl-2-oxazolidinethione [25], previously isolated from seeds or fresh parts of various *Brassica* species including rape. A very weak glucoside-spot, (C), can safely be attributed to sinalbin, a long known glucoside containing *p*-hydroxybenzyl *iso*thiocyanate, on account of the correct $R_F$-value in conjunction with a positive reaction on spraying with diazotized sulphanilic acid [18]. This glucoside has been observed in all *B. napus* species investigated but is consistently present in traces only. Then follow the glucosides giving rise to the volatile mustard oils. First, the progenitor, (D), of the predominant 3-butenyl *iso*thiocyanate [1, 2] for which we have adopted the name gluconapin, introduced in 1905 by Ter Meulen [26] for the glucosidic precursor of the supposedly homogeneous though unidentified volatile mustard oil of rape. With a considerably higher $R_F$-value follows the 4-pentenyl *iso*thiocyanate glucoside (E) for which we propose the name *glucobrassicanapin*. Lastly, a very faint spot, (F), is consistently apparent, attributable to gluconasturtiin, the 2-phenylethyl *iso*thiocyanate glucoside, an assumption supported by the results of André and Delaveau [5].

* *Added in proof*: Recently, the same authors [30] have indeed presented chemical evidence for the identity of the anions of glukorapiferin and progoitrin.

This picture is regarded as an essentially complete and correct account of the *iso*thiocyanates in rape seeds, a subject of much discussion in the literature through more than five decades. Other species of the genus *Brassica* have been similarly studied in this laboratory. The results will be presented in a forthcoming communication, together with some attempts to correlate the cytological and chemical classification within this important genus.

## EXPERIMENTAL

All melting points are uncorrected and determined in capillary tubes in a slowly heated bath.

*Isolation.* Finely divided rape seed cake (30 kg) was suspended in water (60 l), buffered to pH 6.6 with $KH_2PO_4$(850 g) and $Na_2HPO_4$, $2H_2O$ (320 g). Milled seed of white mustard *(Sinapis alba* L.) (5 kg) was added, the suspension was kept at room temperature for 18 hours and steam distilled until about 50 l were collected. The distillate was saturated with salt and extracted three times with a total of 6 l of ether. The extract was dried and the solvent removed over a Vigreux column. The residue was subjected to fractional distillation at 12 mm, using an all-glass column packed with glass-helices and equipped with a total reflux variable take-off head. A forerun, *ca.* 1 g, b. p. 43—60°, was followed by a mustard oil fraction, b. p. 61—70°, redistilled to give 14 g of pure 3-butenyl *iso*thiocyanate (b.p. 64° at 12 mm). Then came a small interfraction (0.6 g), b. p. 71—75°, followed by essentially pure 4-pentenyl *iso*thiocyanate (1.07 g), b. p. 75°. All samples were checked by transformation into thioureas followed by paper chromatography of these in water-saturated chloroform according to our usual method [27]. The last fraction showed a very faint spot only of the 3-butenylthiourea in addition to that of 4-pentenylthiourea and was used directly for preparing the following derivatives.

*1-(4-Pentenyl)-thiourea* (IV). Treatment of a small sample of the preceding mustard oil with ethanolic ammonia at room temperature furnished a brownish oil which was taken up in benzene. Pentane was added to turbidity, and after one week in the ice-box colourless plates separated, embedded in oily material which was removed by pressing between filter paper. Pure N-(4-pentenyl)-thiourea crystallized from water in thin, nacreous plates, m. p. 43.5—44.0° (Ref.[5] 42.5—43.5°). (Found: C 49.75; H 8.31; N 19.46. Calc. for $C_6H_{12}N_2S$: C 49.97; H 8.39; N 19.43). On descending paper chromatography in water-saturated chloroform an $R_{Ph}$-value [27] of 0.96 was determined.

