

(leaves), *Ribes grossularia* (leaves), *Ribes nigrum* (leaves and berries), *Ribes rubrum* (berries), *Spinacia oleracea* (leaves).

Ferns. *Struthiopteris filicastrum* (leaves).

Mosses. *Polytrichum commune*.

Mushrooms. *Amanita muscaria*, *Amanita virosa*, *Boletus luteus*, *Boletus versipellis*.

1. Virtanen, A. I. and Ettala, T. *Suomen Kemistilehti* **B 29** (1956) 107.
2. Virtanen, A. I. and Hietala, P. K. *Acta Chem. Scand.* **9** (1955) 175.
3. Ellfolk, N. and Synge, R. L. M. *Biochem. J. London* **59** (1955) 523.
4. Linko, P. *Suomen Kemistilehti* **B 28** (1955) 96.

Received December 1, 1956.

**isoThiocyanates XXIV*. (+)-,
(-)** and **(+)- α -Methylbenzyl
isoThiocyanate**

ANDERS KJÆR

*Chemical Laboratory of the University
of Copenhagen, Denmark*

In connexion with other work in this laboratory pure specimens of the enantiomeric α -methylbenzyl isothiocyanates became desirable. The racemic mustard oil has been described by Dyson and George¹ as a slightly yellow liquid, b.p. 240–244°, without presentation, however, of additional physical constants or analytical data. Recently, Luskin *et al.*² reported the preparation of (\pm)- α -methylbenzyl isothiocyanate from α -methylstyrene and isothiocyanic acid, as well as from α -methylbenzylamine by the customary decomposition of its dithiocarbamate.

In the present work the method of Schmidt *et al.*³, involving hypochlorite oxidation of dithiocarbamates, was utilized for the synthesis of the racemic mustard oil, further characterized as its benzylthiourea-derivative. The pure, optically active α -methylbenzyl isothiocyanates, (I) and (II), were produced on reaction of the corresponding amines with thiocarbonyl chloride by a slightly modified variation of the described procedure¹. Again, the ben-

* Part XXIII of this series: *Acta Chem. Scand.* **10** (1956) 1358.

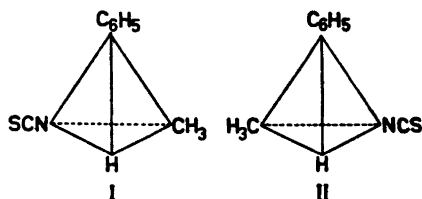


Fig. 1.

zylthiourea-derivatives were synthesized for the purpose of characterization. Attempts to prepare the simple thioureas by reaction of the mustard oils with ammonia did not result in crystalline products.

The symbols (I) and (II) are considered to represent the absolute configurations of (+)- and (-)- α -methylbenzyl isothiocyanate, respectively. The former derives from (-)- α -methylbenzylamine, the transformation of which into (+)-alanine has been effected previously⁴. The configurational relationship of this amino acid with (-)-glyceraldehyde has been established by Wolfrom *et al.*⁵ A unique three-dimensional representation of such molecules is required in consequence of the experimentally established absolute configuration of appropriate optically active molecules⁶. Adopting the recently proposed system for specification of absolute configuration⁷ the sequence of transformations mentioned above is: $S(-)$ -glyceraldehyde \rightarrow $S(+)$ -alanine \rightarrow $S(-)$ - α -methylbenzylamine \rightarrow $S(+)$ - α -methylbenzyl isothiocyanate (I).

Experimental. Melting points are uncorrected and determined in capillary tubes in a slowly heated bath. Rotations are measured in a 1 dm tube.

$S(+)$ - α -Methylbenzyl isothiocyanate (I). To (-)- α -methylbenzylamine (2.02 g, $[\alpha]_D^{24} -39.2^\circ$ (neat)), dissolved in water, was added a chloroform solution of thiocarbonyl chloride (1.91 g). A total of 33.4 ml of 1 N NaOH was added in small portions to the vigorously stirred mixture. The organic layer was separated, the aqueous phase extracted twice with fresh portions of chloroform and the combined organic extracts dried over sodium sulphate. After removal of the solvent, the isothiocyanate (1.12 g) distilled as a colourless oil, b.p. 126° at 16 mm, n_D^{25} 1.5802; $[\alpha]_D^{24} +17.5^\circ$ (c 9.8, CHCl_3). (Found: C 66.50; H 5.52; N 8.91. Calc. for $\text{C}_9\text{H}_9\text{NS}$: C 66.24; H 5.56; N 8.59).

