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, $[\alpha]^{20}\text{D}$ −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, $[\alpha]^{25}\text{D}$ +4.4°.

To determine which isomer had been obtained from apples, refined fusel oil was fractionally distilled. A fraction with $[\alpha]^{25}\text{D}$ −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 $[\alpha]^{25}\text{D}$ +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°, $n^{20}\text{D}$ 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 $[\alpha]^{25}\text{D}$ +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°, $n^{20}\text{D}$ 1.4105, $[\alpha]^{25}\text{D}$ −5.67°, which is 96.1% of the accepted value.[4] The 3,5-dinitrobenzoate of this fraction melted at 83–84°, and had $[\alpha]^{25}\text{D}$ +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.

EASTERN REGIONAL RESEARCH LABORATORY[9]
PHILADELPHIA 18, PENNSYLVANIA

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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, $[\alpha]^{25}\text{D}$ −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; yield, 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.

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[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
CHAPEL HILL, N. C.

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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-

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