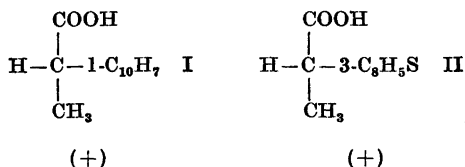


The dextro-rotatory α -(1-naphthyl)-propionic acid has the configuration I. Consequently (+)- α -(3-thianaphthenyl)-propionic acid has a stereo formula corresponding to II.



If the 3-thianaphthenyl group is considered as a substituent on the aliphatic carbon chain, this acid must be assigned to the D-series.

The work described here is part of a stereochemical study of aralkyl carboxylic acids. Full details will be given elsewhere.

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isoThiocyanates XXII*. 3-Benzoyloxypropyl isoThiocyanate, Present as a Glucoside (Glucomalcolmiin) in Seeds of *Malcolmia maritima* (L.) R.Br.

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Paperchromatographic analysis of the isoThiocyanate glucosides in a seed extract of the crucifer *Malcolmia maritima* (L.) R. Br. revealed the presence of two glucosides, (a) and (b), possessing R_B -

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values¹ of 0.34 and 1.36, respectively, in the solvent system: *n*-butanol:ethanol:water (4:1:4). In addition, traces of a third glucoside (R_B 1.03) and substantial amounts of sinapine were recognized in the seed extract, a pattern similar to that obtained elsewhere¹.

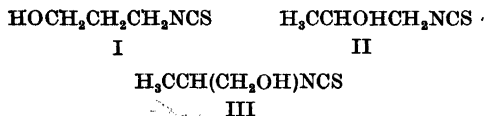
In the present work, the glucoside (a) has been unequivocally identified as glucocheirolin, furnishing cheirolin (3-methylsulphonyl-propyl isothiocyanate) on enzymic hydrolysis, a mustard oil formerly recognized as a constituent of *Cheiranthus cheiri* L.** and other species². Crystalline thiourea derivatives have been obtained from enzymically hydrolyzed seed macerates of *M. maritima* after treatment with aniline and benzylamine, identical with reference specimens prepared from synthetic cheirolin³. The phenylthiourea has been described previously^{2,3} whereas the benzyl derivative is a new compound, m. p. 116° (uncorr.). (Found: C 50.35; H 6.26; N 9.70. Calc. for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{N}_2\text{S}_2$: C 50.31; H 6.33; N 9.78).

The component (b), for which we propose the name *glucomalcolmiin*, is obviously different from all glucosides heretofore encountered in nature. The corresponding optically inactive, non-volatile isothiocyanate, liberated from a paperchromatographically purified specimen of glucomalcolmiin, displays an ultraviolet absorption spectrum indicative of the presence of a strongly chromophoric system (λ_{max} 230 m μ , λ_{min} 213 m μ in water). The new mustard oil has been characterized as a crystalline thiourea, $\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_2\text{S}$, after treatment with ammonia, m. p. 162° (uncorr.). (Found: C 55.40; H 5.91; N 11.75; S 13.59. Calc. for $\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_2\text{S}$: C 55.41; H 5.92; N 11.75; S 13.45); UV-spectrum in ethanol: λ_{max} 237 m μ (ϵ 19 400), λ_{min} 214 m μ (ϵ 11 180) and low-extinction inflections at 270–272 m μ and 278–280 m μ . The IR-spectrum of the solid thiourea in a KBr disc displayed conspicuous bands at: 3.00 (vs), 5.83 (s, ester-CO), 6.05 (s), 6.41 (vs), 6.76 (s), 7.21 (s), 7.49 (s), 7.75 (vs), 8.44 (m), 8.79 (vs), 8.90 (vs), 9.28 (m), 9.48 (m), 9.70 (m), 9.84 (m), 10.64 (w), 11.00 (m), 12.47 (vs), 13.35 (w, broad), 14.03 (vs) and 14.53 μ (m). This pattern, in conjunction with the composition $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NS}$ for the parent mustard oil, points to the new species being a benzoate of a hydroxysubstituted 3-carbon-alkyl isothiocyanate. In accord herewith, alkaline hydrolysis of the thiourea at room temperature afforded benzoic acid in high yield, isolated and identified on comparison with an

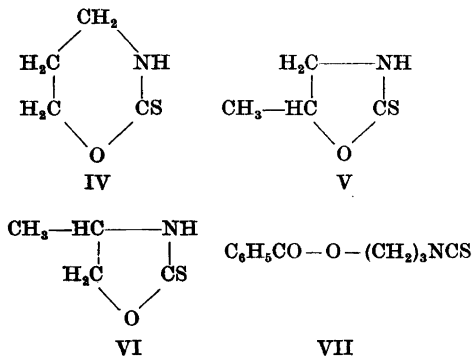
** *Malcolmia maritima* R. Br. is nomen conservandum over *Cheiranthus maritimus* L.

authentic specimen. On paper chromatography in water-saturated chloroform, the thiourea migrates at a rate corresponding to an R_{Fh} -value⁴ of 1.07.

Disregarding the unlikely structures containing a hydroxyl grouping at the α -carbon atom, the alcoholic fragment of the new isothiocyanatoalkyl benzoate may be represented by (I), (II) or (III), the last two structures possessing a centre of asymmetry and thence considered less likely in view of the optically inactive nature of the isothiocyanate.



There are good reasons to expect (I), (II) and (III) to undergo spontaneous cyclization to (IV), (V) and (VI), respectively, the last two formulae representing a ring system formerly recognized in various substances derivable from naturally occurring β -hydroxysubstituted isothiocyanates (cf. Ref.⁵).