A solution of the isothiocyanate (250 mg) and benzylamine (400 mg) in ether (5 ml) rapidly deposited the crystalline (*S*)-1-benzyl-3-(*a*-methylbenzyl)-thiourea. Two recrystallizations from aqueous ethanol afforded colourless needles (267 mg), m. p. 82.5°, $[\alpha]_D^{24} + 22.8^\circ$ (c 2.4, 96% EtOH). (Found: C 71.40; H 6.71; N 10.20. Calc. for $C_{16}H_{18}N_2S$: C 71.09; H 6.71; N 10.36). The UV-spectrum in ethanol displayed a maximum at 243 $m\mu$ (ϵ 14 800), a minimum at 238 $m\mu$ (ϵ 14 100), and strong end-absorption towards the short wave-length region.

R(-)-*a*-Methylbenzyl isothiocyanate (II). This mustard oil was prepared from (+)-*a*-methylbenzylamine ($[\alpha]_D^{24} + 38.9^\circ$ (neat)) in exactly the same way, b. p. 121° at 10 mm, n_D^{25} 1.5801; $[\alpha]_D^{24} - 17.3^\circ$ (c 10.0, $CHCl_3$). (Found: C 66.15; H 5.44; N 8.68. Calc. for C_9H_9NS : C 66.24; H 5.56; N 8.59).

Upon reaction of the mustard oil with benzylamine the (*R*)-1-benzyl-3-(*a*-methylbenzyl)-thiourea was obtained, m. p. 82.5°, $[\alpha]_D^{24} - 23.4^\circ$ (c 2.3, 96% EtOH). (Found: C 71.05; H 6.63; N 10.36. Calc. for $C_{16}H_{18}N_2S$: C 71.09; H 6.71; N 10.36).

(±)-*a*-Methylbenzyl isothiocyanate. Racemic *a*-methylbenzylamine was transformed into the corresponding isothiocyanate according to the directions given by Schmidt *et al.*³ for the preparation of analogous compounds. The yield of pure mustard oil, b. p. 122–123° at 12 mm, was 55%; n_D^{25} 1.5801. (Ref.²: b. p. 135–137°/23 mm, 133–134°/20 mm; n_D^{25} 1.5784, 1.5780).

The racemic 1-benzyl-3-(*a*-methylbenzyl)-thiourea separated in colourless needles from aqueous ethanol, m. p. 100°. (Found: C 71.35; H 6.62; N 9.98. Calc. for $C_{16}H_{18}N_2S$: C 71.09; H 6.71; N 10.36).

The oily thiourea, resulting from the reaction of the isothiocyanate with ammonia, was subjected to paper chromatography in water-saturated chloroform according to our usual method⁸. An R_{Fh} -value of 1.15 was determined, *i. e.* the compound migrates at a rate definitely higher than that of control spots of benzyl- (R_{Fh} 0.93) and the isomeric β -phenylethyl-thiourea (R_{Fh} 1.03).

Microanalyses were made in this laboratory by Mr. P. Hansen. The experimental assistance of Mr. R. Boe Jensen is acknowledged. Dr. Egelund Pedersen of this laboratory kindly furnished the optically pure *a*-methylbenzylamines employed in the present work, which is part of investigations supported by *Statens*

Almindelige Videnskabsfond (The Danish State Research Foundation) and *Carlsbergfondet* (The Carlsberg Foundation).

1. Dyson, G. M. and George, H. J. *J. Chem. Soc.* **125** (1924) 1705.
2. Luskin, L. S., Gantert, G. E. and Craig, W. E. *J. Am. Chem. Soc.* **78** (1956) 4965.
3. Schmidt, E., Zaller, F., Moosmüller, F. and Kammerl, E. *Ann.* **585** (1954) 230.
4. Leithe, W. *Ber.* **64** (1931) 2827.
5. Wolfrom, M. L., Lemieux, R. U. and Olin, S. M. *J. Am. Chem. Soc.* **71** (1949) 2870.
6. Bijvoet, J. M., Peerdeman, A. F. and van Bommel, A. J. *Nature* **168** (1951) 271.
7. Cahn, R. S., Ingold, C. K. and Prelog, V. *Experientia* **12** (1956) 81.
8. Kjær, A. and Rubinstein, K. *Acta Chem. Scand.* **7** (1953) 528.

Received December 11, 1956.

A Rapid Method to Determine Sulphur

ROLF OTTOSSON and
OLLE SNELLMAN

*Institute of Biochemistry, University of
Uppsala, Uppsala, Sweden*

In the method of determining sulphur in organic compounds used earlier here and described by Paulson¹, there were certain difficulties inherent in the combustion of the material. To facilitate the measurements and to obtain a better accuracy some modifications have been introduced in the measuring device and the oxidation of the material has been performed according to a modification of a method described by Schöniger². With this method, sulphur determinations have been performed during the last year and the reproducibility has been very good. The method seems to be both rapid and accurate.

Apparatus. For burning the material a 500 ml bottle with a ground stopper is used. A platinum wire is sealed into the stopper. The wire is 10 cm long and has a diameter of 1 mm. A loop is made on the wire according to Fig. 1.

The same kind of measuring apparatus is used as described by Paulson. The milliam-