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*iso*Thiocyanates XXXVI. * (+)-4-Methyl-2-oxazolidinethione, the Enzymic Hydrolysis Product of a Glucoside (Glucosisymbrin) in Seeds of *Sisymbrium austriacum* Jacq.

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Previous reports on the presence of *iso*thiocyanates and their parent glucosides in various species of the cruciferous genus *Sisymbrium* are discussed.

Paperchromatographic evidence for the presence of three new *iso*thiocyanate glucosides (A, B and C) in seeds of *Sisymbrium austriacum* Jacq. is presented. Upon enzymic hydrolysis the glucosides A and B afford substituted 2-oxazolidinethiones, probably originating in initially formed and spontaneously cyclizing β-hydroxysubstituted *iso*thiocyanates, different from those formerly recognized. Glucoside C, the structure of which has yet to be established, appears to furnish a non-cyclizing mustard oil.

By synthesis of its antipode, the heterocyclic enzymic hydrolysis product produced from glucoside A is proved to be the hitherto unknown (+)-4-methyl-2-oxazolidinethione (V) of established absolute configuration. This represents the first example of a naturally derived 4-substituted 2-oxazolidinethione. The nature of glucoside B is being investigated at the present.

Certain configurational and biogenetical implications are briefly discussed.

The cruciferous genus *Sisymbrium* is of nearly cosmopolitan distribution and comprises about 80 individual species, a few of which have formerly been quoted as sources of *iso*thiocyanate glucosides. Thus, Lepage [1] in 1846 reported on the presence of a mustard oil-producing glucoside in seeds of *S. officinale* Scop.** A few years ago, Schultz and Gmelin [2] recorded paperchro-

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** Another species cited by the same author as a glucoside source, *S. cheiranthoides* Et. et W., is more commonly recognized as *Erysimum cheiranthoides* L.

Like several cruciferous genera that of *Sisymbrium* represents a far from well-defined collection of taxa. Numerous species, at one time regarded as belonging to the genus *Sisymbrium* have subsequently been transferred to other genera and *vice versa*, a fact which calls for attention in chemotaxonomic considerations.

matographic evidence for the presence of sinigrin in fresh plants of *S. officinale* and *S. Loeselii*, a finding which was later supplemented by data indicating the occurrence of the same glucoside also in seeds of the former species [3,4]. Paper chromatography of seed material of *S. strictissimum* revealed a content of two glucosides, tentatively interpreted [5] as glucoputranjivin * and glucocochlearin. In this laboratory the latter assignment was supported by independent studies of volatile mustard oils liberated from seed of *S. strictissimum* L., indicating their identity as *iso*propyl and *sec.*-butyl *iso*thiocyanate [6]. In seed material of the common weed, *Sisymbrium sophia* L.**, the presence of sinigrin was established by formation of paperchromatographically identified N-allylthiourea subsequent to enzymic hydrolysis and ammonia treatment of the liberated mustard oil. Fresh plants of *S. luteum* (Maxim) O. E. Schulz, on the other hand, were found to be devoid of volatile mustard oils [6].

In the course of systematic studies in this laboratory on the distribution of *iso*thiocyanate glucosides in a large number of plant species, the presence of three strong glucoside spots were noticed upon paper chromatography of a methanolic seed extract of *Sisymbrium austriacum* Jacq.*** Paperchromatographic experiments, conducted in various solvent systems and in the presence of several authentic reference glucosides, suggested that the three compounds (A, B and C) were different from all mustard oil glucosides previously encountered in Nature (*cf.* Refs. [7,8]). In butanol:ethanol:water (4:1:4), glucoside A migrated slowly, corresponding to an R_B-value [4] of 0.34, whereas compound B possessed an R_B-value of 0.59. The third glucoside (C) was much more lipophilic (R_B 1.67). Two additional, but weaker spots, located between compounds B and C, were possibly attributable to glucoputranjivin and glucocochlearin, two glucosides affording *iso*propyl and *sec.*-butyl *iso*thiocyanate on enzymic hydrolysis, respectively. Solutions of the individual glucosides, A, B and C, were obtained by elution of the appropriate horizontal zones from paper band chromatograms developed in the same solvent system and subjected to enzymic hydrolysis with a cell-free myrosinase preparation. It appeared that both glucoside A and B afforded Grote-positive hydrolysis products directly, whereas compound C underwent fission to a component which gave positive Grote-reaction only after treatment with ammonia. These observations, supplemented with characteristic UV-absorption patterns of the hydrolysis products derivable from A and B, suggested that the latter belonged to the group of 2-oxazolidinethiones, formerly recognized as cyclized products of initially produced β-hydroxy-substituted *iso*thiocyanates (*cf.* Refs.[7,8]). Glucoside C, in contrast, appeared to yield a reasonably stable mustard oil which was transformed into its thiourea derivative on treatment with ammonia. Upon paper chromatography, with the upper layer of the solvent system benzene:heptane:water (9:2:9) as the mobile phase, the supposable 2-oxazolidine-

