Effect of Ingredients on the Oxygen Uptake of Cooked, Freeze-Dried Combination Foods

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The antioxidant or prooxidant activity of the principal ingredients was determined for eight cooked, freeze-dried combination foods used in Armed Forces operational rations. Each product was made in successive stages or partial formulations with the first stage containing only meat and water and the succeeding stages made by adding one or more ingredients, with the last stage being the complete product. Proportions and processing were maintained as though the final product was being made. The stages were freeze-dried and stored in cans under atmospheric pressure at 40, 70, or 100° F for 12 weeks. Oxygen uptakes of the stages were determined at 2, 4, 8, and 12 weeks. Some ingredients such as rice, chili beans, and vegetable oil were found to have antioxidant properties. Others such as tomato paste, some seasoning mixes, and white sauce were prooxidant. There is evidence that the antioxidant or prooxidant activity of an ingredient varies, depending upon the other ingredients present, and that processing conditions will significantly affect the oxygen uptake of the meat component.

The large surface area resulting from the porous nature of freeze-dried foods makes these products particularly susceptible to oxidation. However, the response of various foods to oxygen differs widely. Hanson (1961) defines oxygen tolerance of freeze-dried foods as the amount of oxygen that can be absorbed by a product without seriously impairing its acceptability over a long period, and states that this property varies with different foods or classes of foods. Roth *et al.* (1965) found that the rates of oxygen absorption by cooked, freeze-dried chicken, beef, carrots, and spinach were very different, and that exposure to oxygen was the primary cause of product deterioration. Tuomy *et al.* (1969) investigated the oxygen uptake of eight cooked, freeze-dried combination items and reported that while these products differed widely in their rates of oxygen uptake and in the total amount of oxygen taken up over a 6-month period, taste panel responses were highly correlated with the quantity of oxygen taken up. The oxygen tolerances of the eight products were practically identical.

Reports in the literature give instances of individual foods exhibiting antioxidant or prooxidant properties. Various spices were shown to have weak to very strong antioxidant activity both in lard (Chipault *et al.*, 1952) and in oil-in-water emulsions (Chipault *et al.*, 1955), although the relative activity was not the same in both cases. Ramsey and Watts (1963) and Pratt and Watts (1964) showed that hot water extracts of some vegetables had antioxidant effects on cooked meat. Bishov *et al.* (1961) showed that in model dehydrated systems proteins generally decreased, and polymeric carbohydrates accelerated oxygen uptake rates. Bishov *et al.* (1967) suggested that hydrolyzed vegetable protein has a stabilizing effect on dry soup mixes.

There is some evidence that cooking of meat reduces susceptibility to oxidation. Abrahami and Naismith (1968) stated that heating of meat to 85° C possibly resulted in antioxidants being formed. Zipser and Watts (1961) stated that antioxidants are produced in meat by prolonged cooking above 100° C but did not attempt to identify the compounds formed.

Investigations concerned with the oxygen uptake of eight freeze-dried combination foods contained in the Food Packet, Long Range Patrol (LRP) (Tuomy *et al.*, 1969, 1970) have shown wide variations in the uptake which are not explainable by comparison of the product formulas. The LRP is a lightweight packet designed to be carried by the individual soldier in operational and combat situations where resupply is difficult or impossible. It has been enthusiastically received by troops in the field, and the combination foods in it, as well as similar freeze-dried foods, are being considered for use in other rations. In addition, similar foods are being introduced in the commercial market. Since oxygen uptake is a very important quality parameter and since the products vary in their rates of oxygen uptake, this study was initiated in an attempt to determine the antioxidant and prooxidant properties of the ingredients used. The products investigated were freeze-dried beef hash, beef stew, beef with rice, chicken and rice, chicken stew, chili con carne, pork with potatoes, and spaghetti with meat.

EXPERIMENTAL

The products were made according to Interim Purchase Description IP/DES S-36-6 Food Packet, Long Range Patrol. Each product was made in successive stages or steps with the first stage containing only the meat and water. The succeeding stages were made by adding one or more formula ingredients until the last stage was the complete product. All ingredients were used in the same relative proportions as in the total formula. Each stage was processed and cooked as closely as possible in the same way and to the same temperatures as it would be if the total product were being made. After processing, the stages were freeze-dried to less than 2% moisture with a platen temperature of 120° F, radiant heat, and a pressure of 400 μ. The vacuum in the freeze-drying chamber was broken with nitrogen and the products packed in No. $2^1/_2$ cans, 125 g per can at atmospheric pressure. The products were packed within 4 hr after the dehydrator was opened.

