

Nb_5Se_4 , Nb_5Te_4 , and Nb_5Sb_4 ,⁹ while V_5Te_4 ¹⁰ has a monoclinic structure of similar dimensions.

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1. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
2. Selte, K. and Kjekshus, A. *To be published.*
3. Schäfer, H. and Dohmann, K.-D. *Z. anorg. u. allgem. Chem.* **299** (1959) 197.
4. Grønvold, F., Kjekshus, A. and Raaum, F. *Acta Cryst.* **14** (1961) 930.
5. Neuberger, M. C. *Z. Krist.* **A 93** (1936) 158.
6. Edwards, J. W., Speiser, R. and Johnston, H. L. *J. Appl. Phys.* **22** (1951) 424.
7. Grønvold, F., Haraldsen, H., Pedersen, B. and Tuftte, T. *To be published.*
8. Røst, E. and Gjertsen, L. *To be published.*
9. Furueth, S. and Kjekshus, A. *To be published.*
10. Grønvold, F., Hagberg, O. and Haraldsen, H. *Acta Chem. Scand.* **12** (1958) 971.

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The Mustard Oils of *Dentaria pinnata* Lmk.

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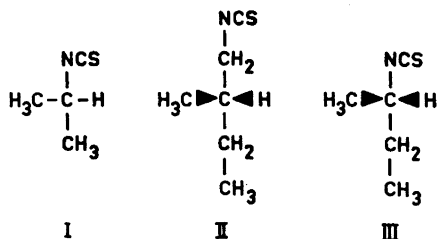
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Recently¹ the production of two volatile isothiocyanates subsequent to disintegration of rhizomes of the crucifer *Dentaria pinnata* Lmk. (*Cardamine pinnata* R.Br.) was reported. The major constituent was identified as isopropyl isothiocyanate (I),¹ a mustard oil deriving from the glucosidic precursor glucoputranjivin and repeatedly

encountered in higher plants (*cf.* Refs.^{1,2}). We now wish to report that the minor isothiocyanate consists of (*S*)-2-methylbutyl isothiocyanate (II), which was only recently established as a mustard oil of natural derivation when it was identified as a minor constituent of the isothiocyanate fraction of seed kernels of *Putranjiva Roxburghii* Wall. (*Euphorbiaceae*).³

The crude thiourea fraction (1.2 g), obtained from 250 g of rhizomes of *D. pinnata*,* was separated into isopropylthiourea and a minor amount of 'thiourea A' (0.25 g) by chromatography on cellulose powder as previously described.¹ Upon recrystallization, first from water and then from benzene:hexane, a pure specimen of 'thiourea A' was obtained as colourless needles, m.p. 73°, $[\alpha]_D^{21} + 9^\circ \pm 1^\circ$ (c 1.0, 96% EtOH). These data, combined with the established elementary composition $C_6H_{14}N_2S$, suggested its identity as (*S*)-1-(2-methylbutyl)-thiourea.³ This was further substantiated upon critical comparison (mixed melting point, paper chromatography, UV-, IR-, and NMR-spectroscopy) with an authentic specimen.³

Paper chromatography of the parent thioglucosides in rhizomes of *Dentaria pinnata* (70% methanolic extract) in butanol:ethanol:water (4:1:4) and butanol:pyridine:water (6:4:3) revealed, as expected, a major spot of glucoputranjivin and a smaller spot of glucojiaputin, the plant precursor of 2-methylbutyl isothiocyanate.³ When larger amounts of the glucoside mixture was applied to the paper, a trace of a third glucoside was noted at about the site of glucocochlearin, in keeping with the previously observed trace amounts of a thiourea, tentatively identified as a derivative of (*S*)-2-butyl isothiocyanate (III), in crude thiourea fractions of certain *Dentaria* collections.¹



* Part LII of a series of papers on naturally derived isothiocyanates. For part LI, see *Acta Chem. Scand.* **17** (1963) 2143.

* The employed material was collected in the field near Bessé en Chandesse, Puy de Dôme (France).

