

is not due to ClO_4^- and is perhaps due to $4f^{13}-4f^{13}5d$ transitions in Tm^{+3} . The three band groups in the range 290–260 $m\mu$ are equivalent to those found by Gobrecht¹³ in solid $\text{Tm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. The multiplet 3P is somewhat perturbed, the most intense band group 263–260 $m\mu$ presumably being due to $^3H_4-^3P_2$.

Since $[S = 1] = 0.02$ for 1I_6 in Tm^{+3} , the transition to this state is still of unusually high probability, if it corresponds to the 358–355 $m\mu$ band group. This is not certain, since the strong intermixing of the states with $J = 4$, viz. 3H_4 , 3F_4 and 1G_4 , may distribute two of the states to 685 and 355 $m\mu$. Bethe and Spedding^{1,14} choose the set of parameters $F_2 = 308 \text{ cm}^{-1}$, $F_4 = 71 \text{ cm}^{-1}$, and $F_6 = 0.86 \text{ cm}^{-1}$ by extrapolation from La^{+3} . If the possibility $^6 F_2 = 450 \text{ cm}^{-1}$, $F_4 = 90 \text{ cm}^{-1}$, and $F_6 = 9 \text{ cm}^{-1}$ is applied to Tm^{+3} with $\zeta = -1400 \text{ cm}^{-1}$, the identifications are changed somewhat. Fig. 1 gives the two sets of calculated wave numbers and the observed. But the question cannot be settled, before J can be determined from crystal field studies. The low intensity of the band at 462 $m\mu$ might support the identification with 1D_2 .

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isoThiocyanates XI.

4-Methylthiobutyl isoThiocyanate, a New Naturally Occurring Mustard Oil

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In a previous communication of this series¹ it was observed that seeds of *Eruca sativa* Mill. contain a volatile mustard oil which is paperchromatographically different from the known, naturally occurring isothiocyanates. We now wish to report on the identity of this mustard oil as 4-methylthiobutyl isothiocyanate (I), a compound first synthesized by Schmid and Karrer².



I



II R = H

III R = $\text{CH}_2\text{C}_6\text{H}_5$

From a larger seed sample, made available to us during the summer of 1954, we isolated the thiourea derivative (II) of the volatile isothiocyanate. The chemical structure was established by analysis and by comparison with a synthetic specimen of (II). Mixed melting point, paper chromatography in various solvents and infrared spectra left no doubt as to the identity of the two preparations.

In Nature (I) occurs as a yet uncharacterized glycoside for which we suggest the name *glucoerucin*. Its presence is disclosed upon paper chromatography according to Schultz and Gmelin³. These authors noticed in seeds of *Eruca sativa*

* Part of the present work was carried out during a visit by one of us (A.K.) to the Department of Physiological Chemistry of the University of Lund, Sweden.

two glucosides one of which was interpreted as belonging to their "SO-group" whereas the higher spot was attributed to glucotropaeolin. Upon paper chromatography of our crude thiourea we could exclude the presence of N-benzylthiourea. Consequently, the spot of presumed glucotropaeolin undoubtedly represented glucoerucin, the two being hardly distinguishable in the usual glucoside chromatography.

In older literature seeds of *Eruca sativa* are reported to contain an unidentified mustard oil⁴ whereas Mohammad and Ahmad⁵ tacitly assumed allyl isothiocyanate to be present in the seeds, known in India as "taramira" and of importance for the local oil production (jamba oil). Sudborough *et al.*⁶ isolated and purified the volatile mustard oil from *Eruca sativa* seeds and transformed it into a derivative, m. p. 83–84°, upon reaction with benzylamine. The composition $C_{19}H_{25}N_3S_3$ was reported for this derivative, apparently without suggestions as to its chemical structure. Therefore, we submitted authentic 4-methylthiobutyl isothiocyanate to reaction with benzylamine and obtained in good yield the expected N-(4-methylthiobutyl)-N'-benzylthiourea (III), $C_{13}H_{20}N_2S_2$, with m. p. 77–78°. We are inclined to believe that the Indian authors have been misled by inaccurate analyses inasmuch as the calculated figures for the two formulae do not deviate very much (see Experimental).

The characteristic radish-like smell and taste of (I) proved of much diagnostic value in our search for the new mustard oil in various species. The taste, in conjunction with paperchromatographic results, points to (I) as being widely distributed in the plant kingdom. So far, we consider 4-methylthiobutyl isothiocyanate to be present in seeds of *Iberis sempervirens* L., *Vesicaria utriculata* L. and *V. sinuata* Poir. *Matthiola annua* R.Br. and various species of *Cheiranthus* and *Brassica oleracea* L., as well as root materials of *Hesperis matronalis* L. and *Farsetia clypeata* R.Br. seem to contain (I) or closely related isothiocyanates.

It is pertinent here to refer to two previously recorded, naturally occurring isothiocyanates with the same carbon skeleton as that of (I). From seeds of *Erysimum Perofskianum* Fisch. et M., Schneider and Kaufmann⁷ isolated erysolin (IV), representing the sulphone corresponding to (I).



