

Short Communications

Steric Relations between α -(1-Naphthyl)-propionic Acid and α -(3-Thianaphthenyl)-propionic Acid

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In connection with stereochemical studies on aralkyl carboxylic acids, α -(3-thianaphthenyl)-propionic acid has been prepared and resolved into its optical antipodes ($[\alpha]_D^{25} = 80.2^\circ$ in abs. alcohol).

Several methods could be used to determine the configuration of α -(3-thianaphthenyl)-propionic acid and sterically relate it to D-glyceraldehyde. At the present time the simplest and most reliable method is perhaps that of quasi-racemates¹, provided it is possible to find some suitable structurally similar compound.

It may be assumed that the angle γ (Fig. 1) in the thianaphthene molecule ought to be between 113° and 120° , since the corresponding angle in the thiophene molecule is 113° ² and in the naphthalene molecule

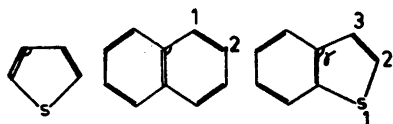


Fig. 1.

120° . The structural dissimilarity between α -(1-naphthyl)-propionic acid and α -(3-thianaphthenyl)-propionic acid should in that case perhaps be small enough to enable a quasi-racemic compound to be formed between the opposite antipodes of these two acids.

The configuration of α -(1-naphthyl)-propionic acid has already been determined by Fredga³ and the pure antipodes of this acid have been put at my disposal.

By thermal analysis according to Kofler⁴ it was shown with the aid of the contact method that a molecular compound was formed between $(-)$ - α -(3-thianaphthenyl)-propionic acid and $(+)$ - α -(1-naphthyl)-propionic acid. After the preliminary experiments the whole curve was determined for this two-component system. As is seen in Fig. 2, a very pronounced quasi-racemic compound is formed from the components in the ratio 1:1.

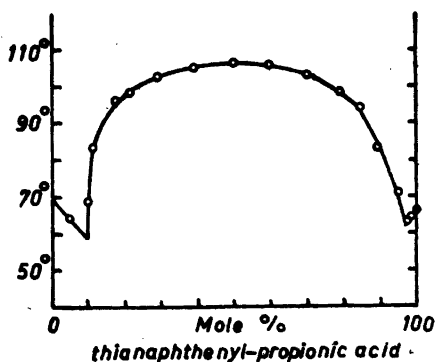
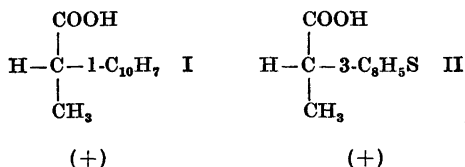


Fig. 2. $(-)$ - α -(3-thianaphthenyl)-propionic acid and $(+)$ - α -(1-naphthyl)-propionic acid.

The melting point curve for the system containing acids with the same direction of rotation was not investigated in detail, but preliminary experiments indicated that no molecular compound was formed.

From the results obtained the conclusion can be drawn that α -(1-naphthyl)-propionic acid and α -(3-thianaphthenyl)-propionic acid with the same direction of rotation (measured in alcohol at the wave-length of the D-line) also have the same configuration.

The dextro-rotatory α -(1-naphthyl)-propionic acid has the configuration I. Consequently (+)- α -(3-thianaphthenyl)-propionic acid has a stereo formula corresponding to II.



If the 3-thianaphthenyl group is considered as a substituent on the aliphatic carbon chain, this acid must be assigned to the D-series.

The work described here is part of a stereochemical study of aralkyl carboxylic acids. Full details will be given elsewhere.

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2. Schomaker, V. and Pauling, L. *J. Am. Chem. Soc.* **61** (1939) 1769.
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isoThiocyanates XXII*. 3-Benzoyloxypropyl isoThiocyanate, Present as a Glucoside (Glucomalcolmiin) in Seeds of *Malcolmia maritima* (L.) R.Br.

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Paperchromatographic analysis of the isothiocyanate glucosides in a seed extract of the crucifer *Malcolmia maritima* (L.) R. Br. revealed the presence of two glucosides, (a) and (b), possessing R_B -

values¹ of 0.34 and 1.36, respectively, in the solvent system: *n*-butanol:ethanol:water (4:1:4). In addition, traces of a third glucoside (R_B 1.03) and substantial amounts of sinapine were recognized in the seed extract, a pattern similar to that obtained elsewhere¹.

In the present work, the glucoside (a) has been unequivocally identified as glucocheirolin, furnishing cheirolin (3-methylsulphonylpropyl isothiocyanate) on enzymic hydrolysis, a mustard oil formerly recognized as a constituent of *Cheiranthus cheiri* L.** and other species². Crystalline thiourea derivatives have been obtained from enzymically hydrolyzed seed macerates of *M. maritima* after treatment with aniline and benzylamine, identical with reference specimens prepared from synthetic cheirolin³. The phenylthiourea has been described previously^{2,3} whereas the benzyl derivative is a new compound, m. p. 116° (uncorr.). (Found: C 50.35; H 6.26; N 9.70. Calc. for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{N}_2\text{S}_2$: C 50.31; H 6.33; N 9.78).

The component (b), for which we propose the name *glucomalcolmiin*, is obviously different from all glucosides heretofore encountered in nature. The corresponding optically inactive, non-volatile isothiocyanate, liberated from a paperchromatographically purified specimen of glucomalcolmiin, displays an ultraviolet absorption spectrum indicative of the presence of a strongly chromophoric system (λ_{max} 230 m μ , λ_{min} 213 m μ in water). The new mustard oil has been characterized as a crystalline thiourea, $\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_2\text{S}$, after treatment with ammonia, m. p. 162° (uncorr.). (Found: C 55.40; H 5.91; N 11.75; S 13.59. Calc. for $\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_2\text{S}$: C 55.41; H 5.92; N 11.75; S 13.45); UV-spectrum in ethanol: λ_{max} 237 m μ (ϵ 19 400), λ_{min} 214 m μ (ϵ 11 180) and low-extinction inflections at 270–272 m μ and 278–280 m μ . The IR-spectrum of the solid thiourea in a KBr disc displayed conspicuous bands at: 3.00 (vs), 5.83 (s, ester-CO), 6.05 (s), 6.41 (vs), 6.76 (s), 7.21 (s), 7.49 (s), 7.75 (vs), 8.44 (m), 8.79 (vs), 8.90 (vs), 9.28 (m), 9.48 (m), 9.70 (m), 9.84 (m), 10.64 (w), 11.00 (m), 12.47 (vs), 13.35 (w, broad), 14.03 (vs) and 14.53 μ (m). This pattern, in conjunction with the composition $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NS}$ for the parent mustard oil, points to the new species being a benzoate of a hydroxysubstituted 3-carbon-alkyl isothiocyanate. In accord herewith, alkaline hydrolysis of the thiourea at room temperature afforded benzoic acid in high yield, isolated and identified on comparison with an

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** *Malcolmia maritima* R. Br. is nomen conservandum over *Cheiranthus maritimus* L.