

LITERATURE CITED

- Casida, J. E., Holmstead, R. L., Khalifa, S., Knox, J. R., Ohsawa, T., *Environ. Qual. Saf.*, in press (1975).
- Casida, J. E., Holmstead, R. L., Khalifa, S., Knox, J. R., Ohsawa, T., Palmer, K. J., Wong, R. Y., *Science* 183, 520 (1974).
- Holmstead, R. L., Khalifa, S., Casida, J. E., *J. Agric. Food Chem.* 22, 939 (1974).
- Jennings, B. H., Herschbach, G. B., *J. Org. Chem.* 30, 3902 (1965).
- Khalifa, S., Mon, T. R., Engel, J. L., Casida, J. E., *J. Agric. Food Chem.* 22, 653 (1974).
- Ohsawa, T., Knox, J. R., Khalifa, S., Casida, J. E., *J. Agric. Food Chem.* 23, 98 (1975).
- Palmer, K. J., Wong, R. Y., Lundin, R. E., Khalifa, S., Casida, J. E., *J. Am. Chem. Soc.* 97, 408 (1975).
- Richey, H. G., Jr., Grant, J. E., Garbacik, T. J., Dull, D. L., *J. Org. Chem.* 30, 3909 (1965).
- Silverstein, R. M., Bassler, G. C., Morrill, T. C., "Spectrometric Identification of Organic Compounds", 3rd ed, Wiley, New York, N.Y., 1974, p 220.

Walter V. Turner
Safy Khalifa
John E. Casida*

Division of Entomology and Parasitology
University of California
Berkeley, California 94720

Received for review March 31, 1975. Accepted April 29, 1975. Supported in part by Public Health Service Grant No. P01 ES00049 and grants from The Rockefeller Foundation and Hercules Incorporated.

Duck Eggs as a Source of Methionine and Threonine

The amino acid composition of duck egg whites and yolks is reported, as well as distribution of protein in whites and yolks. The data indicate that duck egg whites are an excellent source of essential amino acids, especially methionine (6.3

g/16 g of nitrogen), and threonine (6.0 g/16 g of nitrogen). Cost estimations indicate that duck egg white essential amino acids are more economical than commercial sources of L-amino acids.

Essential amino acids are those amino acids that must be supplied in the diet. It is well known that fortification of many vegetable proteins with essential amino acids results in an improvement in the nutritional quality. Howe et al. (1965a,b) have shown that supplementation of major cereal and oilseed crops with only four essential amino acids (lysine, methionine, threonine, and/or tryptophan) is sufficient to raise their protein quality to a level with casein. As the human diet becomes more dependent for protein on cereals and oilseeds, supplemental sources of lysine, methionine, threonine, and tryptophan will become more important.

Amino acid supplementation of a human food is normally accomplished via the addition of free amino acids. However, supplementation with free amino acids is not without its problems, one of which is their flavor. Observations regarding taste have recently been reported and reviewed by Petritschek et al. (1972). Kies et al. (1972) have reported that methionine supplementation of oatmeal made that product unacceptable.

In addition, there are toxicity problems associated with free amino acids, as evidenced by the fact that they have been removed from the GRAS list, and with the exception of D-methionine, all D-amino acids are banned as food additives by the U.S. Food and Drug Administration (Schmidt, 1973). The same regulations also ban D-methionine in infant foods. In general, only the L-amino acids are permitted as food additives in restricted applications.

The purpose of the present paper is to provide information on the amino acid composition of duck eggs, with a view toward their use as a source of essential L-amino acids, particularly methionine and threonine.

An examination of "Amino Acid Composition of Foods" (FAO, 1970) indicated that of the 394 entries, duck egg white protein was highest in both total sulfur containing amino acids and also methionine, and fifth highest in threonine. It also ranks near the top in tryptophan, phenylalanine, and tyrosine. However, the reported analyses were based on only two samples, were for the whites only, and were from unpublished data. Therefore, it was felt that additional data were needed.

METHODS AND MATERIALS

All duck eggs originated from Texas. Three large green-shelled (LG) eggs were obtained from a mixed flock of barnyard ducks fed milo and laying mash. Two medium white shelled (MW) eggs were obtained from the same flock. For the fresh eggs the whites were individually separated from yolks on egg separators, with clinging white scraped off yolks. Each shell was rinsed and blotted dry. Whole egg, yolk, and shell were each weighed and weight of white determined by difference.

A single egg from a wild duck (WD) was obtained, which was boiled and soaked in salt water for preservation. (This egg was about 1 month old when analysis began.) All samples were freeze-dried prior to amino acid analysis.

