methylbutyl 3,5-dinitrobenzoate was encountered during a study of the volatile constituents of apple juice. The melting point of 2-methylbutyl 3,5-dinitrobenzoate is reported as 62°,[1] 70°[2] (both presumably from *d,l* alcohol), and 83–84°[3] (from alcohol of $[\alpha]$ +5.21°). The last value is the only one for a preparation obtained from an active alcohol of a given specific rotation. The stereoisomer available from fusel oil is *d*-2-methylbutanol, $[\alpha]^{20}D$ −5.90.[4] No data were found on the optical activity of the derivative.

An alcohol was obtained from apple juice which gave a dinitrobenzoate with a melting point of 81.5° (all melting points given here are uncorrected); its analysis was that of an amyl derivative. Mixed melting points with all inactive and racemic amyl derivatives were depressed below the melting point of either component except that with *dl*-2-methylbutyl dinitrobenzoate (m. p. 66.5°). The compound was optically active, $[\alpha]^{25}D$ +4.4°.

To determine which isomer had been obtained from apples, refined fusel oil was fractionally distilled. A fraction with $[\alpha]^{25}D$ −5.67° was obtained, equivalent to a purity of 96%. From this was prepared a 3,5-dinitrobenzoate, which melted at 83–84° and had $[\alpha]^{25}D$ +4.9°. This identified the alcohol from apples as *d*-2-methylbutanol, *i. e.*, the same as present in fusel oil.

Experimental

Dinitrobenzoate from Apple Fraction.—A distillate fraction (the full procedure appears elsewhere,[5] 0.98 g. b. p. (150 mm.) 90–100°, $n^{20}D$ 1.4104, yielded a chromatographically[6] homogeneous 3,5-dinitrobenzoate on treatment with dinitrobenzoyl chloride in the presence of pyridine. It had a m. p. of 81.5–82.5°, analyzed as an amyl derivative, and failed to depress the m. p. of only the *dl*-2-methylbutyl derivative (m. p. 66.5°), in which case the melting range was 67–79°. It was then found to have $[\alpha]^{25}D$ +4.4° (4.8% in acetone). *Anal.* Calcd. for $C_{12}H_{14}O_6N_2$: C, 51.10, H, 4.96, N, 9.93. Found: C, 51.09; H, 5.04; N, 9.99.[7]

Distillation of *d*-2-Methylbutanol from Fusel Oil.—One gallon (3.78 l.) of "isoamyl alcohol"[8] was fractionated at atmospheric pressure in a Podbielniak column operated with intermittent take-off; it yielded 200 ml. of crude *d*-2-methylbutanol, b. p. 128–129°, estimated to be 53% pure. When redistilled, this fraction yielded 65 ml. of the alcohol, 93% pure. This material, redistilled in turn, yielded a fraction, b. p. 128.5°, $n^{20}D$ 1.4105, $[\alpha]^{25}D$ −5.67°, which is 96.1% of the accepted value.[4] The 3,5-dinitrobenzoate of this fraction melted at 83–84°, and had $[\alpha]^{25}D$ +4.9° (6.4% in acetone). *Anal.* Calcd. for $C_{12}H_{14}O_6N_2$: C, 51.10; H, 4.96. Found: C, 51.00; H, 5.00. A mixed melting point with the product from apple juice was 82–84°; therefore the alcohol from apples was -*d* 2-methylbutanol.

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(1) Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 1948, p. 226.

(2) Reichstein, *Helv. Chim. Acta*, **9**, 799 (1926).

(3) Gordon, *J. Am. Pharm. Assoc.*, **16**, 419 (1927).

(4) W. Markwald and A. McKenzie, *Ber.*, **34**, 485 (1901).

(5) White, THIS JOURNAL, in press.

(6) Chromatography was on silicic acid-rhodamine 6G by the method of White and Dryden, *Anal. Chem.*, **20**, 853 (1948).

(7) The authors are indebted to C. L. Ogg for the microanalyses.

(8) This alcohol, $[\alpha]^{25}D$ −1.06°, was kindly donated by Publicker Industries, Inc.

