TABLE II

ALKYL γ-DIETHYLAMINOPROPYLCARBAMATES

Alkyl group	Molecular formula	B. p. °C.	B. p. Mm.	$n^{20}D$	d^{20}_{20}	MD Calcd.	MD Found	Nitrogen, % Calcd.	Nitrogen, % Found	Soly. in water at 25°, g./100 g. solvent
Methyl	$C_9H_{20}O_2N_2$	125–127	9	1.4535	0.9713	52.84	52.42	14.97	15.02	∞
Ethyl	$C_{10}H_{22}O_2N_2$	138	9	1.4515	.9631	57.46	56.59	13.85	13.82	12.5
n-Propyl	$C_{11}H_{24}O_2N_2$	147–149	11	1.4520	.9479	62.08	61.65	12.95	12.91	5.0
n-Butyl	$C_{12}H_{26}O_2N_2$	158–161	11	1.4519	.9318	66.70	66.78	12.21	12.20	0.9
Isobutyl	$C_{12}H_{26}O_2N_2$	144–147	8	1.4504	.9310	66.70	66.64	12.21	12.13	1.1
n-Amyl	$C_{13}H_{28}O_2N_2$	159–163	9–10	1.4531	.9304	71.32	71.11	11.47	11.35	0.5
Isoamyl	$C_{13}H_{28}O_2N_2$	139–143	2	1.4575	.9286	71.32	71.69	11.47	11.41	.6
n-Hexyl	$C_{14}H_{30}O_2N_2$	172–176	10	1.4540	.9241	75.94	75.67	10.85	10.78	.2

rated removed by filtration. The filtrate was concentrated to half its volume and again filtered. Potassium carbonate was added to the solution until it was neutral and then solid potassium hydroxide added until no more would dissolve. The γ-diethylaminopropylamine separated as a brown oil. It was removed and distilled. The fraction boiling between 110 and 172° was collected and dried with magnesium sulfate for two days. Fractional distillation yielded 48 g. (48%) of a light yellow oil boiling at 167–170°: d^{20}_{20} 0.8283; $n^{20}D$ 1.4437; MD calcd., 41.96; MD found, 41.69.

Anal. Calcd. for $C_7H_{18}N_2$: N, 21.54. Found: N, 21.45.

The phenylthiourea was prepared by treatment with phenyl isothiocyanate. Recrystallization of this derivative from alcohol yielded colorless crystals melting at 116–116.5°.

Anal. Calcd. for $C_{14}H_{23}N_3S$: N, 15.85. Found: N, 15.80.

Alkyl γ-Diethylaminopropylcarbamates.—A solution of 10 g. of γ-diethylaminopropylamine in 100 cc. of ether was added to 8 g. of powdered potassium carbonate mixed with just enough water to make a thick paste. To this mixture was added slowly a solution of the alkyl chlorocarbonate[4] in 100 cc. of ether. The mixture was shaken vigorously and cooled to prevent too vigorous a reaction. After standing at room temperature for twenty hours with occasional shaking, the ether layer was decanted and the residue extracted four times with 25 cc. of ether. The combined ether extracts were dried with magnesium sulfate, the ether distilled and the residual oil fractionally distilled *in vacuo*. The urethans were obtained as pleasant smelling oils. The yields were 65–70%. The properties and analyses are given in Table II.

Summary

A series of alkyl γ-diethylaminopropylcarbamates has been synthesized by the following sequence: potassium phthalimide → γ-bromopropylphthalimide → γ-diethylaminopropylphthalimide → γ-diethylaminopropylamine → alkyl γ-diethylaminopropylcarbamate. Their local anesthetic action has been studied.

(4) Adams, Kamm and Marvel, "Org. Chem. Reagents. I," *Univ. of Ill. Bull.*, **43**, 42 (1919).

URBANA, ILLINOIS RECEIVED JANUARY 6, 1939

[CONTRIBUTION FROM THE U. S. CITRUS PRODUCTS STATION, FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Characteristics and Composition of Watermelon Seed Oil (Cuban Queen Variety)[1]

BY ARTHUR J. NOLTE AND HARRY W. VON LOESECKE

The Cuban Queen variety of watermelon (*Citrullus Vulgaris*) is round or slightly oval with a rind alternately striped with dark and light green, giving it the appearance of being ribbed. The seeds are brownish black.

According to Jamieson[2] the seeds of watermelon contain from about 20 to over 40% of oil depending upon the variety and locality. The oil is said to be used for cooking or as an illuminant. The seeds are alleged to have diuretic properties, although there is no convincing evidence to substantiate this contention.

Jamieson[2] gives the range of the characteristics for watermelon seed oil (varieties not stated); Power and Salway[3] examined a sample of the seed oil and found it to consist of the glycerides of linoleic, oleic, palmitic and stearic acids. Other than the work of Power and Salway, no further study of the composition of the oil seems to have

(1) Food Research Division Contribution No. 409.

(2) Jamieson, "Vegetable Fats and Oils," Chemical Catalog Company, Inc., New York, 1932, p. 222.

