

Table 1. Total and hydrolyzable phosphorus of the thiamine compounds separated as in Fig. 1.

Hydrolyzable phosphorus is determined after heating the compounds in 2 N HCl at 100° for 10 min., after which all thiamine polyphosphates appear as thiamine monophosphate. Total phosphorus is determined after wet ashing. Thiamine is oxidized with alkaline ferricyanide to thiochrome, and the fluorescence estimated in a Beckman spectrophotometer with fluorescence attachment.

| Compound | hydrolyz- able P | P | R_F value |
|----------|---------------------|----------|--------------------|
| | total P | thiamine | |
| 1 | — | — | 0.87 |
| 2 | — | — | 0.79 |
| 3 | — | 1 | 0.77 |
| 4 | 1/2 | 2 | 0.68 |
| 5 | 2/3 | 3 | 0.55 |
| 6 | 3/4 | 4 | 0.46 |
| 7 | 4/5 | 5 | 0.36 |
| 8—10 | | >5 | 0.24, 0.21 0.16 |

8—10 have more than five phosphate groups per molecule of thiamine.

The described method has been used for isolating biological thiamine triphosphate from yeast¹², and was found satisfactory for this purpose. The R_F value, however, is somewhat lower than for the synthetic compound depending on the contamination with impurities from the yeast.

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isoThiocyanates XXIII*. I (—)-9-Methylsulphinylnonyl isoThiocyanate, a New Mustard Oil Present as a Glucoside (Glucosarabin) in *Arabis* Species

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In the course of a systematic investigation of glucosidically bound isothiocyanates in seeds of various species of the cruciferous genus *Arabis*, it was observed that a glucoside, obviously different from all compounds heretofore recognized in Nature, was present in, e. g., *Arabis alpina* L., a popular flower-garden subject. Paper chromatograms of seed extracts¹ indicated the presence of two glucosides both possessing R_F -values well above that of glucotropaeolin (cf. Ref.²).

When a purified, methanolic extract of a larger seed sample was subjected to enzymic hydrolysis in a buffered solution (pH 6.5), an ether-soluble isothiocyanate fraction was formed. Homogeneous, optically active, crystalline thioureas were obtained upon reaction of the isothiocyanate solution with various amines. The analytical data clearly indicated the composition $C_{11}H_{21}ONS_2$ for the parent mustard oil. The thiourea, recrystallized from ethyl acetate, had the m. p. 103.5—104.5° (uncorr.). (Found: C 50.00; H 9.13; N 10.45; S 24.40. Calc. for $C_{11}H_{21}ON_2S_2$: C 49.96; H 9.15; N 10.60; S 24.25), $[\alpha]_D^{24.5} -66^\circ$ (96% EtOH, $c = 2.1$). The infra-red spectrum in a KBr-wafer showed a characteristic strong band at 9.78 μ , attributable to a sulphoxide-grouping. The phenylthiourea separated from ethyl acetate in colourless prisms, m. p. 121—122° (uncorr.) (Found:

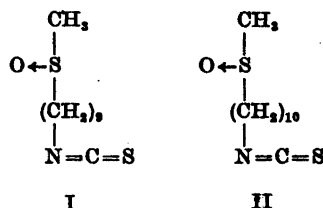
* Part XXII of this series: *Acta Chem. Scand.* **10** (1956) 1193.

C 60.00; H 8.24; N 8.21. Calc. for $C_{17}H_{28}ON_2S_2$: C 59.97; H 8.29; N 8.23, $[\alpha]_D^{25} -54^\circ$ (96 % EtOH, $c = 0.84$), whereas the *benzylthiourea* crystallized from acetone as thin, colourless needles, m. p. 119° (uncorr.) (Found: C 60.90; H 8.61; N 7.60; S 18.00. Calc. for $C_{18}H_{30}ON_2S_2$: C 60.97; H 8.53; N 7.90; S 18.09), $[\alpha]_D^{25} -64^\circ$ (MeOH, $c = 0.44$). Treatment of the latter derivative with silver nitrate furnished in high yield (79 %) the corresponding urea-derivative, separating from ethyl acetate in colourless needles, m. p. 120.5° (uncorr.) (Found: C 63.75; H 8.96; N 8.32; S 9.37. Calc. for $C_{18}H_{30}O_2N_2S$: C 63.87; H 8.93; N 8.23; S 9.47), $[\alpha]_D^{25} -56^\circ$ (96 % EtOH, $c = 0.95$). Reduction of the latter with zinc dust in HCl-containing ethanol proceeded in quantitative yield, and was accompanied by disappearance of the optical rotation and the characteristic sulphoxide-band in the infra-red spectrum. The reduced benzyl-urea separated from ethyl acetate as tiny, colourless needles, m. p. 99.5° (uncorr.) (Found: C 66.85; H 9.31; N 8.58. Calc. for $C_{18}H_{30}ON_2S$: C 67.01; H 9.38; N 8.69). Hydrogenolysis of this compound with W4-Raney nickel afforded a sulphur-free urea-derivative, which was proved to be identical with an authentic specimen of the previously unknown 1-benzyl-3-nonylurea, m. p. $99.0-99.5^\circ$ (uncorr.) (Found: C 73.75; H 10.23; N 10.05. Calc. for $C_{17}H_{28}ON_2$: C 73.88; H 10.21; N 10.14), synthesized by oxygen-sulphur exchange with silver nitrate from 1-benzyl-3-nonylthiourea, m. p. 75.5° (uncorr.) (Found: C 69.90; H 9.65; N 9.71. Calc. for $C_{17}H_{28}N_2S$: C 69.81; H 9.65; N 9.58), which was, in turn, produced from benzyl isothiocyanate and *n*-nonylamine.

The above sequence of reactions establishes the structure of the new *Arabis* mustard oil as a methylsulphinyl-nonyl isothiocyanate, the optical activity of which resides solely in the sulphoxide grouping. This fact, in conjunction with the close analogy to previously recorded natural representatives of the ω -methylthioalkyl isothiocyanates³⁻⁵, strongly suggest that the *Arabis* mustard oil has its methylsulphinyl-grouping located at the terminal carbon-atom*. The physical data, notably

the rotation values, are closely comparable to those of the homologous 1(-)-10-methylsulphinyldeoyl isothiocyanate (II) which we recently established⁶ as a naturally occurring species.

Therefore, we conclude that seeds of *Arabis alpina* L. contain 1(-)-9-methylsulphinyl-nonyl isothiocyanate (I) in the traditional glucosidic combination, for which we wish to introduce the name *glucoarabin*. On paper chromatography in various solvent systems, the presence of glucose and sulphate in glucoarabin has been established. A detailed account of this work, supplemented by confirmatory synthetic evidence for the structure (I), will form the subject of a forthcoming communication in this journal.



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* Note added in proof: This supposition has now been verified by synthesis.