(9) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration.

2,2-Disubstituted-thiazolidine-4-carboxylic Acids

BY RICHARD H. WILEY AND J. F. JEFFRIES

The present report describes the application of the method of Woodward and Schroeder,[1] first used to prepare thiazolidine carboxylic acids from cysteine and acetone, to cysteine and three other ketones to form the corresponding substituted thiazolidine carboxylic acids.

2-Methyl-2-ethylthiazolidine-4-carboxylic acid.—One gram of cysteine[2] was refluxed with 200 ml. of methyl ethyl ketone, b. p. 79–80°, in a 300-ml. flask attached by ground glass connection to a reflux condenser. After three hours the cysteine had nearly all dissolved. The solution was filtered, evaporated to 15 ml., and cooled to deposit crystals which were recrystallized from methyl ethyl ketone; yie d, 1.0 g., 70% of the theoretical amount, m. p. 131°. No reaction took place when rubber stoppered equipment was used.

Anal. Calcd. for $C_7H_{13}NO_2S$: C, 48.00; H, 7.42; N, 7.98; S, 18.28. Found: C, 47.75; H, 7.19; N, 8.02; S, 18.38.

2-Methyl-2-isopropylthiazolidine-4-carboxylic acid was prepared from methyl isopropyl ketone as in the preceding example; yield, 0.69 g. from 1 g. of cysteine, 44% of the theoretical amount, m. p. 154° recrystallized from methyl isopropyl ketone.

Anal. Calcd. for $C_8H_{15}NO_2S$: C, 50.8; H, 7.92; N, 7.40; S, 16.90. Found: C, 50.9; H, 7.94; N, 7.51; S, 17.20.

2,2-Tetramethylenethiazolidine-4-carboxylic acid was prepared from cysteine and cyclopentanone; yield 0.86 g. from 1 g. of cysteine, 56% of the theoretical amount, m. p. 138°, recrystallized from cyclopentanone.

Anal. Calcd. for $C_8H_{13}NO_2S$: C, 51.2; H, 6.94; N, 7.48; S, 17.10. Found: C, 50.8; H, 6.92; N, 7.34; S, 16.90.

(1) Woodward and Schroeder, THIS JOURNAL, **59**, 1690 (1937).

(2) Toennies and Bennett, *J. Biol. Chem.*, **121**, 323 (1937).

CONTRIBUTION FROM THE
VENABLE CHEMICAL LABORATORY
UNIVERSITY OF NORTH CAROLINA
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NEW COMPOUNDS

Esters of Mono-, Di- and Tri-chloro-acetic Acids[1]

The new esters of mono-, di-, and tri-chloro-acetic acids, listed in Table I, have been synthesized by refluxing the alcohol with a slight molar excess of the acid in the presence of benzene. A Dean–Stark moisture trap was included in the apparatus to collect the water produced during the reaction. Refluxing was continued until the theo-

(1) Work done at the American Home Products Corp. Development Laboratory, New York, N. Y.

retical amount of water was collected. The reaction mixture was then cooled, washed with dilute bicarbonate solution and dried over anhydrous sodium sulfate. The product was isolated by vacuum distillation. Yields were in the neighborhood of 80–90%.

TABLE I

Esters of	B. p. °C.	mm.	Chlorine, % Calcd.	Found
Monochloroacetic acid				
2-Phenylcyclohexyl	141–143	1.5	14.05	14.38
Butyl cellosolve	85–87	1.5	18.25	18.10
Dichloroacetic acid				
2-Phenylcyclohexyl	149–151	1.5	24.70	24.42
Cyclohexyl	80–82	1.5	33.60	33.76
Butyl cellosolve	90–93	1.5	31.00	31.25
Trichloroacetic acid				
2-Phenylcyclohexyl	157–159	1.5	32.50	32.70
Cyclohexyl	85–88	2	43.00	43.30

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1-Benzyl-3-phenyl-2-thiohydantoin

Ethyl N-Benzylglycinate.—Ethyl chloroacetate was condensed with benzylamine according to the directions of Mason and Winder.[1] The yield of ethyl N-benzylglycinate on the second distillation, 128–131° at 6 mm., was 55%. The picrate derivative was prepared by mixing ethereal solutions of the two substances and scratching to induce crystallization. These yellow plates, washed with ether, melted 166–168° (micro-block).[2] A benzoyl derivative was also attempted but it could not be prepared by either the Schotten–Baumann method or by boiling with benzoyl chloride in benzene solution. This unexpected behavior prompted the attempt to form a thiourea derivative.

