

*iso*Thiocyanates XXV*. Methyl
4-*iso*Thiocyanatobutyrate, a New
Mustard Oil Present as a Glucoside
(Glucoerypestrin) in *Erysimum*
Species

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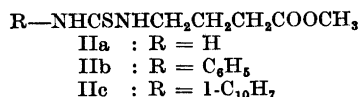
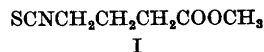
A few years ago it was noticed in this laboratory¹ that seeds of various species of the genus *Erysimum* (*Cruciferae*) contain a mustard oil glucoside which is different from those formerly recognized in Nature. A substantial seed sample of *Erysimum rupestre* DC., procured by cultivation of the plant on a larger scale**, has now made it possible to characterize and identify the new glucoside for which we wish to introduce the name *glucoerypestrin****.

According to paperchromatographic analysis, glucoerypestrin is accompanied by minor amounts of glucocheirolin in seed extracts of *E. rupestre*. The partly purified, glassy glucoside fraction yielded a crystalline product on acetylation. Fractional crystallization of this from 90% ethanol afforded a homogeneous specimen of *glucoerypestrin tetraacetate monohydrate*, decomposing at 188–190° (uncorr.) †; $[\alpha]_D^{23} -18.0^\circ$ (H₂O, *c* = 1.7). (Found ††: C 37.40; H 4.85; N 2.05; K 6.19. Calc. for C₂₀H₂₈O₁₅NS₂K·H₂O (643.7): C 37.32; H 4.70; N 2.18; K 6.07). The infra-red spectrum was of the usual type^{3,4} and did not provide much information as to structural details.

Deacetylation with 1.5 N methanolic ammonia, under carefully controlled con-

ditions, furnished the alkali-labile, paperchromatographically homogeneous glucoerypestrin which, in turn, was subjected to enzymic hydrolysis with myrosinase at pH 6.7. The resulting mustard oil, isolated by ether extraction or distillation at diminished pressure, yielded a crystalline, optically inactive *thiourea* (IIa), C₆H₁₂O₂N₂S, m.p. 93° (uncorr.) (Found: C 40.85; H 6.83; N 15.65; S 18.60; OCH₃ 17.58. Calc.: C 40.90; H 6.87; N 15.90; S 18.20; OCH₃ 17.61), on treatment with methanolic ammonia, again under strictly controlled conditions. The ultra-violet spectrum of the thiourea (in EtOH) was of the usual type (λ_{\max} 243 m μ (ϵ 12 600), λ_{\min} 223 m μ (ϵ 1 500)). A very strong band at 1 728 cm⁻¹ in the infra-red spectrum (in KBr) was suggestive of the presence of an ester grouping in the thiourea. On paper chromatography in water-saturated chloroform, the new thiourea travelled at a rate corresponding to an *R_F*-value of 0.65⁵.

Reaction of the *isothiocyanate* with aniline and 1-naphthylamine in methanolic solutions afforded the nicely crystalline *phenylthiourea* (IIb), C₁₂H₁₆O₂N₂S, m.p. 91° (uncorr.) (Found: C 57.00; H 6.39; N 11.01. Calc.: C 57.12; H 6.39; N 11.11), and (*1-naphthyl*)-*thiourea* (IIc), C₁₆H₁₈O₂N₂S, m.p. 132° (uncorr.) (Found: C 63.70; H 5.85; N 9.03. Calc.: C 63.56; H 6.00; N 9.27), respectively.



The cumulate data suggested that the new mustard oil was *methyl 4-isothiocyanatobutyrate* (I), an assumption fully verified through the following synthesis.

† It has been observed in this laboratory that the decomposition temperature of most acetylated *isothiocyanate* glucosides is very dependent on the rate of heating. The present value was determined in capillary tubes by inserting the sample at 140° and raising the temperature at a rate of 8° per min.

Polymorphism may also in some cases contribute to the widely varying values observed (M. G. Ettlinger, private communication).

†† A Karl Fischer titration gave: 2.85% H₂O. Calc. for the monohydrate: 2.80%.

* Part XXIV of this series: *Acta Chem. Scand.* 11 (1957) 184.

** We are much indebted to the *Botanical Garden of the University of Copenhagen* for the cultivation of this and other biennial *Erysimum* species.

*** This name has been preferred to the more consistent designation "glucoerysimin" in order to avoid confusion with the cardiac glucoside erisimin of similar provenance (cf. Ref.²).

