AN INVESTIGATION INTO THE EFFECTIVENESS OF VARIOUS ANTOXIDANTS ON THE PRESERVATION OF FRESH GROUNDNUT OIL (FOOD GRADE) B.P.

By G. A. Birchall and R. I. Felix

From the Distillers Company (Biochemicals) Limited, Speke, Liverpool

Received May 23, 1960

Of several compounds examined the n-propyl, n-octyl and n-dodecyl esters of gallic acid alone or in combination with certain chelating agents are the most effective preservatives of groundnut oil.

Vegetable oils will maintain their freshness only for a limited period and upon storage progressively deteriorate, developing a detectable rancidity.

Rancidity may be induced by a number of factors, but the most frequent is spontaneous oxidation of the double bonds by atmospheric oxygen which leads to the formation of organic peroxides.

Reducing agents are effective against oxidising agents and atmospheric oxygen and antoxidants are effective against atmospheric oxygen only. It has been suggested that antoxidants act by disrupting the chain reactions which lead to the production of peroxides[1], and they are of value only when added to oils which have not already deteriorated. In addition, chelating agents such as citric acid and acetone dicarboxylic acid, will complex with contaminating trace metals such as iron or copper which catalyse oxidation, and consequently enhance the action of some antoxidants. Furthermore, the activity of a combination of certain antoxidants is greater than when each is present separately.

An ideal antoxidant should possess the following characteristics.

No toxicity and no irritant properties even after prolonged usage.

No influence on colour, taste or odour of the substrate.

Ready solubility in the substrate.

Effectiveness in low concentration.

Be chemically inactive with other constituents and neutral in reaction.

Be non-volatile thus ensuring no fall in concentration after prolonged storage.

Experimental

Determination of Peroxides

The method was essentially that described by Heaton and Uri[2] but the period of nitrogen sparging and the reaction time was reduced.

Reagents. Solvent solution. The solution consists of two volumes of glacial acetic acid B.P. and one volume of carbon tetrachloride, and is stored in a closed container and used within three days of preparation. *Saturated solution of potassium iodide.* A saturated solution of potassium iodide in distilled water. 0·002N *Sodium thiosulphate.* Freshly prepared. *Starch indicator.* 1 per cent w/v soluble starch in distilled water.

Method of Peroxide Determination

Six boiling tubes are arranged in series and connected by a reducing valve to a source of oxygen-free nitrogen. Accurately weighed samples

TABLE I

EVALUATION OF ANTOXIDANTS IN SAMPLES OF GROUNDNUT OIL (FOOD GRADE) B.P. STORED AT 37° RECORDING PEROXIDE VALUE AGAINST STORAGE INTERVAL IN DAYS