* This glucoside was differently interpreted in Ref. [3], *viz.* as sinigrin.

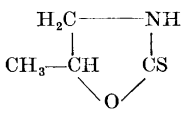
** This plant is now more commonly recognized as a species of the genus *Descurainia*, *viz.* *D. sophia* (L.) Webb; *cf.* foot note on p. 1575.

*** This species is indigeneous to the mountain areas of Middle Europe. The authenticity of the seed material employed in the present studies has been controlled through the courtesy of the *Botanical Garden of the University of Copenhagen* by sowing and subsequent botanical determination of the resulting plants.

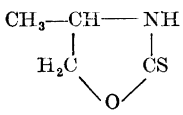
thiones derived from glucoside A and B ('THIOX A' and 'THIOX B') migrated at a rate corresponding to an R_{Ph}-value * of 0.27 and 0.62, respectively. These figures, as well as direct chromatography with various 2-oxazolidinethiones as reference substances, indicated that both compounds, and hence the glucosides A and B, were different from all previously encountered natural compounds. The present communication reports on the structural elucidation of 'THIOX A' and hence glucoside A for which the name *glucosisymbrin* is proposed. The chemical identity of the glucosides B and C will form the subject of forthcoming papers.

In a preliminary isolation experiment a small specimen of pure, crystalline 'THIOX A' was secured after a rather long and tedious series of purification steps (see Exptl. Part). The crystalline product proved very helpful as seeding material for a subsequently obtained portion of 'THIOX A', isolated from a larger sample (220 g) of seeds of *Sisymbrium austriacum* Jacq.** The seed material was finely ground, defatted with carbon tetrachloride and thoroughly extracted with 70 % methanol. After removal of impurities with lead acetate, the resulting solution was enzymically hydrolyzed with myrosinase, and the ether-extractable reaction products purified by means of alumina to give an almost colourless oil (1.6 g). After extraction with water and lyophilization of the aqueous solution an oil remained which on seeding with the previously obtained, crystalline specimen of 'THIOX A' yielded a portion of crystals (133 mg) which was repeatedly recrystallized from various solvents to yield an analytically pure sample of chromatographically homogeneous 'THIOX A', m.p. 64°, which proved to be *dextro*rotatory in ethanol solution.

The analytical composition, C_4H_7ONS, in conjunction with the ultra-violet and infra-red spectra, strongly suggested that 'THIOX A' was a methyl-substituted 2-oxazolidinethione. Of these, both the (±)-5-methyl-derivative (I) [9,10] (m.p. 72-73°[9], 74.5-75.0°[10]) and the racemic 4-methyl-2-oxazolidinethione [11]



I



II

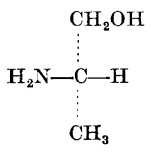
(II) (m.p. 75-76°) had been formerly described. Previous experience within this series has indicated that the racemic compounds often melt higher than the enantiomorphs and deviate considerably from the latter in their infra-red spectra. Careful paper chromatography in benzene:heptane:water (9:2:9), however, showed that 'THIOX A' travelled at a slightly, but consistently, higher rate than a specimen of racemic (I), prepared in this laboratory. Again, it was noticed that in the same solvent system (±)-4-vinyl-2-oxazolidinethione

* *i.e.* the ratio between the distances travelled by the said substance and (±)-5-phenyl-2-oxazolidinethione on the same chromatogram.