A total of 45 cans were closed for each stage. Fifteen cans of each were stored at 40, 70, and 100° F to be withdrawn at 2, 4, 8, and 12 weeks, three cans at each withdrawal.

Headspace gas analysis was performed by chromatographic means in accordance with the procedure outlined by Bishov and Henick (1966). Sample size was 250 to 500 μl. Experience indicates an anticipated error for the method of approximately $\pm 0.25\%$.

Total headspace volume in the cans was determined by compressing 125 g of product from each stage in a laboratory press at 5000 lb per in.^{2} for 10 sec and subtracting the volume of the resulting bar from the total volume of the can. This method is not completely accurate; however, since the volume

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Table I. Composition of the Stages for the Eight Combination Meat Items

Product	Stage 1	Stage 2	Stage 3	Stage 4	Formula %
Beef hash	Beef, raw	Beef, raw	Beef, raw	...	42.5
	Water	Water	Water	...	13.5
		Potatoes, raw	Potatoes, raw	...	41.0
			Seasoning, mix	...	3.0
Beef stew	Beef, cooked	Beef, cooked	Beef, cooked	Beef, cooked	38.8
	Water	Water	Water	Water	32.0
		Potatoes, raw	Potatoes, raw	Potatoes, raw	16.0
		Peas, raw	Peas, raw	Peas, raw	3.3
		Oil, vegetable	Oil, vegetable	Oil, vegetable	2.0
			Seasoning, mix	Seasoning, mix	3.3
				Carrots, raw	4.6
Beef with rice	Beef, raw	Beef, raw	Beef, raw	Beef, raw	35.0
	Water	Water	Water	Water	47.0
		Rice, instant	Rice, instant	Rice, instant	11.3
			Cream of onion soup	Cream of onion soup	6.03
				Seasoning	0.67
Chicken and rice	Chicken, cooked	Chicken, cooked	Chicken, cooked	Chicken, cooked	38.5
	Water	Water	Water	Water	41.5
		Rice, instant	Rice, instant	Rice, instant	9.6
			Seasoning, mix	Seasoning, mix	5.6
				Oil, vegetable	4.8
Chicken stew	Chicken, cooked	Chicken, cooked	Chicken, cooked	...	29.0
	Water	Water	Water	...	32.0
		Potatoes, raw	Potatoes, raw	...	21.0
		Peas, raw	Peas, raw	...	4.5
		Carrots, raw	Carrots, raw	...	5.0
		Oil, vegetable	Oil, vegetable	...	2.5
			Seasoning mix	...	6.0
Chili con carne	Beef, raw	Beef, raw	Beef, raw	Beef, raw	42.25
	Water	Water	Water	Water	20.5
		Beans, dry	Beans, dry	Beans, dry	21.5
			Seasoning, mix	Seasoning, mix	3.75
				Tomato paste, light	12.0
Pork with potatoes	Pork, raw	Pork, raw	Pork, raw	...	26.0
	Water	Water	Water	...	28.9
		White sauce, dry	White sauce, dry	...	8.6
			Potatoes, raw	...	33.5
			Peppers, green	...	1.0
			Pimientos, canned	...	1.5
			Onions, dehydrated	...	0.5
Spaghetti with meat sauce	Beef, raw	Beef, raw	Beef, raw	Beef, raw	51.2
	Water	Water	Water	Water	14.2
		Spaghetti, dry	Spaghetti, dry	Spaghetti, dry	13.0
			Seasoning mix	Seasoning mix	2.6
				Tomato paste, light	19.0

of headspace was so large in comparison with the absolute volume of the products, any resulting error was considered to be insignificant.

