along [010] (Fig. 1 b) are given. The form of the organic part of the complex necessarily leads to overlapping in any projection. In the [010] projection overlapping of two amine molecules occurs. A difference synthesis — with subtraction of the bromine atoms — led to a chart in which the organic part was better resolved than in Fig. 1 a. All further details of the investigation — now practically finished — will be given in a forthcoming publication.

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isoThiocyanates XVII. o-Methoxybenzyl isoThiocyanate and some Derivatives

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Recently, Ettlinger and Lundeen \(^1\) isolated \(m\)-methoxybenzyl isoThiocyanate \((\text{II})\) from seeds of the American plant \(Lamannthus douglasii\) \(\text{R.Br.}\). Coincidentally, \(p\)-methoxybenzyl isoThiocyanate \((\text{III})\) was recognised in this laboratory as the glucocone of a glucoside, named glucouabretin, occurring in various species of the crucifer genus \(Aubrietia\) \(^4\). Both \((\text{II})\) and \((\text{III})\) were synthesised in the course of these investigations.

\[
\begin{align*}
\text{I} & \quad \begin{array}{c}
\text{OCH}_3 \\
\text{CH}_3\text{NCS}
\end{array} \\
\text{II} & \quad \begin{array}{c}
\text{OCH}_3 \\
\text{CH}_3\text{NCS}
\end{array} \\
\text{III} & \quad \begin{array}{c}
\text{CH}_3\text{O} \\
\text{CH}_3\text{NCS}
\end{array}
\end{align*}
\]

On this background it became of interest to prepare the heretofore unknown \(o\)-methoxybenzyl isoThiocyanate \((\text{I})\). The requisite \(o\)-methoxybenzylamine was obtained by Leuckart-reaction on \(o\)-methoxybenzaldehyde, according to Lewis \(^2\), but in somewhat better yield \((40 \%)\). The amine was converted into \((\text{I})\) by the convenient modification of Kuhn's synthesis which was recently introduced by Hodgkins and Ettlinger \(^4\), and used also for the synthesis of \((\text{II})\) \(^1\) and \((\text{III})\) \(^4\). Contrary to the latter two, which are liquids at ordinary temperature, the mustard oil \((\text{I})\) appeared as a low-melting solid. Its ultra-violet absorption spectrum in 2,2,4-trimethylpentane has a shoulder at about 255 \(\mu\) \((\text{ca. } 1550)\), maxima at 271 \(\mu\) \((2400)\) and 277 \(\mu\) \((2400)\) and minima at 236 \(\mu\) \((850)\) and 275 \(\mu\) \((2200)\). These data are in accord with those reported for the \(meta\)-isomeride \((\text{II})\) \(^4\), but differ considerably from the values determined for \((\text{III})\) in the same solvent, \textit{viz.} shoulders at about 250 \(\mu\) \((2300)\) and 285 \(\mu\) \((1900)\), maxima at 228 \(\mu\) \((1100)\) and 276 \(\mu\) \((1730)\) and a broad minimum around 269 \(\mu\) \((1550)\). In the wave-length region below 11 \(\mu\), the infra-red spectrum of \((\text{I})\) was comparable to that of \((\text{II})\), both displaying bands which deviated considerably from those reported for the \(meta\)-compound \(^4\).

For the purpose of characterisation, \((\text{I})\) was converted into \(N\text{-o-methoxybenzylthiourea}\) and \(N\text{-benzyl-N'\text{-o-methoxybenzylthiourea}}\) on reaction at room temperature with ammonia and benzylamine, respectively. The mustard oil reacted much more sluggishly than generally experienced for isoThiocyanates, a fact suggesting a certain steric influence of the neighbouring methoxy-grouping. In an attempt to enforce the reaction between \((\text{I})\) and benzylamine under more drastic conditions, amine exchange occurred, resulting in the formation of \(N\text{-iN'-dibenzyliothiourea}\). This reaction presents no novelty in thiourea chemistry. Recently, Ettlinger and Hodgkins \(^5\) observed the formation of thio-carbanilide in the reaction of \(N\text{-t-butyl-N'}\text{-phenylthiourea}\) with aniline in boiling benzene, and referred to further examples in the literature. In the present case, it seems likely that steric factors interfere with the usual thiamide-resonance, thus favouring the displacement of \(o\)-methoxybenzylamine. This view is supported by the infra-red spectra of the thioureas corresponding

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to (I), (II) and (III). Whereas the latter two exhibit normal "thiourea" absorption bands at 6.58 \( \mu \) and 6.57 \( \mu \), a displacement of the band to 6.58 \( \mu \) is noticed in the spectrum of o-methoxybenzylthiourea.