Antoxidant	w/v per cent	Sample of oil	Storage interval in days																								
			0	6	11	14	26	27	28	30	41	46	50	55	66	67	73	74	82	90	91	92	105	122	134	144	323
1. Propyl gallate	0·01	A	4·2	5·5	—	—	—	6·6	—	—	8·8*	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
2. Propyl gallate	0·015	A	4·5	5·3	—	—	—	6·2	—	—	7·3	—	—	—	—	—	—	—	9·9	—	—	—	11·3	—	12·1	—	—
3. Propyl gallate	0·02	A	4·2	5·6	—	—	—	5·9	—	—	7·8	—	—	—	—	—	—	—	8·6	—	—	—	10·7	—	11·2	—	—
4. Propyl gallate + Citric acid	0·015 0·01	A	4·1	5·9	—	—	—	5·7	—	—	7·1	—	—	—	—	—	—	—	8·6	—	—	—	10·4	—	10·1	—	—
5. Octyl gallate	0·01	A	4·2	6·7	—	—	—	7·8	—	—	11·5*	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
6. Octyl gallate	0·015	A	4·3	5·8	—	—	—	6·7	—	—	8·5	—	—	—	—	—	—	—	10·1	—	—	—	11·1	—	13·8	—	—
7. Octyl gallate + Citric acid	0·015 0·01	A	4·5	5·7	—	—	—	5·8	—	—	7·7	—	—	—	—	—	—	—	8·9	—	—	—	11·7	—	12·7	—	—
8. Control	—	A	4·8	7·9	—	—	—	12·4	—	—	19·0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
9. Dodecyl gallate	0·01	B	2·4	—	—	—	—	—	—	6·5	—	—	—	7·4	—	—	—	—	—	—	—	6·7	—	10·0	—	—	30·8
10. Dodecyl gallate	0·015	B	4·7	—	—	—	—	—	—	6·0	—	—	—	6·1	—	—	—	—	—	—	—	9·8	—	10·6	—	—	17·3
11. Dodecyl gallate + Citric acid	0·015 0·01	B	2·9	—	—	—	—	—	—	7·7	—	—	—	7·0	—	—	—	—	—	—	—	7·5	—	9·4	—	—	17·5
12. Propyl gallate + Citric acid	0·02 0·01	B	2·8	—	—	—	—	—	—	8·5	—	—	—	5·4	—	—	—	—	—	—	—	7·1	—	7·2	—	—	13·0
13. Butylated hydroxy toluene + Butylated hydroxy anisole	0·01 0·01	B	4·9	—	—	—	—	—	—	7·2	—	—	—	7·6	—	—	—	—	—	—	—	12·5	—	21·8	—	—	—
14. Butylated hydroxy toluene + Butylated hydroxy anisole	0·02 0·02	B	6·0	—	—	—	—	—	—	8·1	—	—	—	8·6	—	—	—	—	—	—	—	29·3	—	—	—	—	—
15. Butylated hydroxy anisole + Propyl gallate + Citric acid	0·02 0·006 0·004	B	3·4	—	—	—	—	—	—	6·0	—	—	—	6·9	—	—	—	—	—	—	—	16·4	—	21·2	—	—	—
16. Propyl gallate	0·02	B	3·0	—	—	—	—	—	—	5·2	—	—	—	—	—	—	—	—	—	—	—	5·4	—	6·5	—	—	14·2
17. Control	—	B	5·9	—	—	—	—	—	—	15·2	—	—	—	16·6	—	—	—	—	—	—	—	>30	—	—	—	—	—
18. Butylated hydroxy anisole	0·01	C	6·2	—	—	7·2	12·4*	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
19. Butylated hydroxy anisole	0·015	C	7·3	—	—	10·4	14·8*	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
20. Butylated hydroxy anisole	0·02	C	7·1	—	—	11·6	13·9*	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
21. Butylated hydroxy toluene	0·01	C	7·6	—	—	8·8	10·1*	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
22. Butylated hydroxy toluene	0·015	C	7·4	—	—	7·8	8·7	—	—	—	—	9·2	—	—	—	26·1	—	—	—	—	—	—	—	—	—	—	—
23. Butylated hydroxy toluene	0·02	C	7·9	—	—	9·1	9·4	—	—	—	—	7·9	—	—	—	15·3	—	—	—	16·2	—	—	—	—	—	—	—
24. Control	—	C	6·7	—	—	12·1	14·2	—	—	—	—	20·3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
25. Acetone dicarboxylic acid	0·02	D	0·9	—	4·2	—	—	—	11·3	—	—	—	11·8	—	16·6	—	18·0	21·7	—	—	—	—	—	—	—	—	—
26. Propyl gallate	0·02	D	0·5	—	2·4	—	—	—	1·8	—	—	—	1·4	—	2·1	—	—	1·6	—	—	1·4	—	—	—	—	2·7	—
27. Propyl gallate + Acetone dicarboxylic acid	0·02 0·02	D	1·7	—	2·0	—	—	—	3·8	—	—	—	3·0	—	—	—	1·1	3·4	—	—	2·8	—	—	—	—	3·5	—
28. Dodecyl gallate	0·02	D	0·8	—	1·8	—	—	—	2·2	—	—	—	1·9	—	—	—	—	3·4	—	—	1·8	—	—	—	—	2·8	—
29. Control	—	D	1·2	—	1·8	—	—	—	3·1	—	—	—	6·4	—	4·6	—	10·5	12·5	—	—	16·6	—	—	—	—	31·5	—

* Discontinued, ineffective at 60°.

of the oil (about 1 g.) are introduced into tubes 2–5. Tube 1 contains only solvent solution, to saturate the nitrogen stream. 20·0 ml. of the solvent solution is added and nitrogen bubbled through at a constant rate for 30 minutes. 0·5 ml. of potassium iodide solution is introduced into tubes 2–6. The nitrogen is passed for a further five minutes to ensure complete mixing of the solutions. The tubes are then sealed and stored in the dark for 30 minutes. The contents of tubes 2–6 are transferred into conical flasks containing 30 ml. of distilled water and each titrated with 0·002N sodium thiosulphate using starch as indicator. A "blank" determination is carried out on tube 6. The peroxide value is determined by the following equation, titre of sample–titre of blank/wt. of sample in g.

Experimental Method

The additives were dissolved in groundnut oil, 50 ml. of which was put into 2 oz. open glass jars stored at 37° and 60°. The peroxide values were determined at intervals.

Initial determinations were made on all samples and a sample of untreated oil was used as the control. Accelerated tests at 37° and 60° were also made.

Four samples of different batches of oil, obtained from the same supplier were examined.

Antoxidants Examined

The antoxidants examined are those permitted for use in foodstuffs.[3] They were n-propyl gallate, n-octyl gallate, n-dodecyl gallate, butylated hydroxy anisole, butylated hydroxy toluene, combinations of the above, and combinations of the above with citric acid and acetone dicarboxylic acid.

Results

The results have been tabulated under their storage conditions. Table I records the peroxide values obtained at 37° and Table II at 60°.

The quantitative work was stopped when undesirable rancidity was evident. This corresponded to a peroxide value of about 20.