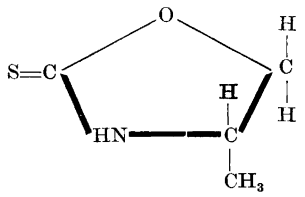
** The seed material employed was produced by cultivation on a larger scale through 1957—58 in the *Botanical Garden of the University of Copenhagen*. The authors are very grateful to the Garden for its valuable assistance.

migrated slightly faster than the (±)-5-isomeride *. This fact, in conjunction with the observation that 'THIOX A' compared with the 4-vinyl-isomeride, produced more blue and stable colours with Grote's reagent than the 5-methyl- and 5-vinyl-substituted ring compounds, supported the belief that 'THIOX A' was, in fact, one of the stereoisomeric 4-methyl-2-oxazolidinethiones (II). Accordingly, the correctness of this assumption was tested by the following synthetic approach.

The 2-amino-alcohol required for the synthesis of one of the optically active 4-methyl-2-oxazolidinethiones (II) is either (+)- or (−)-2-amino-1-propanol (alaninol). Consequently, natural L(+)-alanine was reduced with lithium aluminium hydride in tetrahydrofuran as described by Vogl and Pöhm [12] to give (+)-2-amino-1-propanol (III) in 78 % yield. The amino-alcohol was characterized as its acid oxalate [12,13], whereas a neutral oxalate with the reported m.p. [12–14] could not be obtained despite many attempts, possibly on account of the formation of unresolvable solid solutions of the acid and neutral salts.

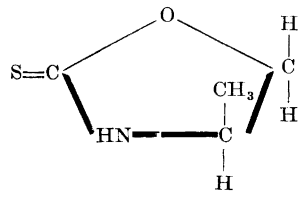


III



(−)

IV



(+)

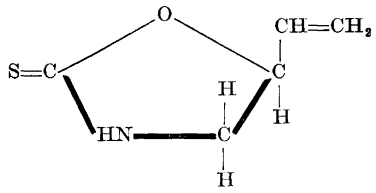
V

L-Alaninol (III) was then treated with thiocarbonyl chloride and triethylamine in chloroform solution to give an oil which was induced to crystallize only after seeding with 'THIOX A'. As shown below the synthetic compound constitutes, in actuality, the antipode of 'THIOX A'. Hence, the successful seeding should probably be attributed to a case of oriented overgrowth on crystals of intermediately formed traces of the racemic compound (*cf. e.g.* Ref.[15]). The synthetic preparation was indistinguishable from 'THIOX A' on paper chromatography and furthermore possessed the same elementary composition and melting point as well as ultra-violet and infra-red spectra as 'THIOX A'. Its optical rotation, however, was similar in magnitude *but opposite in sign* to that of the naturally derived, *dextro*rotatory 2-oxazolidinethione. The enantiomorphous relationship between the two compounds further appeared from the fact that a mixture of equal amounts of the two separated from methanol as the racemic 4-methyl-2-oxazolidinethione (II) possessing the m.p. 75—76°, in agreement with the value previously reported [11]. Not unanticipated, the infra-red spectrum of the latter deviated considerably from that of the enantiomers (Fig. 1).

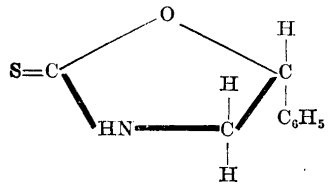
* Synthetic specimens of the vinyl-substituted 2-oxazolidinethiones were kindly supplied by Dr. M. G. Ettlinger of the Chemistry Department, Rice Institute, Houston, Texas, U.S.A.

The above synthetic route, departing from configurationally known (+)-alanine, immediately establishes the absolute configuration (IV) for the *levo*rotatory, synthetic product *. Consequently, (V) depicts the absolute configuration for the naturally derived, *dextro*rotatory 4-methyl-2-oxazolidinethione ** ('THIOX A').

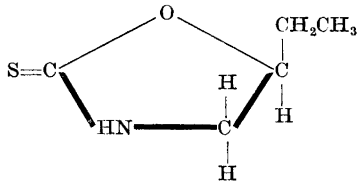
The new 2-oxazolidinethione represents the first example of a 4-substituted derivative of natural provenance. Previously reported compounds of this type include 5,5-dimethyl-[17], (−)-5-vinyl-[18] and (−)-5-phenyl-2-oxazolidinethione [19]. To the last two of these we have assigned the absolute configurations (VI)[20] and (VII)[21], respectively. Furthermore, it has been pointed out [20] that the synthetic, *levo*rotatory 5-ethyl-derivative possesses the absolute configuration (VIII).