(3) Power and Salway, THIS JOURNAL, **32**, 360 (1910).

been made. Dorn and Erastova[4] investigated the constants for watermelon seed oil and its action after polymerization when applied as a lacquer.

The present work was undertaken to supply more detailed information relative to the composition of the oil from seeds of a known variety of watermelon.

The melons used were culls and grown in South Central Florida. The seeds were obtained by mashing the fruit and flushing with large quantities of water. The seeds thus obtained still had small fragments of adhering pulp. This was removed by allowing the packed seeds to undergo fermentation followed by subsequent screening, washing, and drying.

The air-dried seeds, upon analysis, gave the following results:

	%
Moisture	8.84
Water-soluble ash	0.05
Water-insol. ash	2.31
Total ash	2.36
Protein (N × 6.25)	17.31
Fat (ether extract)	26.52
Undetermined	44.97

Preparation of the Oil.—The oil was prepared by extracting the air-dried, ground seeds with warm petroleum ether. The extracted seeds contained a residual oil content of 3.2%. The solvent was removed by distillation and the last traces removed by warming to 120° under a vacuum of 15 mm. The filtered oil contained 0.06% of volatile constituents.

Physical and Chemical Examination.—The oil was yellow in thin layers and brownish in moderately thick layers. It had a bland odor and taste. The chemical and physical properties of the oil were determined by the usual procedures[5] with the results given in Table I.

TABLE I

CHEMICAL AND PHYSICAL CHARACTERISTICS OF WATERMELON SEED OIL (CUBAN QUEEN VARIETY)

Specific gravity 25°/25°	0.9197
Refractive index, $n^{20}D$	1.4669
Acid value	0.42
Saponification value	197.4
Iodine no. (Hanus)	133.8
Unsaponifiable matter, %	1.19
Unsaturated acids, % (corr.)	78.96
Saturated acids, % (corr.)	14.56
Iodine no. of unsatd. acids	166.6
Reichert-Meissl no.	0.29
Polenske no.	.72
Acetyl value	7.5
Hehner value (corr. for unsap. matter)	89.2

The Reichert-Meissl and Polenske numbers show small amounts of glycerides of volatile acids; this fact is confirmed also by the Hehner value.

Examination of Unsaturated Acids.—The unsaturated acids were separated by the lead salt–ether method and dried in a current of carbon dioxide. The iodine number of the unsaturated acids was 166.6, the neutralization value 195.2 and the mean molecular weight 287.8.

Bromination of the unsaturated acids failed to yield ether-insoluble hexabromides, indicating the absence of linolenic acid. Since only linoleic and oleic acids were found to be present, the percentage of these acids was calculated by the formula given by Lewkowitsch[6] with the following results.

	In unsatd. acids, %	Original oil, %	Glyceride in original oil, %
Linoleic	83.99	65.85	68.38
Oleic	16.01	12.55	13.03
	100.00	78.40	81.41

Examination of the Saturated Acids.—The saturated acids were esterified and the mixed methyl esters (7.86 g.) fractionally distilled *in vacuo* with the results given in Table II.

TABLE II

RESULTS OF ANALYSES OF FRACTIONS OBTAINED BY DISTILLING METHYL ESTERS OF SATURATED ACIDS OF WATERMELON SEED OIL

Fractions		1	2	Residue
Temperature, °C.		130–155	155–162	...
Pressure, mm.		1.0	1.0	1.0
Iodine number		2.84	5.37	12.83
Sapn. values of esters of satd. acids		200.4	198.3	175.8
Esters of unsatd. acids, %		1.16	3.39	8.09
Esters of satd. acids, %		98.84	96.61	91.91
Mean mol. wt. of esters of satd. acids		279.9	282.9	319.1
Composition of methyl esters of saturated acids, %	Palmitate	65.8	55.2	...
	Stearate	34.2	44.8	26.1
	Arachidate	...	...	74.9

The iodine numbers and saponification values of the different fractions were determined and the mean molecular weights of the esters calculated according to Baughman and Jamieson.[7] These results are also given in Table II.

To confirm the data in Table II, the acids were isolated from the different fractions and fractionally crystallized from 95% ethyl alcohol.

Palmitic Acid.—From fraction 1 was obtained an acid melting at 63–64° which was considered to be evidence of palmitic acid.

Stearic Acid.—Fraction 2 yielded an acid melting at 69–71.5° which was considered to be stearic acid.

Arachidic Acid.—From the residue remaining in the distilling flask an acid melting at 74–75° was obtained. This

TABLE III

SATURATED ACIDS IN WATERMELON SEED OIL

Acids	Grams	Yield, %	Acids in oil, %	Glycerides in oil, %
Palmitic	4.63	58.08	8.46	8.84
Stearic	2.48	37.13	5.41	5.61
Arachidic	0.58	4.79	0.70	0.72
			14.57	15.17

(4) Dorn and Erastova, *Trudui Nauch.-Issledovatel. Inst. Lakov. i. Krasok.* No. 1 (*Film-forming substances*), p. 7 (1935); *C. A.*, **30**, 7879 (1936).

(5) Association of Official Agricultural Chemists, "Methods of Analysis," Washington, D. C., 4th ed., 1935, pp. 404–418.