Discussion

Of the antoxidants examined, the esters of gallic acid, alone or in combination with citric acid or acetone dicarboxylic acid, are the most effective in delaying the onset of oxidative rancidity. Propyl gallate 0·02 per cent w/v alone is more efficient than dodecyl gallate 0·02 per cent w/v alone. However, the gallate moiety is the active group and the use of an identical concentration of the higher molecular weight ester on a weight basis, results in a lower content of the gallate radical and consequently, antoxidant activity.

Acetone dicarboxylic acid alone appears to accelerate the rate of oxidation and no marked antoxidant activity is evident even in combination with propyl gallate.

TABLE II

EVALUATION OF ANTOXIDANTS IN SAMPLES OF GROUNDNUT OIL (FOOD GRADE) B.P. STORED AT 60° RECORDING PEROXIDE VALUE AGAINST STORAGE INTERVAL IN DAYS

Antoxidants	w/v per cent	Sample of oil	Storage interval in days																						
			0	2	3	5	6	7	10	13	17	19	20	21	25	26	31	35	40	47	52	54	55	66
1. Propyl gallate	0·01	A	4·2	5·3	—	—	5·3	6·6	6·9	—	—	10·5	—	—	—	13·5	—	21·8	—	—	—	—	—	—
2. Propyl gallate	0·015	A	4·5	5·9	—	—	—	6·7	6·8	—	—	7·8	—	—	—	11·7	—	13·9	16·2	17·1	—	—	33·8	—
3. Propyl gallate	0·02	A	4·2	5·3	—	—	—	6·6	6·7	—	—	8·1	—	—	—	18·6	—	13·3	17·3	14·7	—	—	20·6	—
4. Citric acid + Propyl gallate	0·01 + 0·015	A	4·1	5·5	—	—	—	6·4	6·4	—	—	8·7	—	—	—	10·4	—	13·0	14·4	13·6	—	—	16·1	—
5. Octyl gallate	0·01	A	4·2	5·8	—	—	—	7·1	7·6	—	—	9·5	—	—	—	12·8	—	17·8	27·7	—	—	—	—	—
6. Octyl gallate	0·015	A	4·3	4·9	—	—	—	6·1	7·6	—	—	9·4	—	—	—	12·4	—	17·5	19·8	—	—	—	—	—
7. Octyl gallate + Citric acid	0·015 + 0·01	A	4·5	4·9	—	—	—	6·1	4·2	—	—	9·8	—	—	—	11·4	—	14·7	16·4	19·1	—	—	—	—
8. Control	—	A	4·8	7·7	—	—	—	14·0	16·5	21·3	—	—	—	—	—	—	—	—	—	—	—	—	—	—
9. Butylated hydroxy anisole	0·01	C	6·2	—	—	—	22·0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
10. Butylated hydroxy anisole	0·015	C	7·3	—	—	—	20·7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
11. Butylated hydroxy anisole	0·02	C	7·1	—	—	—	22·0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
12. Butylated hydroxy toluene	0·01	C	7·6	—	—	—	—	—	—	13·2	—	—	18·3	—	32·1	—	—	—	—	—	—	—	—	—
13. Butylated hydroxy toluene	0·015	C	7·4	—	—	—	—	—	—	12·1	—	—	17·1	—	23·4	—	—	—	—	—	—	—	—	—
14. Butylated hydroxy toluene	0·02	C	7·9	—	—	—	—	—	—	11·2	—	—	17·1	—	20·1	—	—	—	—	—	—	—	—	—
15. Control	—	C	6·7	—	—	—	17·7	—	—	26·2	—	—	—	—	—	—	—	—	—	—	—	—	—	—
16. Acetone dicarboxylic acid	0·02	D	0·9	—	4·3	15·3	—	14·2	36·8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
17. Propyl gallate	0·02	D	0·5	—	2·3	2·4	—	2·6	2·5	—	4·7	—	—	4·8	—	—	9·2	—	11·0	—	16·0	16·4	—	53·0
18. Propyl gallate + Acetone dicarboxylic acid	0·02 + 0·02	D	1·7	—	2·3	3·0	—	3·2	4·8	—	7·0	—	—	13·2	—	—	9·7	—	13·3	—	—	—	—	—
19. Dodecyl gallate	0·02	D	0·8	—	2·1	3·3	—	3·2	4·4	—	5·2	—	—	3·8	—	—	11·5	—	14·6	—	>100	—	—	—
20. Control	—	D	1·2	—	4·8	5·0	—	10·8	14·1	—	>100	—	—	—	—	—	—	—	—	—	—	—	—	—

Butylated hydroxy anisole and butylated hydroxy toluene, at the concentrations used, either alone or in combination are much less effective than the gallates, butylated hydroxy toluene having a greater activity than butylated hydroxy anisole which has little effect.

Acknowledgements. The authors wish to thank Miss E. Kelly and Miss B. Jepson for technical assistance.

REFERENCES

1. Shotton, *Antoxidants, Pharm. J.*, October 2, 1954.
2. Heaton and Uri, *J. Sci. Food Agric.*, 1958, **9**, 781.
3. Stat. Inst. 1958, No. 1454—The Antioxidant in Food Regulations—1958.

After Mr. Felix presented the paper there was a DISCUSSION.