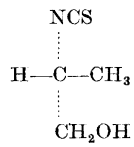
VI



VII



VIII



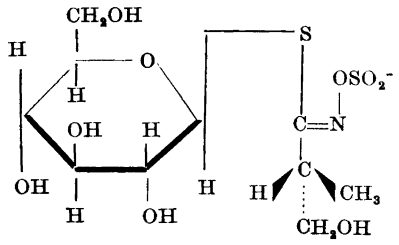
IX

It is of interest to note that exchange of a vinyl- or ethyl-grouping in 5-position with a methyl-substituent in 4-position on the same side of the ring plane, results in a change in sign of rotation, whereas no such alteration accompanies the exchange of the 5-phenyl- with the 4-methyl-substituent. It is expected that further insight into the relationship between configuration and optical rotation in the present class of substances will be obtained from rotatory dispersion studies at present under way.

On the very likely premises that *dextro*rotatory 4-methyl-2-oxazolidinethione (V) results from spontaneous intramolecular cyclization of an initially produced β-hydroxy*iso*propyl *iso*thiocyanate, the above determination of the absolute configuration of (V) immediately establishes the spatial arrangement (IX) around the asymmetric carbon atom of the latter.

* *(S)*-4-Methyl-2-oxazolidinethione in the specification system of Cahn *et al.*[16]

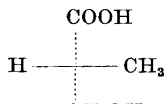
** *(R)*-4-Methyl-2-oxazolidinethione in the same system.



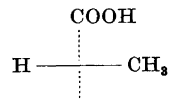
X

Although no experimental proof is available, it appears likely that the configuration depicted in (IX) is that prevailing also in the side-chain of the parent glucoside glucosisymbrin which, therefore, should be formulated as (X), in accordance with the revised general glucoside structure forwarded by Ettlinger and Lundeen [22]. In an analogous case, *viz.* that of glucocochlearin which on enzymic hydrolysis affords (+)-2-butyl *iso*thiocyanate, the same authors [22] suggested that the intramolecular rearrangement accompanying the enzymic reaction would probably proceed with retention of configuration as a consequence of the reaction mechanism involved.* This view has indirectly received some support from the establishment in this laboratory of the same absolute configuration of naturally derived (+)-2-butyl mustard oil as that prevailing around the β-carbon atom of natural *iso*leucine [23] which may be envisaged as biogenetically related with glucocochlearin.

The structural elucidation of glucosisymbrin raises the question as to its biogenetic relationship with glucoputranjivin, the glucoside producing *iso*propyl *iso*thiocyanate and present in *inter alia* several *Sisymbrium* species [24]. It appears likely that one may be derivable from the other by enzymic oxidation or reduction, a possibility which, however, needs further clarification. A reaction sequence analogous to the well-established valine catabolism in animal tissues, proceeding *via iso*butyryl-CoA and β-hydroxy*iso*butyric acid [25], may conceivably be operative also in higher plants. In this connexion attention should be drawn to the establishment by Suchý *et al.*[26] of one of the enantiomorphous β-hydroxy*iso*butyric acids as the acid moiety of the sesquiterpene lactone arctiopicrin.



XI



XII

* *Added in proof.* Provided this assumption proves tenable, acid hydrolysis of glucosisymbrin, analogous to that recorded for other *iso*thiocyanate glucosides by Ettlinger and Lundeen [22], should afford optically active β-hydroxy*iso*butyric acid possessing the absolute configuration (XI).