RESULTS AND DISCUSSION

Four of the products (beef hash, beef with rice, chili con carne, and spaghetti with meat sauce) are made with raw ground beef and the first stage of each of these products consisted of beef and water, but in different proportions (Table I) and with somewhat different cooking procedures. The oxygen uptake data suggested that there was considerable difference between the products. Analysis of variance showed that there was a difference significant at the 1% level and that about 26.5% of the variance found was due to the different products and their interactions with storage time and temperature. Further analysis showed that there was no statistical difference for spaghetti with meat sauce and beef hash. However, chili con carne and beef with rice had significantly higher oxygen uptakes and beef with rice had a significantly higher uptake than chili. Review of the formulas and processing showed that the beef in spaghetti with meat sauce and beef hash was processed about the same amount, and the proportion of beef to water was about the same. However, with the other two products, the amount of water was greater and the meat was processed for a longer time, with the beef with rice being boiled for at least 5 min. Since the four products were processed at different times and from different lots of meat, these results cannot be taken as conclusive. Further

Table II. Oxygen Uptake of Stages Divided by Oxygen Uptake of Stage 1 Adjusted for Meat Present at the End of 12 Weeks at 100° F

Product	Stage 2	Stage 3	Stage 4
Beef hash	1.01	1.22	...
Beef stew	0.79	0.92	1.43
Beef with rice	0.79	0.42	0.33
Chicken and rice	0.31	1.39	0.56
Chicken stew	0.90	0.93	...
Chili con carne	0.91	0.85	1.83
Pork with potatoes	2.30	2.35	...
Spaghetti with meat sauce	0.96	0.73	4.15

work is indicated on the effect of cooking procedures on the oxygen uptake. However, it is evident that the meat is the most prooxidant ingredient of the combination foods studied, except possibly for tomato paste, when the quantity of the ingredients normally used in these types of foods is considered.

In order to establish differences in oxygen uptake which could be attributed to different ingredients, the oxygen uptakes of the stage 1's (meat and water) were used as 0 reference points. The percentage of meat dry solids in a given stage was considered to have the same relative oxygen uptake potential as in the corresponding stage 1. This uptake was subtracted from the observed uptake of the stage in question. A negative result meant that the oxygen uptake of the stage was less than should be expected from the quantity of meat solids present, a positive result that the uptake was more. For simplicity, the term antioxidant is used for negative results and prooxidant for positive. The differences found were subjected to analysis of variance and further analyzed for the percentage of variance due to the various factors by the method of Hicks (1956). In addition, the Duncan Multiple Range test was used to determine if there were significant differences between the uptake means for the stages of each product. Table II shows the oxygen uptake of the various stages divided by the oxygen uptake of stage 1 adjusted for the meat present stored at 100° F. Table III shows that the total variances due to stages and the stage X temperature stage X time interactions were substantial, indicating antioxidant or prooxidant activity. The variance due to the stage X temperature interaction was generally low, which would tend to indicate little effect of temperature on the antioxidant or prooxidant activity. However, the variance due to the stage

Table III. Analysis of Variance Significance and Components of Variance in Percent of Total Variance for Oxygen Uptake

	Beef hash		Beef stew		Beef with rice		Chicken and rice		Chicken stew		Chili con carne		Pork with potatoes		Spaghetti with meat sauce	
Factor	Sig	%	Sig	%	Sig	%	Sig	%	Sig	%	Sig	%	Sig	%	Sig	%
A (stage)	*a*	27.1	*a*	15.1	*a*	30.5	*a*	22.8	*a*	12.9	*a*	41.1	*a*	14.8	*a*	33.8
B (temp)	n.s.[c]	...	*a*	8.4	n.s.	...	*a*	2.8	*a*	1.8	*a*	1.0	*a*	21.3	*a*	2.1
C (time)	*a*	2.7	*a*	14.0	*a*	18.7	n.s.	...	*a*	8.5	*a*	7.8	*a*	19.1	*a*	7.3
AB	n.s.	...	*b*	4.1	n.s.	...	*a*	13.5	*b*	1.1	*a*	2.4	*a*	11.9	*a*	11.4
AC	*a*	15.9	*a*	14.3	*a*	17.5	*a*	26.5	*a*	7.3	*a*	40.0	*a*	8.2	*a*	37.0
BC	*a*	27.9	*a*	7.2	*a*	5.1	*a*	9.7	*a*	59.1	*a*	3.1	*a*	13.1	*a*	1.9
Remainder	...	26.4	...	36.9	...	28.2	...	24.7	*a*	9.3	...	4.6	...	11.6	*a*	6.5

[a] Significant at the 1% level. [b] Significant at the 5% level. [c] n.s. = not significant at the 5% level.