(6) Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 6th ed., Vol. I, 1921, p. 574.

(7) Baughman and Jamieson, THIS JOURNAL, **42**, 156 (1920).

was considered to be arachidic acid. The composition of the saturated acids is given in Table III.

Summary

A study has been made of the composition of the glycerides of watermelon seed oil (Cuban Queen Variety). The fatty acids consist of 8.84% palmitic acid, 5.61% of stearic acid, 0.72% of arachidic acid, 13.03% of oleic acid and 68.38% of linoleic acid. The unsaponifiable matter amounts to 1.19%.

The presence of arachidic acid in watermelon seed oil has not been mentioned by previous investigators.

WINTER HAVEN, FLA. RECEIVED FEBRUARY 6, 1939

[CONTRIBUTION NO. 691 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

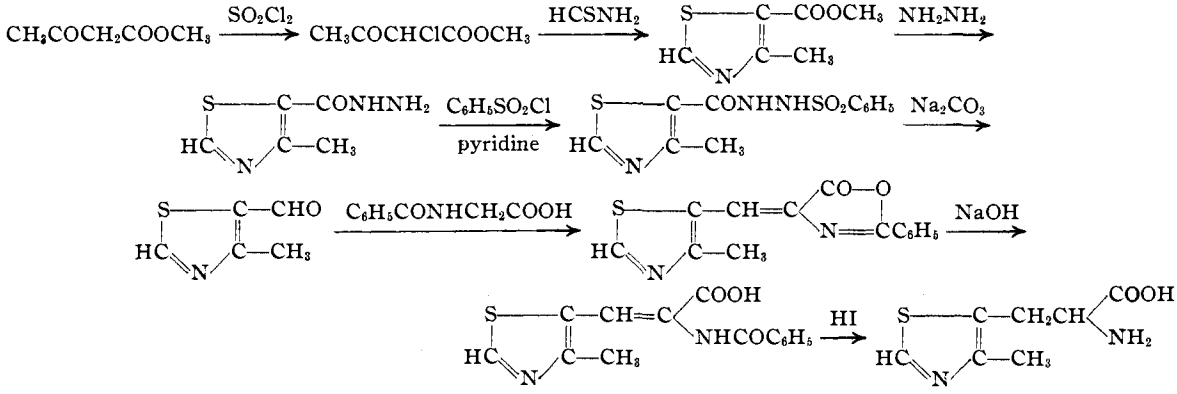
Thiamin Analogs. I.[1] β-(4-Methylthiazolyl-5)-alanine[2]

BY EDWIN R. BUCHMAN AND EDWIN M. RICHARDSON

The thiamin (vitamin B_1) molecule comprises two parts which may be referred to as the pyrimidine half and the thiazole half, the vitamin itself being a quaternary salt of its thiazole half. Not only may the synthesis of the vitamin be accomplished *in vitro*[3] by a coupling of the two halves but also the same transformation may be effected enzymatically[4] in certain organisms, so that it is reasonable to assume that this reaction represents the last step in the natural biogenesis of the substance.

The thiazole half, with its $-CH_2CH_2OH$ group, bears a certain resemblance to β-phenylethyl alcohol, tyrosol, and tryptophol, substances which may be derived from the amino acids, phenylalanine, tyrosine, and tryptophan by the action of fermenting yeast[5] and whose β-hydroxyethyl side chain results from the degradation of the alanine grouping. We have seen in this similarity a clue to a possible precursor of the vitamin thiazole and accordingly have synthesized the appropriate amino acid, β-(4-methylthiazolyl-5)-alanine, in order to investigate its biological significance.[6]

The synthesis was accomplished in a straightforward manner as indicated below



The transformation of the thiazole ester to the aldehyde represents an extension to the thiazole series of the recently published[7] method of Stevens for converting aromatic acids to the corresponding aldehydes. The over-all yield of amino acid from acetoacetic ester is about 6% or a yield of 9 g. from 100 g. of the starting material.

The evidence accumulated to date does not permit definite conclusions regarding the biological role of the amino acid. It is of interest that

(1) Paper 18 in the R. R. Williams series.

(2) Presented before the Pacific Division of the American Association for the Advancement of Science at the San Diego meeting, June, 1938.

(3) R. R. Williams and J. K. Cline, THIS JOURNAL, **58**, 1504 (1936); J. K. Cline, R. R. Williams and J. Finkelstein, *ibid.*, **59**, 1052 (1937).

(4) J. Bonner and E. R. Buchman, (a) *Proc. Natl. Acad. Sci.*, **24**, 431 (1938); (b) *ibid.*, in press.

(5) F. Ehrlich, *Ber.*, **40**, 1047 (1907); **44**, 139 (1911); **45**, 883 (1912).

(6) Professor C. R. Harington in a communication to one of us (E. R. B.) has disclosed that, independently motivated by considerations similar to those which have influenced us, he also has synthesized this amino acid and investigated some of its biological properties. We have been privileged to view Professor Harington's manuscript prior to publication and take this opportunity again to thank him for the extended courtesy.

(7) J. S. McFayden and T. S. Stevens, *J. Chem. Soc.*, 584 (1936).