IV



V

Sulphoraphen, the characteristic isothiocyanate of radish seed (*Raphanus sativus* L.), was shown by Schmid and Karrer⁸ to possess the structure (V), differing from (I) in being unsaturated and containing a sulphoxide-grouping. It is interesting in this connection that Lavine⁹ demonstrated the intermediate formation of a "dehydro"-derivative in the oxidation of methionine to its sulphoxide.

The isolation and characterization of further isothiocyanates, structurally related to (I), will form the subject of future communications.

Experimental. Isolation and structure proof of (II). A preliminary argentometric analysis of the air-dried, fatty seeds of *Eruca sativa* Mill. showed a content of 1.4 % of volatile mustard oil, calculated as methylthiobutyl isothiocyanate.

A homogenized mixture of 25 g of seeds of *Eruca sativa* (fat-containing) and 500 ml of water was placed at 35° for 3 hours. The volatile constituents were removed by steam distillation, 500 ml of distillate being collected and transformed into thiourea upon standing for 24 hours with 100 ml of conc. ammonia. Evaporation *in vacuo* left a brownish, crystalline residue which was taken up in hot water, treated with a little charcoal, filtered and cooled. Colourless, nacreous plates separated and were recrystallized twice from water and once from ethyl acetate and petroleum ether before analysis. The yield was 0.25 g, m. p. 53° (Fisher-John's block), undepressed on admixture with an authentic specimen of N-(4-methylthiobutyl)-thiourea (II). (Found: C 40.71; H 7.87; N 15.62. Calc. for $C_6H_{14}N_2S_2$: C 40.42; H 7.91; N 15.72). Paper chromatography with chloroform as the solvent¹⁰ gave the R_{F_2} -value 0.97, whereas in the following systems: 1) pyridine : amyl alcohol : water (35:35:30); 2) heptane : 90 % formic acid : *n*-butanol (20:20:15)¹²; 3) heptane : 90 % formic acid : *n*-butanol (20:10:22)¹³, R_F -values of 0.82, 0.13 and 0.76 were found, respectively, for both the natural and the synthetic specimen. The infra-red spectra were determined in potassium bromide discs and proved to be completely identical.

Synthesis of (I) and (II). 4-Methylthiobutylamine (6.3 g), prepared by our previously

recorded method¹¹, was dissolved in water (45 ml), and a solution of thiocarbonyl chloride (6.1 g) in chloroform (50 ml) was added. To the vigorously shaken mixture 1.4 N NaOH (76 ml) was slowly added. After 0.5 hour, the chloroform layer was separated, dried and evaporated. Distillation *in vacuo* of the residue afforded 5.1 g (60 %) of the isothiocyanate, b.p. 136° at 12 mm, with a characteristic smell of radish. Ref.³ lists b. p. 130—140° at 9 mm.

The mustard oil was dissolved in ethanol, previously saturated with ammonia at 0°, and left at room temperature for 3 days. The solvent was removed and the residue recrystallized twice from water and once from chloroform and petroleum ether before analysis. M. p. 53° (Fisher-John's block). Ref.³ reports m. p. 55—56°. (Found: N 15.80; S 36.07. Calc. for $C_6H_{14}N_2S_2$: N 15.72; S 35.96).

N-(4-Methylthiobutyl) - *N'*-benzylthiourea (III). A solution of (I) (615 mg) and benzylamine (735 mg) in ethanol (3 ml) was kept at 40° for 18 hours. The solvent was then removed and the residue taken up in ether. The solution was shaken with small portions of 0.5 N HCl and water in order to remove the excess amine. During these operations the separation of the crystalline thiourea started (900 mg). Before analysis, the sample was recrystallized twice from 70 % ethanol and once from ethyl acetate and petroleum ether, m. p. 77—78° (water bath). (Found: C 58.25; H 7.55; N 10.45. Calc. for $C_{13}H_{20}N_2S_2$: C 58.15; H 7.51; N 10.44. Calc. for $C_{11}H_{18}N_2S_2$: C 58.28; H 6.44; N 10.81).

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The Calculation of Sedimentation Velocity from Experiments with Concentrated Mixtures

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A sedimenting boundary in the ultracentrifuge is by no means mathematically simple even in the case of a dilute solution of an ideal solute, as is seen from Faxén's¹ solution of the concentration function in a centrifuge cell. Additional complications, to which considerable attention has been paid, arise from thermodynamic and frictional effects, and from polydispersity. Thus the situation may be very complicated and is still more accentuated if the solution is concentrated *in a more hydrodynamic sense*², in which case the general form of the differential equation describing the course of the concentration change in the cell is intricate, even apart from effects of the non-constancy of the thermodynamical and frictional coefficients.

In such a situation it may sometimes seem more natural to use the concentration decrease in the middle of the sector-shaped cell than to use an analytical property of the boundary. This well-known possibility is evident from the considerations of Rinde^{3,4}, of Trautman and Schumaker⁵ and others.

In a part of the cell, not reached by the diffusion gradient regions at the top and bottom, the determination of the actual sedimentation coefficients of a two-com-