The amino acid analyses were performed with a Beckman Model 120 C analyzer. Cystine content was determined after oxidation to cysteic acid. Tryptophan was determined by the method of Kohler and Palter (1967). Each observation was made once for each of six eggs.

RESULTS AND DISCUSSION

The weights of whites and yolks are reported in Table I. It may be noted that the fraction of total protein in the whites ranged from 0.43 to 0.58 for the three types of eggs, a difference which is statistically significant. This difference is also important because of the difference in amino acid content of white and yolk, to be discussed.

The amino acid contents of the whites and yolks are reported in Tables II and III. Besides the amino acids reported, an unidentified component was observed which was presumably a basic amino acid. This component is present at ca. the 1% level in the white and ca. 0.4% in the yolk (percent of protein). The unidentified peak was eluted 7 min before lysine with elution conditions of 55°, pH 5.27, 0.35 N citrate buffer. The data from the limited sample analyzed indicate that there is little difference in amino acid composition for the different kinds of eggs. The amino acid composition of the whites is in fair agreement with published data (FAO, 1970). May (1960) has shown that amino

Table I. Weights and Moisture and Protein Contents of Whites and Yolks

Type egg	LG ^c	MW ^c	WD ^c	Std ^b dev
Total weight, g	87.1	74.3	64.4	2.7
Shell, g	9.2	7.7	4.0	0.2
Yolk, g	28.6	28.2	22.9	0.3
White, g	49.3	38.4	37.5	2.2
Moisture contents				
Yolk, %	48.3	45.2	39.1	1.7
White, %	86.9	89.5	83.3	0.8
Protein content ^a				
Freeze-dried yolk, %	30.0	29.3	27.6	0.6
Freeze-dried white, %	83.8	84.0	84.0	0.8
Total protein				
Yolk, g	4.4	4.4	3.4	0.2
White, g	5.4	3.3	4.6	0.1
Whole egg, g	9.8	7.7	8.0	0.4

^a Protein is taken as N × 6.25. The 6.25 factor is recommended for eggs in USDA Handbook No. 8. ^b Standard deviation of single analysis. ^c The two-letter designations indicate type of duck egg. LG means large green shelled (average analysis for three eggs); MW means medium white shelled (two eggs); and WD means wild duck (one egg).

Table II. Amino Acid Composition of Duck Egg White^a

Amino acid	LG	MW	WD	Av
Essential				
Ile	4.4	4.3	4.3	4.3
Leu	8.6	8.2	8.5	8.4
Lys	6.7	6.5	6.6	6.6
(Total aromatic)	(13.5)	(13.0)	(13.8)	(13.4)
Phe	8.7	8.5	9.1	8.8
Tyr	4.8	4.5	4.7	4.7
(Total S-containing)	(9.2)	(9.1)	(8.8)	9.0
Cys	2.8	2.6	2.7	2.7
Met	6.4	6.5	6.1	6.3
Thr	6.3	6.0	5.8	6.0
Trp	2.0	2.0	<i>b</i>	2.0
Val	6.9	6.7	6.9	6.8
Total essential	57.6	55.8	54.7	56.0
Nonessential				
His	2.0	2.0	2.0	2.0
Arg	4.5	4.5	4.5	4.5
Asp	10.0	9.4	9.7	9.7
Glu	15.6	14.1	15.9	15.2
Ser	7.6	7.5	8.0	7.7
Pro	3.9	3.7	3.5	3.7
Ala	5.0	4.7	4.9	4.9
Gly	3.7	3.5	3.6	3.6
Total	109.9	105.2	106.8	107.3

^a All units are grams of amino acid/16 g of nitrogen. Standard deviation of single analysis is 0.2 g/16 g of nitrogen. ^b No observation.

acid protein of chicken egg proteins is not affected by strain. Based on these observations, it is assumed that the average amino acid compositions reported in Tables II and III apply to duck eggs in general, and not only to the samples analyzed.

The data in Tables II and III indicate that the egg white protein is particularly rich in methionine, with 2.7 times the amount of methionine in the 1957 FAO provisional pattern (FAO, 1965). Both the white and yolk are also high in