The infra-red spectrum, determined in a potassium bromide disc, showed prominent bands at 2.90 (v.s.), 3.27 (m.), 6.08 (v.s.), 6.35 (v.s.), 6.79 (s.), 6.98 (s.), 7.29 (v.s.), 7.60 (m.), 8.27 (m.), 8.54 (m.), 8.79 (w.), 10.01 (s.), 10.92 (v.s.), 11.78 (w.), 13.46 (w.) and 14.06 $\mu$ (m.). The bands at 10.01 and 10.92 $\mu$ are particularly important in this connexion because they strongly indicate the presence of a vinyl grouping [29]. The ultra-violet absorption spectrum in ethanol was of the usual type, $\lambda_{max}$ 242 m$\mu$ ($\varepsilon_{max}$ 14 150), $\lambda_{min}$ 225 m$\mu$ ($\varepsilon_{min}$ 5 100).

*1-(1-Naphthyl)-3-(4-pentenyl)-thiourea* (V). A solution of the natural mustard oil (50 mg) and freshly recrystallized 1-naphthylamine (65 mg) in ethanol (3 ml) was heated to reflux for 2 hours. Removal of the solvent left an oil which crystallized on being rubbed with a few drops of ethanol. Two recrystallizations from aqueous ethanol afforded the pure thiourea (73 mg) as needles, m. p. 102°. (Found: C 70.95; H 6.60; N 10.25. Calc. for $C_{16}H_{18}N_2S$: C 71.06; H 6.71; N 10.36). A week later, the m. p. was found to be 126°, obviously a case of dimorphism. A sample prepared from synthetic 4-pentenyl *iso*thiocyanate and 1-naphthylamine (see below) still appeared as the low-melting form after two recrystallizations from aqueous ethanol, but changed to the high-melting modification on a third recrystallization from the same solvent. Once the high-melting form had appeared, it was no longer possible to realize the low-melting modification. Polymorphism has frequently been observed within the class of thioureas, the present case closely resembling that of *e. g.* 1-(*m*-methoxybenzyl)-3-phenyl-thiourea, recently discussed by Ettlinger and Lundeen [28].

*Synthesis of 4-pentenyl isothiocyanate* (III). The reaction of 4-penten-1-ol [7] (VIII) and phosphorus tribromide in pyridine, following described directions [8], furnished in somewhat lower yield (70 %) 5-bromo-1-pentene (IX), b. p. 58° at 70 mm. The latter was converted into N-(4-pentenyl)-phthalimide (X) in 75 % yield according to Kharasch and Fuchs [9], b. p. 163° at 2 mm (lit.[9] 155—157° at 2 mm). A sample of the phthalimide, recrystallized twice from aqueous ethanol, melted at 34° (lit.[9] 40°). (Found: C 72.45; H 6.15; N 6.49. Calc. for $C_{13}H_{13}NO_2$: C 72.56; H 6.09; N 6.51).

Hydrazinolysis was performed by refluxing the phthalimide (26 g) and hydrazine hydrate (6.7 ml) in ethanol (150 ml) for one hour. The suspension was digested for another hour at 100° with 500 ml of 6 N HCl, whereupon the ethanol was removed by distillation. The phthalylhydrazide was filtered off, the filtrate concentrated to about 200 ml and made strongly alkaline. Salt was added to saturation, the amine extracted with ether, the extract dried over KOH pellets, and the ether removed over a column. The crude 4-pentenylamine (8.5 g) was further dried over fresh KOH for two days and distilled in a system protected from the atmosphere, b. p. 98°. Analysis indicated that water was still present in the product, though less than corresponding to a monohydrate. (Found: N 15.0. Calc. for $C_5H_{11}N$: N 16.5; for $C_5H_{13}NO$: N 13.6). The amine acid oxalate hemihydrate formed colourless needles from ethanol, m. p. 139.0—139.5° (lit.[11] 129—130°). (Found: C 45.70; H 7.47; N 7.61. Calc. for $C_5H_{11}N$, $C_2H_2O_4$, 0.5 $H_2O$: C 45.63; H 7.66; N 7.61). Drying of the salt at 100° over $P_2O_5$ resulted in weight loss, but the extremely hygroscopic nature of the anhydrous product made a quantitative determination of the water of crystallization impossible.