Table IV. Oxygen Activity of Components in the Eight Combination Meat Items

Ingredient	Product	Solids in formula dry basis %	Effect on oxygen uptake[b] 40° F	70° F	100° F	overall
Beans, kidney	Chili con carne	43.3	a[a]	a	a	a
Carrots, raw	Beef stew	1.9	n[a]	n	n	p[c]
Cream of onion soup	Beef with rice	18.3	n	n	a[d]	n
Oil, vegetable	Chicken and rice	15.6	n	a	a	a
Potatoes, raw	Beef hash	26.9	n	n	n	n
Rice, instant	Beef with rice	32.2	a	a	a	a
Rice, instant	Chicken and rice	28.2	n	n	a	n
Seasoning mix	Beef hash	10.0	p[a]	p	p	p
Seasoning mix	Beef stew	10.9	n	n	n	p[c]
Seasoning mix	Beef with rice	2.1	n	n	a[d]	n
Seasoning mix	Chicken and rice	9.0	n	p	p	p
Seasoning mix	Chicken stew	23.16	n	n	n	n
Seasoning mix	Chili con carne	8.36	n	n	n	n
Seasoning mix	Spaghetti with meat sauce	6.25	n	n	n	n
Spaghetti	Spaghetti with meat sauce	28.4	n	n	n	n
Tomato paste, light	Chili con carne	6.9	p	p	p	p
Tomato paste, light	Spaghetti with meat sauce	11.6	p	p	p	p
Vegetables	Beef stew	19.0	n	n	n	p[c]
Vegetables	Chicken stew	32.6	a	a	a	a
Vegetables	Pork with potatoes	26.2	n	n	p	n
White sauce	Pork with potatoes	30.97	p	p	p	p

[a] a = antioxidant; p = prooxidant; n = neutral. [b] Determined by the Duncan Multiple Range Test significant at the 5% level. [c] Individually, the components of stages 2, 3, and 4 of beef stew were statistically neutral. Combined in stage 4 they were significantly prooxidant. [d] Individually, cream of onion soup and seasoning mix in beef with rice were statistically neutral. Stored at 100° F, they combined to be significantly antioxidant.

X time interaction was generally substantial, showing that time affected the activity.

Table IV is a listing of the various ingredients in the eight products, the percentage they contributed to the total dry solids in the formula, and whether the antioxidant or prooxidant activity they contributed to the product was significant under the conditions of this study. In several cases inspection of the raw data would indicate that ingredients noted as neutral actually had antioxidant or prooxidant effects, since all or almost all individual readings had the same sign. However, the remainders (error factors) in this study were large enough to prevent them from showing up as significant.

Examination of Tables I and IV gives explanations for some of the differences found in the oxygen uptakes of the eight products studied previously (Tuomy *et al.*, 1970). It is evident that the oxygen uptake of a freeze-dried combination item is not simply the addition of the oxygen uptakes of individual ingredients. The rice in beef with rice acted as an antioxidant, while the other ingredients (cream of onion soup and seasoning mix) were either neutral or slightly antioxidant. Thus, beef with rice was the most stable of the eight items. On the other hand, tomato paste in spaghetti with meat sauce was highly prooxidant, while the other ingredients (spaghetti and seasoning mix) were essentially neutral. Thus, spaghetti with meat sauce was the least stable of the eight items.

There is some evidence in this study that the antioxidant or prooxidant activity of an ingredient varies, depending upon the other ingredients present. For example, with chicken and rice and beef with rice the rice component as shown by the stage 2 results in Table II did not produce equivalent results in the two products. Tomato paste does not have as much prooxidant effect on chili con carne as it does with spaghetti with meat sauce, even taking into account the differences in tomato paste contents.

While this study gives some evidence as to why there were substantial differences in the oxygen uptakes of the eight items and which ingredients could be classified as antioxidant or prooxidant, it is evident that further work is needed on the mechanisms involved. Since there is some evidence that a given ingredient acts differently with different ingredients, results from an empirical study of one product cannot be depended upon for transfer to another product.

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