Table III. Amino Acid Composition of Duck Egg Yolk^a

Amino acid	LG	MW	WD	Av value
Essential				
Ile	4.8	5.0	5.3	5.0
Leu	8.3	8.5	9.1	8.6
Lys	7.5	7.5	7.9	7.6
(Total aromatic)	(9.1)	(9.3)	(10.3)	9.6
Phe	4.6	4.6	5.3	4.8
Tyr	4.5	4.7	5.0	4.7
(Total S-containing)	(4.1)	(4.1)	(4.6)	4.3
Cys	1.6	1.6	1.9	1.7
Met	2.5	2.5	2.7	2.6
Thr	5.2	5.2	5.0	5.1
Trp	1.9	2.2	<i>b</i>	2.0
Val	5.3	5.6	5.9	5.6
Total essential	46.2	47.4	48.1	47.2
Nonessential				
His	2.5	2.5	2.7	2.6
Arg	6.7	6.8	7.3	6.9
Asp	8.4	8.7	9.3	8.8
Glu	11.8	12.6	13.2	12.5
Ser	7.1	7.2	7.7	7.3
Pro	3.8	3.7	3.9	3.8
Ala	4.8	4.9	5.3	5.0
Gly	2.9	2.9	3.1	3.0
Total	94.2	96.7	100.6	97.2

^a All units are grams of amino acid/16 g of nitrogen. Standard deviation of single analysis is 0.2 g/16 g of nitrogen. ^b No observation.

threonine (2.1 and 1.8 times the FAO pattern, respectively). The whites and yolks are also good sources of lysine and tryptophan.

Compared to chicken egg whites (FAO, 1970) the duck egg whites contain more of the four most critical essential amino acids. The duck egg whites contain 60% more methionine, 45% more total S-containing amino acids, 30% more threonine, 25% more tryptophan, and equal lysine.

The compositional data suggest that duck egg white might be used as a source of methionine, threonine, tryptophan, and lysine, providing this is feasible and economically practical.

One possible form for duck egg utilization is as a dried product, which would allow separate marketing of whites and yolks. The drying of duck eggs is a technically feasible operation (Iyengar et al., 1969). Current (Oct., 1974) U.S. bulk price for chicken egg powder is \$3.80/kg, for either dry whites or yolks.

A variety of ducks called Khaki Campbell has been developed which reportedly average ca. 360 eggs per year and has a feed conversion ratio (weight eggs per weight feed) equal or superior to chickens (Hutt, 1952; Sullivan and Adams, 1961). The feed conversion ratio is important because feed costs constitute ca. 70% of the cost of egg production.

Based on these considerations, it would seem safe to assume that dried duck egg white could also be produced to sell at ca. \$3.80/kg, and consequently some calculations can be made regarding the economics of using duck egg white as a source of amino acids.

However, it may be noted here in passing that the use of whole duck eggs would be expected to result in an even cheaper source of amino acids. Whole duck eggs are a common food in China, India, Europe, the Philippines, and elsewhere.

Based on the analyses in Table II and current prices of L-amino acids (Anjinomoto USA, Inc., price list effective 1974, for quantities of 30 kg and up) 1 kg of dried duck egg

white would provide 50 g of L-threonine worth \$3.50, 53 g of L-methionine worth \$2.00, 17 g of L-tryptophan worth \$1.50, and 55 g of L-lysine worth \$0.60. (Values were rounded to nearest \$0.1.) This represents an estimated total market value of \$7.60 for only threonine, methionine, tryptophan, and lysine, which is twice the \$3.80 estimated cost for the kilogram of dried duck egg white. The threonine alone almost covers the cost of the whole product.

This little exercise in price comparisons would seem to suggest that dried duck egg whites be considered as a currently economical source of the L-amino acids. Future price comparisons will depend on price trends of feed as compared to L-amino acid prices.

This discussion has centered on duck eggs as a source of economical amino acids. However, this is only a special case for an approach to nutrition that is not new but is sometimes overlooked in the confrontation between plant breeding and amino acid fortification as to which is the best answer to the world's protein problem. The data and discussion of this paper would suggest that an alternate approach to human protein nutrition be selection of appropriate supplementary foods that contain large amounts of the most needed essential amino acids. These might then be consumed as food additives (e.g. dried duck egg white) or as a separate food (e.g. whole duck egg).

It has been suggested that even the fortification of a vegetable protein with an animal protein can be practical if the

right animal protein is selected. Even more economy might be achieved by production of vegetable proteins high in the most needed essential amino acids.