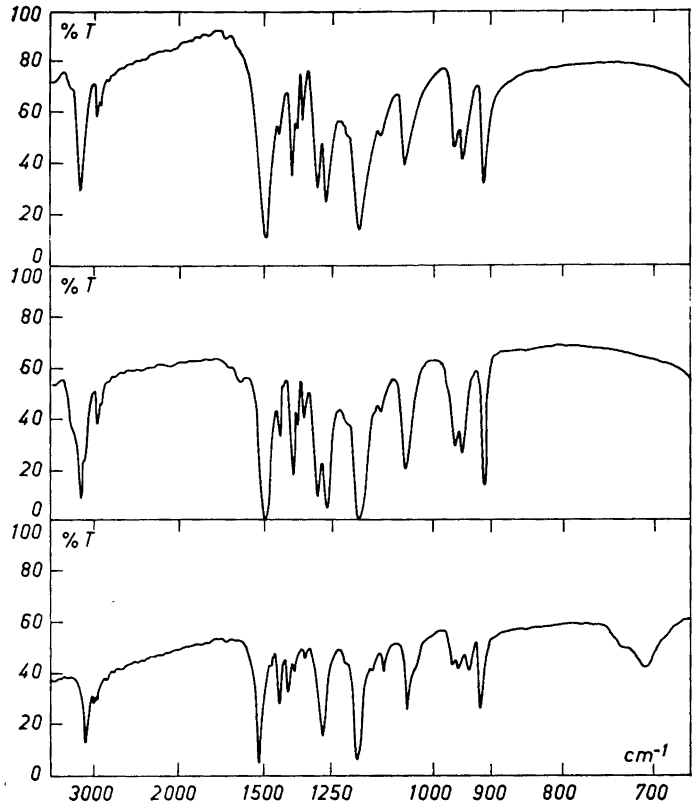


Fig. 1. Infra-red spectra, determined in KBr pellets. Upper curve: naturally derived, *dextro*rotatory 4-methyl-2-oxazolidinethione ('THIOX A'). Middle curve: synthetic, *levo*rotatory enantiomer of the same substance. Lower curve: racemic 4-methyl-2-oxazolidinethione.

Very recently, Asen *et al.*[27] isolated (−)-β-amino*iso*butyric acid from bulbs of *Iris tingitana*. The determination by Balenović and Bregant [28] of the absolute configuration (XII) for *levo*-rotatory β-amino*iso*butyric acid establishes identical configurations around the asymmetric β-carbon atom of (XI) and (XII), both derivable from plant sources. Again, it appears interesting that methylmalonic acid semialdehyde, a product on the catabolic pathway of β-hydroxy*iso*-butyric acid in mammalian tissues, has been shown to undergo a reversible transamination with glutamate to furnish β-amino*iso*butyric acid [25].

EXPERIMENTAL

All melting points reported are uncorrected and, if not otherwise stated, determined in capillary tubes in a slowly heated bath. Rotations are measured in a 1 dm tube. Infra-red spectra are determined in KBr pellets on a Perkin-Elmer "Infracord" instrument.

Exploratory paperchromatographic investigations. A glucoside solution, prepared by boiling a finely ground seed sample of *Sisymbrium austriacum* Jacq. (0.5 g) with 70 % methanol (5 ml), was chromatographed descendingly on Schleicher and Schüll paper

No. 2243b together with a reference sample of glucotropaeolin, with the upper layer of the solvent system *n*-butanol:ethanol:water (4:1:4) as the mobile phase. Three spots were easily distinguishable upon dipping the chromatogram through methanolic silver nitrate, and were attributed to the glucosides A, B and C with R_B-values [4] of 0.34, 0.59 and 1.67, respectively. In *n*-butanol:pyridine:water (6:4:3) the R_B-values were: 0.65, 0.80 and 1.19. That the three spots in this solvent system also represented the glucosides A, B and C in the same sequence was proved by chromatographing the individual compounds, obtained by elution with water of the appropriate zones from chromatograms run as bands in the neutral system, in the pyridine solvent.

To the individual aqueous eluates, each of a volume of 1 ml, were added a phosphate buffer (pH 6.7, 1/15 M, 0.25 ml) and 3 drops of a cellfree myrosinase solution. After 1 h at room temperature, the three solutions were extracted with chloroform. The extracts derivable from the glucosides A and B yielded a strong blue colour with Grote's reagent in contrast to that originating from compound C. The first two solutions, together with a reference solution of (±)-5-phenyl-2-oxazolidinethione [19], were subjected to descending chromatography on Whatman paper No. 1 with the upper layer of the solvent system benzene:heptane:water (9:2:9) as the mobile phase. On spraying with Grote's reagent two blue spots were observed, derivable from glucoside A and B and possessing R_{Ph}-values of 0.27 and 0.62, respectively. Neither of these spots could be assigned to any previously encountered product of natural origin but both exhibited the same characteristic UV-spectrum in ethanol (λ_{max} 243 mμ, λ_{min} 219 mμ), very similar to the pattern previously registered for 2-oxazolidinethiones. After treatment with a chloroform solution of dry ammonia the reaction product of glucoside C yielded a Grote-positive derivative, travelling near the solvent front in water-saturated chloroform.