The co-occurrence of the glucosidic progenitors of isopropyl (I), 2-butyl (III), and 2-methylbutyl isothiocyanate (II) in *Putranjiva* and *Dentaria* probably reflects a common or related biosynthetic pathway of thioglycosides with branched side-chains. Since there is strong evidence that amino acids, or their keto acid analogues, may serve as precursors for the mustard oil glucosides,^{4,5} it appears likely that valine, or 2-oxo-isovaleric acid, functions as a natural precursor of glucoputranjivin. Likewise, isoleucine, or the corresponding keto-acid, can easily be visualized as progenitors of glucocochlearin, producing 2-butyl isothiocyanate on enzymic hydrolysis.

The biosynthesis of leucine from valine in higher plants has recently been shown to follow essentially the same path as in microorganisms, involving the participation of an acetate unit and proceeding through transformations similar to those operating in the citric acid cycle.^{6,7} Hence, it is surprising that a thioglucoside with the isobutyl side-chain has not yet been encountered in nature. Still, however, the formation of glucojiaputin from 2-amino-4-methylhexanoic acid, or the corresponding keto-acid, which, in its turn, may arise from the keto acid corresponding to isoleucine by a formally similar series of reactions, appears to be an attractive biogenetic hypothesis.

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1. Delaveau, P. G. and Fromageot, F. *Phytochem.* **2** (1963) 237.
2. Kjær, A. *Fortschr. Chem. Org. Naturstoffe* **18** (1960) 122.
3. Kjær, A. and Friis, P. *Acta Chem. Scand.* **16** (1962) 936.
4. Benn, M. H. *Chem. Ind. (London)* **1962** 1907.
5. Underhill, E. W., Chisholm, M. D. and Wetter, L. R. *Can. J. Biochem. Physiol.* **40** (1962) 1505.
6. Satyanarayana, T. and Radhakrishnan, A. N. *Biochim. Biophys. Acta* **56** (1962) 197.
7. Butler, G. W. and Shen, L. *Biochim. Biophys. Acta* **71** (1963) 456.

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Isolierung und Synthese von γ -Hydroxy-L-glutamin

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γ -Hydroxy-L-glutaminsäure ($\text{HO}_2\text{C}-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{CO}_2\text{H}$; I) wurde in diesem Laboratorium zum erstenmal aus *Phlox decussata* isoliert und chemisch charakterisiert.¹ Das Amid dieser neuen Aminosäure, γ -Hydroxy-L-glutamin ($\text{H}_2\text{NOC}-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{CO}_2\text{H}$; II), wurde von Fowden² in einer unbekanntenen Verbindung aus einer *Hemerocallis*-Art vermutet, da sie leicht zu (I) hydrolysiert wurde. Wir haben jetzt das Amid aus *Phlox* isoliert und aus (I) synthetisiert.

Auf Papierchromatogrammen von Extrakten frischer Pflanzen von *Phlox decussata* wurde in diesem Laboratorium vor einiger Zeit eine neue Aminosäure entdeckt,

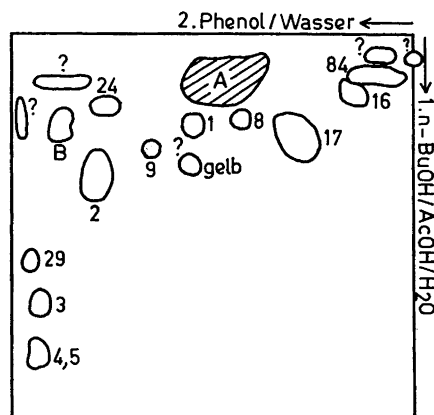


Abb. 1. Mit Ninhydrin nachweisbare Substanzen auf einem zweidimensionalen Papierchromatogramm eines Extraktes aus Samen von *Phlox decussata*.

A. γ -Hydroxy-L-glutamin

B. $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_6$ (4)

- | | |
|---------|------------------------------|
| 1. Gly | 9. Thre |
| 2. Ala | 16. Asp |
| 3. Val | 17. Glu |
| 4. Ileu | 24. Glu-NH ₂ |
| 5. Leu | 29. NH ₂ -Butters |
| 8. Ser | 84. γ -HO-Glu |