LITERATURE CITED

- FAO, "Amino Acid Composition of Foods", Rome, 1970.
 FAO, "Protein Requirements", Rome, 1965.
 Howe, E. E., Gilfillan, E. W., Milner, M., *Am. J. Clin. Nutr.* 16, 321 (1965a).
 Howe, E. E., Jansen, G. R., Gilfillan, E. W., *Am. J. Clin. Nutr.* 16, 315 (1965b).
 Hutt, F. B., *J. Hered.* 43, 277 (1952).
 Iyengar, J. R., Sripathy, N. V., Rao, R. S., *J. Food Sci. Technol.* 6, 123 (1969).
 Kies, C., Peterson, M. R., Fox, H. M., *J. Food Sci.* 37, 306 (1972).
 Kohler, G. O., Palter, R., *Cereal Chem.* 44, 512 (1967).
 May, K., *J. Am. Diet. Assoc.* 37, 568 (1960).
 Petritschek, A., Lynen, F., Belitz, H. D., *Lebensm.-Wiss. Technol.* 5, 47 (1972).
 Schmidt, A. M., *Fed. Regist.* 38(143), 20036 (1973).
 Sullivan, T. W., Adams, J. L., *Nebr. Exp. Stn. Q.*, 3 (Fall, 1961).

Robert Hagenmaier

Food Protein Research and Development Center
 Texas A&M University
 College Station, Texas 77843

Received for review October 29, 1974. Accepted March 25, 1975.

In Vitro Biotransformations of

1-(*o*-Chlorophenyl)-1-(*p*-chlorophenyl)-2,2-dichloroethane (*o,p'*-DDD) and 1,1-Bis(*p*-chlorophenyl)-2,2-dichloroethane (*p,p'*-DDD) by Bovine Adrenal

In vitro biotransformations of ¹⁴C-labeled 1-(*o*-chlorophenyl)-1-(*p*-chlorophenyl)-2,2-dichloroethane (*o,p'*-DDD) and 1,1-bis(*p*-chlorophenyl)-2,2-dichloroethane (*p,p'*-DDD) by bovine adrenal homogenates were studied. Homogenates were found to oxidize *o,p'*-DDD to *o,p'*-dichlorodiphenylacetic acid (*o,p'*-DDA), while *p,p'*-DDD was converted to bis(*p*-chlorophenyl)acetic acid (*p,p'*-DDA) and 1,1-bis(*p*-chlorophenyl)-2,2-dichloroethanol. Transformation products were

identified by thin-layer chromatography and mass spectra of band extracts. The mitochondrial fraction was found to be the most active of the cortex subcellular fractions in transforming the substrates with some contribution by the soluble fraction. Transformation by the microsomal fraction was negligible. An NADPH generating system was necessary for these transformations, and they did not occur with boiled enzyme preparations.

The compound *o,p'*-DDD [1-(*o*-chlorophenyl)-1-(*p*-chlorophenyl)-2,2-dichloroethane] produces atrophy of the adrenal cortex, inhibition of ACTH stimulation of steroid production, and alteration of liver cortisol metabolism (Hart and Straw, 1971a). *o,p'*-DDD has Food and Drug Administration approval for human use in the treatment of Cushing's Syndrome, secondary to adrenal carcinoma (Verdon et al., 1960) or hyperfunction (Hellman et al., 1970).

The adrenal effects of *o,p'*-DDD occur in dogs and humans, but it is inactive in rats, mice, rabbits, and monkeys (Gaunt et al., 1965). Weber et al. (1958) reported that technical DDD caused adrenal atrophy in cattle. It has been reported that *p,p'*-DDD [1,1-bis(*p*-chlorophenyl)-2,2-dichloroethane], the main component of technical DDD, is relatively inactive while the presence of *o,p'*-DDD is responsible for the adrenal effects of technical DDD (Nichols, 1961). Hart et al. (1973) found that equal doses of both isomers eventually produced cortex necrosis and inhibited adrenal steroid production in dogs, but *o,p'*-DDD was faster acting than *p,p'*-DDD.

A number of in vivo metabolites of *o,p'*-DDD in the

human (Sinsheimer et al., 1972; Reif et al., 1974) and the rat (Reif and Sinsheimer, 1975) have been identified in these laboratories. Metabolism involved alkyl oxidation to *o,p'*-DDA [*o,p'*-dichlorodiphenylacetic acid] and aromatic hydroxylation in both species. Peterson and Robison (1964) identified a number of metabolites of *p,p'*-DDT [1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane] in the rat which could also be metabolites of *p,p'*-DDD. There was evidence of *p,p'*-DDA [bis(*p*-chlorophenyl)acetic acid] formation, but aromatic hydroxylation of para,para'-substituted isomers has not been reported.

Since DDD concentrates in the adrenal gland (Moy, 1961) and the adrenal cortex is the target organ for the drug, the biotransformation of DDD isomers by adrenals is of interest. Of particular interest would be the possible para hydroxylation of *o,p'*-DDD by the adrenal cortex as the basis for the increased rate of activity of this isomer. The few reports of in vitro conversions of xenobiotics by adrenals have involved incubations with whole gland homogenates and would include transformations by both cortex and medulla. Jellinck et al. (1967) showed that rat