Preliminary isolation experiment. Dry seeds (220 g) of *Sisymbrium austriacum* Jacq. were covered with carbon tetrachloride (500 ml) and finely ground in a Waring blendor without cooling. The process was repeated with fresh solvent (500 ml) and the suspension was finally refluxed for 1 h. The filtered, defatted seed powder (155 g) was then extracted with three 1 l portions of 70 % methanol. After filtration through Celite, the extract was concentrated *in vacuo* to a sticky brown mass, which was dissolved in the lower phase (200 ml) of the solvent system employed for paper chromatography (*n*-butanol:ethanol: water, 4:1:4). The solution was introduced into No. 1 of a total of 11 separatory funnels, all preloaded with the corresponding upper phase (200 ml in each funnel). The crude mixture was now distributed in a counter-current manner through all vessels. Troublesome emulsion formation was overcome by centrifugation before the next following transfer. Paper chromatography indicated that glucoside C was primarily concentrated in the separatory funnels No. 5—8, supplemented with the upper phase of funnel No. 9, whereas the lower layer of the latter plus the vessels No. 10 and 11 contained essentially a mixture of glucoside A and B, contaminated with considerable quantities of an almost black syrup. To a solution of the crude fraction containing A and B in water (400 ml), a 10 % solution of basic lead acetate was added until the separation of a yellow-brown precipitate ceased (a total of *ca.* 120 ml). The latter was removed by filtration through Celite, and hydrogen sulphide was introduced into the filtrate to precipitate excess lead ions. The filtered solution was concentrated *in vacuo* to an almost colourless syrup. This was redissolved in water (400 ml), equal volumes (20 ml) of 1/15 M solutions of primary and secondary potassium phosphate were added, followed by 25 ml of a myrosinase solution. After having been kept for 3 h at room temperature, the solution was extracted with four 300 ml portions of ether which were pooled and dried. The residual yellow oil (1.3 g) was dissolved in benzene (20 ml) and rapidly washed through a small column of alumina (4 × 0.8 cm) with additional benzene, until the Grote-reaction became negative. This procedure yielded an almost colourless oil (1.1 g) which was thereafter subjected to careful adsorption chromatography on neutral alumina (column diameter: 2.2 cm, height of packing: 25 cm) with 1 % of methanol in benzene as the eluant. Fractions of 5 ml were taken; the Grote-positive constituents were located in fractions No. 147—178. Paper chromatography revealed that the fractions No. 147—155 contained exclusively 'THIOX B', No. 170—181 solely 'THIOX A' and the intermediate fractions a mixture of the two.

The 'THIOX A'-fractions were taken to dryness, redissolved in pure benzene and a small insoluble residue discarded. The oily product (134 mg) was subjected to fractional sublimation at 0.2 mm Hg. At 40° (bath temperature) an oily fraction distilled and was discarded. The bath was slowly raised to 80° when a deposit of crystalline material

(34 mg) on the 'cold finger' was noticed. The somewhat oily preparation was recrystallized from anhydrous ether at low temperature to give thin colourless prisms, $[\alpha]_D^{24}$ +22.1° (*c* 0.85, MeOH). The recovered material from the rotation determination, supplemented by a fraction of crystalline material obtained directly from fraction No. 166–169 on seeding, was purified by repeated recrystallizations from a mixture of benzene and petroleum ether to give a pure specimen (16.8 mg) of 'THIOX A' as colourless prisms with m. p. 64–65°.