1-Benzyl-3-phenyl-2-thiohydantoin.—Approximately equal amounts of ethyl N-benzylglycinate and phenyl isothiocyanate were mixed in alcoholic solution and boiled for a minute or two. The product which separated on cooling was recrystallized from alcohol to give a good yield of long flat needles, m. p. 188.5–189.5° (micro-block). Instead of the expected thiourea the product indicated by analysis was the 2-thiohydantoin which resulted from cyclization of the thiourea by splitting out of ethanol. This type of cyclization is not unusual, though it generally requires higher temperatures[3] or acid catalysis.[4] *Anal.* Calcd. for $C_{16}H_{14}N_2OS$: C, 68.06; H, 5.00; N, 9.92. Found: C, 68.05; H, 5.12; N, 9.93.

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(1) Mason and Winder, *J. Chem. Soc.*, 188 (1894).

(2) Slight decomposition—as evidenced by the evolution of a distillate—was noticeable as low as 150°. This might bear some relationship to the 154° m. p. reported by Mason and Winder.[1]

(3) Wheeler and Brautlecht, *Am. Chem. J.*, **45**, 446 (1911).

(4) Morton, "The Chemistry of Heterocyclic Compounds," McGraw-Hill Book Co., N. Y., 1946, p. 459.

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COMMUNICATIONS TO THE EDITOR

STUDIES OF FIBRINOGEN AND FIBRIN WITH THE ELECTRON MICROSCOPE

Sir:

Electron micrographs of metal-shadowed bovine Fraction I and human fibrinogen have been obtained showing that these materials consist largely of filamentous elements which are nodous in outline, somewhat like a string of beads, about 40 Å in diameter. Since the filaments tend to intermingle, it is difficult to measure all lengths with certainty, but such filaments as can be discerned vary in length from 300 to 1100 Å., with an average of about 600 Å. From flow-birefringence data it has been concluded that the fibrinogen particle can be represented by a prolate ellipsoid with a major axis of 700 Å. and an axial ratio of 18:1.[1] The widths observed are not appreciably different from the calculated minor axis. Numerous filaments occur with lengths close to the 700 Å. predicted, but the correlation is unsatisfactory in that flow-birefringence data indicate a constancy in length, while the electron microscope observations show a distribution of lengths. The discrepancy might be due to differences in samples or to difficulties inherent in the electron microscope methods.

An axial periodicity of about 250 Å. has been reported in bovine fibrin[2] after staining with phosphotungstic acid. The macroperiod is superficially similar to that in collagen[3] and certain other protein fibrils. In the present investigation, electron micrographs were obtained with improved resolution, showing that in bovine and human fibrin, the macroperiod consists of narrow stain-receptive bands midway between denser and wider stain-receptive bands whose average distance center-to-center along the fibril axis is about 230 Å. The spacing is constant to about 3% in individual fibrils, but varies by as much as 20% between separate fibrils. The fibrils appear to consist of particles having diameters in the range 30 to 50 Å. Metal-shadowing shows that the stain-receptive bands represent higher portions, indicating that the intervening regions have shrunk during drying. It is concluded that the periodic structure represents regular fluctuations in protein concentration in the originally hydrated system.

(1) J. T. Edsall, J. F. Foster and H. Scheinberg, THIS JOURNAL, **69**, 2731 (1947).

(2) C. V. Z. Hawn and K. R. Porter, *J. Exp. Med.*, **86**, 285 (1947).

(3) C. E. Hall, M. A. Jakus and F. O. Schmitt, THIS JOURNAL, **64**, 1234 (1942).