

isoThiocyanates XXVIII*. A New isoThiocyanate Glucoside (Glucobarbarin) Furnishing (-)-5-Phenyl-2-oxazolidinethione upon Enzymic Hydrolysis

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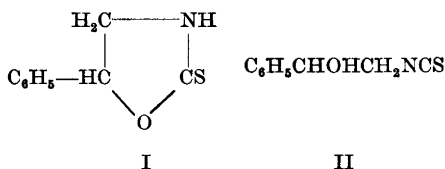
Paperchromatographic analysis in this laboratory of the *isothiocyanate* glucoside contents in seed extracts of several species of the genus *Barbarea* (*Cruciferae*) revealed the presence of two glucosides, one of which was gluconasturtiin, enzymically hydrolyzed to the steam-volatile 2-phenylethyl *isothiocyanate* and recognized many years ago by Gadamer¹ as a constituent of, *inter alia*, *Barbarea praecox* R. Br.

The second, and preponderant, glucoside, for which we propose the name *glucobarbarin*, does not seem to have been recognized previously. Its identity has now been established by investigation of a purified seed extract of *Barbarea vulgaris* R. Br.** On paper chromatography in *n*-butanol: ethanol:water (4:1:4), glucobarbarin travels at the same rate as glucotropaeolin, the glucoside producing benzyl mustard oil, while gluconasturtiin possesses a definitely higher R_F -value. The new glucoside does not afford steam-volatile material on enzymatic hydrolysis but possesses the notable property of yielding a compound with ultra-violet absorption data suggestive of a cyclic thiocarbamate structure (*cf. e. g.* Ref.³), in keeping also with the blue-green colour produced with Grote's reagent. In addition, the enzymic hydrolysis results in the formation of the traditional fragments, sulphate and glucose, the latter identified by paper chromatography in two solvent systems.

On a preparative scale, a seed extract of *B. vulgaris*, purified by passing through

a column of anionotropic alumina, was buffered to pH 6.7 and subjected to enzymic hydrolysis with a cell-free myrosinase preparation. The semi-crystalline, Grote-positive reaction product, isolated by chloroform extraction, was transformed into thin, colourless needles on repeated recrystallizations from aqueous ethanol and ethyl acetate-hexane mixtures, m. p. 125° (uncorr.), $[\alpha]_D^{25} - 70.8^\circ \pm 1.5^\circ$ (*c* 2.0, MeOH).

Analytical data suggested the composition C_9H_9NOS for the new compound (Found: C 60.30; H 4.96; N 7.76; S 17.78. Calc. C 60.31; H 5.06; N 7.82; S 17.89). Its UV-spectrum in 96% ethanol exhibited a minimum at 224 $m\mu$ (ϵ 4300), and a maximum at 245 $m\mu$ (ϵ 19000), the latter displace hypsochromically on addition of alkali, a pattern characteristic for 2-oxazolidinethiones^{2,3}. Subtraction of the elements of the heterocyclic ring from the empirical formula above, leaves a phenyl grouping to be accommodated. Previous evidence that 5-substituted 2-oxazolidinethiones are secondarily formed from enzymically liberated 2-hydroxy-substituted *isothiocyanates*^{2,5,6}, renders it very likely that the new compound is (-)-5-phenyl-2-oxazolidinethione (I), a cyclic artifact deriving from one of the stereoisomeric 2-hydroxy-2-phenylethyl *isothiocyanates* (II), enzymically liberated from glucobarbarin.



For the purpose of comparison, (\pm)-5-phenyl-2-oxazolidinethione (I) has been synthesized. Racemic 2-amino-1-phenylethanol, prepared by lithium aluminium hydride reduction of (\pm)-mandelonitrile, was transformed into optically inactive (I), following the procedure designed by Hodgkins and Ettlinger⁴ for the synthesis of *isothiocyanates* from amines. An analytical specimen separated from benzene in colourless needles, m. p. 140° (uncorr.) (Found: C 60.25; H 5.16; N 7.88. Calc. for C_9H_9NOS : C 60.31; H 5.06; N 7.82). On paper chromatography in three solvent systems, the racemic compound was indistinguishable from the

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** The seed material was commercially obtained from H. Bornträger, Offstein/Kr. Worms, Germany.

levorotatory, natural isomeride. Their identity, save for the steric arrangement around 5-C, is further supported by their nearly coinciding infra-red spectra.

More recently, the synthesis of both isomerides of (I) from the enantiomeric 2-amino-1-phenylethanols⁷ has been accomplished in this laboratory. Upon critical comparison, the synthetic, levorotatory enantiomorph proved identical with the specimen of natural origin.

The synthesis of levorotatory (I) from (-)-2-amino-1-phenylethanol further establishes its absolute configuration, and hence that of the mustard oil derivable from glucobarbarin, because the (-)-amine results from a series of reactions not involving inversions and starting with (-)-mandelic acid⁷ whose relationship with (+)-glyceraldehyde has been established by several investigators (cf. Ref.⁸). Consequently, the heterocyclic enantiomorph of natural provenance should be depicted as (I), yet with the bonds to the hydrogen atom and phenyl grouping in 5-position projecting above and below the plane of the paper, respectively.

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Infrared Investigation of the Location of the Ethylenic Bonds in the Newly Discovered Palustric Acid

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Recently Loeblich, Baldwin and Lawrence^{1,2} isolated a new acid, which they named palustric acid, from the oleoresin of *Pinus palustris* and *Pinus caribaea* by means of partition chromatography. Palustric acid is a primary acid of the abietic type which these authors also isolated as an intermediate product in the acid and heat isomerization of levopimaric acid to abietic acid. This new member of the abietic series is interesting from the standpoint of rosin acid chemistry and may be of value for the elucidation of the conversion of rosin acids into one another.

Palustric acid is reported to contain two conjugated double bonds which according to the location of the maximum in the ultraviolet spectrum appear to be situated between carbon atoms 5-6 and 7-8 (Fig. 1). On the other hand, the close relationship between palustric and *l*-abietic acid shown by the heat isomerization of levoabietic suggests a structure for palustric acid in which the double bonds are located between carbon atoms 7-8 and 13-14^{1,2}.

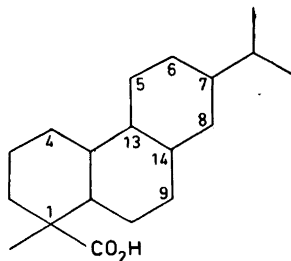


Fig. 1.