

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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*iso*Thiocyanates XVII. *o*-Methoxybenzyl *iso*Thiocyanate and some Derivatives

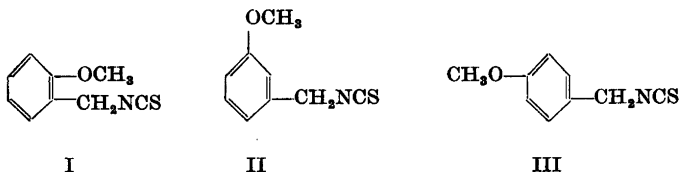
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Recently, Ettlinger and Lundeen¹ isolated *m*-methoxybenzyl *iso*thiocyanate (II) from seeds of the American plant *Limnanthes douglasii* R.Br. Coincidentally, *p*-methoxybenzyl *iso*thiocyanate (III) was recognised in this laboratory as the aglucone of a glucoside, named glucoaubrietin, occurring in various species of the crucifer genus *Aubrietia*². Both (II) and (III) were synthesised in the course of these investigations.

Ettlinger⁴, and used also for the synthesis of (II)¹ and (III)². Contrary to the latter two, which are liquids at ordinary temperature, the mustard oil (I) appeared as a low-melting solid. Its ultra-violet absorption spectrum in 2,2,4-trimethylpentane has a shoulder at about 255 $m\mu$ (ϵ ca. 1 550), maxima at 271 $m\mu$ (ϵ 2 400) and 277 $m\mu$ (ϵ 2 400) and minima at 236 $m\mu$ (ϵ 850) and 275 $m\mu$ (ϵ 2 200). These data are in accord with those reported for the *meta*-isomeride (II)¹, but differ considerably from the values determined for (III) in the same solvent, *viz.* shoulders at about 250 $m\mu$ (ϵ 2 300) and 285 $m\mu$ (ϵ 1 000), maxima at 228 $m\mu$ (ϵ 11 600) and 276 $m\mu$ (ϵ 1 730) and a broad minimum around 269 $m\mu$ (ϵ 1 550). In the wave-length region below 11 μ , the infra-red spectrum of (I) was comparable to that of (III), both displaying bands which deviated considerably from those reported for the *meta*-compound¹.

For the purpose of characterisation, (I) was converted into *N*-*o*-methoxybenzylthiourea and *N*-benzyl-*N'*-*o*-methoxybenzylthiourea on reaction at room temperature with ammonia and benzylamine, respectively. The mustard oil reacted much more sluggishly than generally experienced for *iso*thiocyanates, a fact suggesting a certain sterical influence of the neighbouring methoxy-grouping. In an attempt to enforce the reaction between (I) and benzylamine under more drastic conditions, amine exchange occurred, resulting in the formation of *N,N'*-dibenzylthiourea. This reaction presents no novelty in thiourea chemistry. Recently, Ettlinger and Hodg-



On this background it became of interest to prepare the heretofore unknown *o*-methoxybenzyl *iso*thiocyanate (I). The requisite *o*-methoxybenzylamine was obtained by Leuckart-reaction on *o*-methoxybenzaldehyde, according to Lewis³, but in somewhat better yield (40 %). The amine was converted into (I) by the convenient modification of the Kaluza-synthesis which was recently introduced by Hodgkins and

kins⁵ observed the formation of thio-carbanilide in the reaction of *N*-*t*-butyl-*N'*-phenylthiourea with aniline in boiling benzene, and referred to further examples in the literature. In the present case, it seems likely that sterical 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

to (I), (II) and (III). Whereas the latter two exhibit normal "thiourea" absorption bands at 6.58μ and 6.57μ , a displacement of the band to 6.38μ is noticed in the spectrum of *o*-methoxybenzylthiourea.

The three methoxybenzylthioureas were subjected to descending paper chromatography in water-saturated chloroform and the R_{F1} -values ⁷ 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 isomeride in solution. So far, the mustard oil (I) has not been encountered in nature.

Experimental *. *o*-Methoxybenzylamine. *o*-Methoxybenzaldehyde ⁸ (50 g) was treated with ammonium formate (200 g), and the mixture subsequently hydrolysed with conc. HCl (400 ml) as previously described ³, 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 ¹. The isothiocyanate distilled at 133° and 4 mm, and solidified to a colourless crystalline mass, m. p. 28° , yield 6.8 g (68 %). (Found: C 60.50; H 5.03; N 7.70; S 17.97. Calc. for C_9H_9ONS : 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 13.23μ (v. s.).

N-*o*-Methoxybenzylthiourea. A solution of (I) (500 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 $C_9H_{11}ON_2S$: 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 14.20μ .

N-Benzyl-*N'*-*o*-methoxybenzylthiourea. An ether solution of (I) (500 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 $C_{16}H_{18}ON_2S$: 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. $149-150^\circ$. (Found: C 70.30; H 6.21; N 10.64. Calc. for $C_{15}H_{16}N_2S$: C 70.29; H 6.29; N 10.93). The composition, in conjunction with reported values for the m. p., *e. g.* $147-148^\circ$, indicated the identity of the reaction product as *N*-*N'*-dibenzylthiourea.

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* Melting points are uncorrected and determined in capillary tubes in a water- or glycerol-bath.