The three methoxybenzylthioureas were subjected to descending paper chromatography in water-saturated chloroform and the \( R_f \)-values \( 1 \). 1.14, 0.99 and 1.02 determined for the o-, m- and p-derivative, respectively. The high value of the ortho-compound indicates a rather pronounced chelation of this isomeric in solution. So far, the mustard oil (I) has not been encountered in nature.

Experimental. o-Methoxybenzylamine. o-Methoxybenzaldehyde (50 g) was treated with ammonium formate (200 g), and the mixture subsequently hydrolysed with conc. HCl (400 ml) as previously described, except that the reaction time was increased to 6 hours. The amine distilled at 114° at 14 mm, yield 20 g (40 %); the previously reported yield was 30%.

o-Methoxybenzyl isothiocyanate (I). The above amine (7.6 g) was converted to (I) by the method formerly used for preparing the corresponding m-derivative. The isothiocyanate distilled at 133° and 4 mm, and solidified to a colourless crystalline mass, m. p. 28°, yield 6.8 g (85 %). (Found: C 60.50; H 5.03; N 7.70; S 17.97. Calc. for \( C_9H_8ON_2S \): C 60.31; H 5.06; N 7.82; S 17.89.) The infra-red spectrum, determined in a KBr disc, showed bands at 3.33, 4.65 (very strong, N=C=S), 6.18, 6.57, 6.86, 6.90, 7.40, 7.70, 8.05 (v. s., aryl ether), 8.49, 8.87, 9.45, 9.70, 11.98 and 13.23 \( \mu \) (v. s.).

N-o-Methoxybenzylthiourea. A solution of (I) (600 mg) in ethanol (5 ml), saturated with dry ammonia, was set aside at room temperature for 4 days. The separated thiourea crystallised from water, containing a little ethanol, as colourless needles (361 mg), m. p. 122°. (Found: C 54.90; H 6.35; N 14.12. Calc. for \( C_9H_8ON_2S \): C 55.05; H 6.17; N 14.27.) The infra-red spectrum (KBr pellet) had prominent bands at: 2.93, 3.08, 6.04, 6.38, 6.64 (weak), 6.89, 7.34, 7.51 (w.), 7.68, 7.98, 8.54, 8.87, 9.50, 9.64, 9.86, 10.71, 11.91, 12.74, 13.14 (strong), 13.36 and 14.20 \( \mu \).

N-Benzyl-N'-o-methoxybenzyl-thiourea. An ether solution of (I) (600 mg) and benzylamine (2 ml) was kept at room temperature for 4 weeks. The solvent was removed and the oily residue treated with dilute HCl. After being kept at 0° for some hours the syrup crystallised. After two recrystallisations from 70 % ethanol, an analytical specimen was obtained as colourless needles (494 mg), m. p. 82.5°. (Found: C 66.90; H 6.38; N 9.86. Calc. for \( C_{13}H_{13}ON_2S \): C 67.10; H 6.34; N 9.78.)

In an attempt to enforce this reaction, (I) (500 mg) was heated to reflux for one hour in benzylamine (10 ml). Excess amine was removed in vacuo and the residue triturated with dilute HCl. The now crystalline product was recrystallised twice from ethanol, yielding colourless prisms (329 mg), m. p. 149—150°. (Found: C 70.30; H 6.21; N 10.64. Calc. for \( C_{13}H_{13}ON_2S \): C 70.29; H 6.29; N 10.93.) The composition, in conjunction with reported values for the m. p., e. g. 147—148°, indicates the identity of the reaction product as N,N'-dibenzylthiourea.

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