To a solution of thiophosgene (2.08 g) in chloroform (25 ml) was added another solution of 4-pentenylamine (1.7 g) in water (7 ml). 1 N NaOH (39.5 ml) was slowly added to the stirred solution, and the yellow colour gradually disappeared. The chloroform layer was dried, the solvent removed and the residue distilled *in vacuo*. Pure 4-pentenyl *iso*thiocyanate III) (0.9 g) was obtained as a colourless oil possessing a characteristic mustard oil smell, though less penetrant than that of 3-butenyl *iso*thiocyanate, b. p. 75° at 12 mm, $n_D^{25}$ 1.5118 (lit. 73.7°/11.5 mm[4], 76—77°/10 mm[5]; $n_D^{18}$ 1.5187 [4], $n_D^{20}$ 1.5172 [5]). (Found: C 56.30; H 7.28; N 10.97. Calc. for $C_6H_9NS$: C 56.65; H 7.13; N 11.01).

The synthetic *iso*thiocyanate was transformed into its thiourea derivative with 1-naphthylamine as described above for the natural mustard oil. The stable modification was obtained as colourless needles, m. p. 125°, alone or in admixture with the natural derivative. (Found: C 71.15; H 6.67; N 10.40. Calc. for $C_{16}H_{18}N_2S$: C 71.06; H 6.71; N 10.36). The infra-red spectra were determined for both specimens and found to be identical.

*1-(1-Naphthyl)-3-(4-pentenyl)-urea* (VI). The thiourea (714 mg), dissolved in ethanol (40 ml), was treated with a solution of silver nitrate (896 mg) in 75 % ethanol (15 ml), resulting in instantaneous separation of silver sulphide. Sodium hydroxide (1 N) was added dropwise to neutral reaction, and the mixture was heated to reflux for two hours. The suspension was filtered through Celite, the precipitate thoroughly washed with ethanol, and the joint filtrate and washing liquor diluted with half the volume of water, resulting in precipitation of the crystalline urea. The product was recrystallized twice from 90 % ethanol and pure 1-(1-naphthyl)-3-(4-pentenyl)-urea (VI) separated as tiny, colourless needles (470 mg), m. p. 152°. (Found: C 75.30; H 7.13; N 11.10. Calc. for $C_{16}H_{18}N_2O$: C 75.58; H 7.13; N 11.02).

*1-(1-Naphthyl)-3-pentyl-urea* (VII). On mixing equimolecular amounts of naphthyl *iso*cyanate and *n*-pentylamine in ether solution, 1-(1-naphthyl)-3-pentylurea crystallized spontaneously. It separated from aqueous ethanol in colourless needles, m. p. 146.5—147.0°. (Found: C 74.45; H 7.96; N 11.15. Calc. for $C_{16}H_{20}N_2O$: C 74.74; H 7.87; N 10.93).

No depression of the m. p. was observed when this product was mixed with a specimen prepared by catalytic hydrogenation of the corresponding unsaturated urea described above. The reduction was performed in ethanolic solution at ordinary pressure with Adam's platinum catalyst. The infra-red spectra of the two specimens were determined and found to be identical.

*Paper chromatography.* In the present work, all paper chromatograms were run by the descending technique on Whatman paper No. I in a constant temperature room. Methanolic extracts of the various seed samples were employed without further puri-

fication in the paperchromatographic analyses of the glucoside contents, the spraying and development being performed essentially as described elsewhere[17]. The identity of (B) (Fig. 1) as progoitrin (glukorapiferin) was proved in the following way. A rape seed extract was applied to an 18 cm broad paper strip as a band and chromatographed in the usual way. A small strip, cut from each edge, was developed in order to locate the component (B). The corresponding section of the main strip was cut out, eluted with water and the eluate subjected to enzymic hydrolysis by adding a droplet of a myrosinase solution. After 4 hours, the solution was extracted with ether, the solvent removed and the ultra-violet absorption spectrum determined for an ethanolic solution of the residue. An absorption pattern was obtained, identical with that previously reported for 5-vinyl-2-oxazolidinethione [25]. The other glucoside spots on the paper chromatogram were found devoid of characteristic absorption when tested in a similar way.

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