Isolation of (+)-4-methyl-2-oxazolidinethione. Another seed portion (220 g) was processed exactly as described above with the sole exception that the cumbersome countercurrent extraction was omitted. The lead-purified glucoside extract was enzymically hydrolyzed as described in the foregoing. Again, yellow contaminants were partially removed from the ethereal extract by means of a small alumina column. The residue was treated with water (80 ml) causing a considerable amount of a gummy product (polymerisation?) to separate. The latter was thoroughly washed and the aqueous solution lyophilized to give a colourless oil. This was taken up in ether (5 ml), the solution was cooled to 0° and seeded with previously obtained crystals of 'THIOX A' when the separation of crystalline, but slightly oily 'THIOX A' (133 mg) started. Two recrystallizations from a mixture of benzene and petroleum ether (1:1), followed by another two from anhydrous ether afforded a pure specimen of 'THIOX A' (17 mg), m. p. 63.5°–64.5°. (Found: C 41.06; H 6.15; N 11.81. Calc. for C_4H_7ONS: C 40.99; H 6.02; N 11.95.)

An additional 9.6 mg of the same purity was secured by repeated recrystallizations of the mother liquor preparation, m. p. 64°; $[\alpha]_D^{24}$ +21.1° (*c* 0.72, EtOH). The infra-red spectrum is reproduced in Fig. 1.

Synthesis of (−)-4-Methyl-2-oxazolidinethione. L-Alanine (8.01 g, $[\alpha]_D^{28}$ +14.7° (*c* 7.0, 1 N HCl)) was reduced by means of a solution of $LiAlH_4$ (10.5 g) in tetrahydrofuran (120 ml), according to the procedure described by Vogl and Pöhm [12]. Distillation *in vacuo* afforded L(+)-alaninol in 78 % yield as a colourless oil, b. p. 67°/8 mm, n_D^{25} 1.4487, $[\alpha]_D^{25}$ +22.0° (*c* 6.45, 96 % EtOH). Literature values: b. p. 78–80°/12 mm, $[\alpha]_D^{17}$ +20.1° (alcohol) [13]; b. p. 85°/10 mm, $[\alpha]_D^{17}$ +20.3° (EtOH) [12].

The amino-alcohol was characterized as its acid oxalate, produced by mixing hot solutions of the former and of oxalic acid dihydrate (20 % excess). The salt separated from ethanol in colourless needles, m. p. 151°, $[\alpha]_D^{26}$ +13.8° (*c* 2.5, H_2O). (Found: C 36.35; H 6.56; N 8.55. Calc. for C_3H_9ON, $C_2H_2O_4$: C 36.35; H 6.71; N 8.48). Literature values: m. p. 140–141°[13]; m. p. 141–142°[12]; (no rotation data reported). Repeated attempts to prepare the formerly described neutral oxalate proved unsuccessful, despite variations in the procedure and amounts of reactants employed. Beautiful, crystalline salts were obtained with the reported rotation value ($[\alpha]_D^{23}$ +18.0° (*c* 2.3, H_2O)) but invariably melting over a wide temperature range (*e. g.* 125–140°).

To a cooled and stirred solution of thiocarbonyl chloride (1.16 g) in chloroform (15 ml), another solution of L(+)-alaninol (0.65 g) and triethylamine (1.76 g) in chloroform (10 ml) was added in the course of 10 min. Shortly after the addition of the amino-alcohol was completed the thiophosgene smell disappeared, and the yellow solution was evaporated to dryness *in vacuo*. Repeated extractions with ether removed the Grote-positive product from triethylamine hydrochloride. The concentrated extract was decolourized with Norite, filtered and again concentrated to a final volume of 7 ml. Only after addition of seed crystals of 'THIOX A' a crystalline precipitate appeared. Next day, the product (346 mg) was recrystallized thrice from ether to give an analytical specimen (180 mg) of *(−)-4-methyl-2-oxazolidinethione*, m. p. 65°, $[\alpha]_D^{26}$ −22.9° (*c* 1.12, 96 % EtOH). (Found: N 11.77; S 27.42. Calc. for C_4H_7ONS: N 11.95; S 27.36.) The infra-red spectrum of the synthetic preparation was indistinguishable from that of 'THIOX A' (Fig. 1). The latter, therefore, is the antipodal (+)-4-methyl-2-oxazolidinethione.

Racemate formation. Synthetic material (2.36 mg) was mixed with 'THIOX A' (2.36 mg) and the solid dissolved in a few drops of methanol. The residual oil crystallized on scratching, and the racemate was recrystallized from two drops of water to give thin, colourless needles, m. p. 75.5–76.0° (microscope). Literature value: m. p. 75–76°[11].

The infra-red spectrum, which is conspicuously different from that of the optically active forms, is presented in Fig. 1.

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