When the thiourea-mixture, obtained by enzymic hydrolysis, solvent extraction and ammonia treatment of a purified seed extract of *M. maritima*, was chromatographed on paper, the pattern shown in Fig. 1 was observed. The results can be interpreted according to the following scheme, and strongly suggest that the new mustard oil is 3-benzoyloxypropyl isothiocyanate (VII).

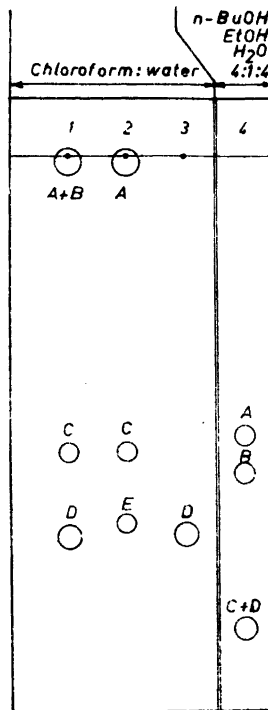
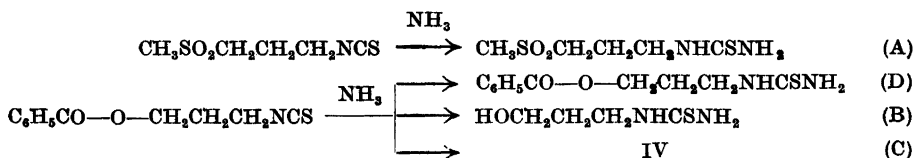


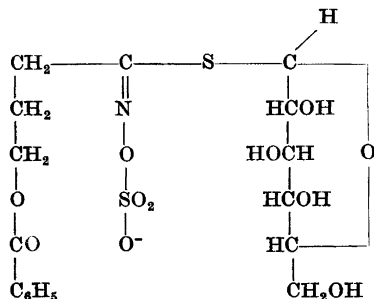
Fig. 1. Schematic, descending paper chromatograms. 1 and 4: thiourea mixture obtained from seeds of *Malcolmia maritima*; 2 and 3: synthetic reference samples. A: cheirolinthiourea; B: 3-hydroxypropylthiourea; C: tetrahydro-1,3-oxazine-2-thione (IV); D: 3-benzoyloxypropylthiourea; E: (\pm)-5-methyl-2-oxazolidinethione (V).

The normal thiourea formation is partly accompanied by ammonolysis of the ester linkage, resulting in the formation of (B) as well as the previously unknown tetrahydro-1,3-oxazine-2-thione (IV). An authentic specimen of the latter, prepared from 3-amino-1-propanol by the method of Hodgkins and Fittlinger⁶ for the synthesis of isothiocyanates, was obtained as colourless plates, m. p. 129° (uncorr.). (Found: C 41.05; H 6.21; N 11.86. Calc.

for C_6H_7ONS : C 40.98; H 6.02; N 11.95). The compound migrated on paper chromatograms at a rate definitely lower than that of a reference sample of (\pm)-5-methyl-2-oxazolidinethione (V)^{7,8} (Fig. 1); it appears likely that the isomeride (VI)⁹ will not differ markedly from (V) in its chromatographic behaviour. Synthetic experiments are now in progress to verify the structure (VII).

The possible existence in *Malcolmia* seeds of an additional glucoside, containing (B) as the aglucone and located at the site of glucosylchirolin in the paper chromatogram, has been ruled out by chromatography on paper of the free isothiocyanates in chloroform (spray reagent: ammoniacal silver nitrate). Only cheirolin and (VII) were detectable, both travelling near the solvent front, whereas no trace of the expected ring compound (IV) was observed. The present results explain the appearance of two spots in the low R_F -region of the paper chromatogram of *Malcolmia*-thioureas, reported by Schultz and Wagner¹. One is attributable to cheirolinthiourea (A) whereas the other spot probably represents the artefact (B). In the present work it has been further established that our previously recorded occurrence of methyl isothiocyanate in *Malcolmia* seeds¹⁰ is incorrect.

The presence of glucose and sulphate in glucomalcolmiin has been verified by paper-chromatographic methods. The glucoside thence appears to be of the usual type. Unpublished results from this laboratory, supplemented by the conclusive work of Ettlinger and Lundeen¹¹ on the revised mustard oil glucoside structure, favour the following expression for the glucomalcolmiinate ion:



A detailed account of the present work will appear in this journal.

Microanalyses by Mr. P. Hansen of this laboratory. The work is part of investigations supported by *Statens Almindelige Videnskabsfond* (The Danish State Research Foundation) and *Carlsbergfondet* (The Carlsberg Foundation).

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A New Modification of Titanium Monoxide

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According to Ehrlich¹, titanium monoxide has a structure of sodium chloride type with randomly distributed vacancies in both the titanium and oxygen frameworks and a very broad range of homogeneity. Samples of this phase were prepared by melting mixtures of titanium metal and titanium dioxide (both of high purity) under argon atmosphere in an electric arc furnace. The following data, which are in fair agreement with Ehrlich's results, were obtained for a few of the compositions studied.

The unit cell dimensions were obtained from powder photographs taken in a Guinier focusing camera with strictly monochromatized $\text{CuK}\alpha_1$ radiation using potassium chloride as an internal standard.

The arc-melted samples were sealed in evacuated silica tubes, heated at 800°C for several days and quenched in water. The Guinier photographs of the preparations TiO_x ($x < 1$) then showed the pattern