4. Foreman, H. D., and Brown, J. B., Oil and Soap, *21*, 183-7 (1944).
5. Gascard, A., and Damoy, G., Compt. Rend., *177*, 1224, 1442 (1923).
6. Haskell, T. H., Ph.D. Dissertation, Ohio State University (1949).
7. Hill, U. T., Anal. Chem., *19*, 932 (1947).
8. Ikuta, H., Analyst, *59*, 161 (1934).
9. Khan, N. A., Ph.D. Dissertation, Ohio State University (1950).
10. Knight, B. H., Anal. Chem., *19*, 359 (1947).
11. Koonce, S. D., Ph.D. Dissertation, Ohio State University (1943).
12. Koonce, S. D., and Brown, J. B., Oil and Soap, *21*, 231-4 (1944).
13. Koonce, S. D., and Brown, J. B., Oil and Soap, *22*, 217-8 (1945).
14. Kreger, D. R., Rec. Trav. Botan. Neerland., *41*, 603-736 (1949).
15. McLoud, E. S., personal communication.
16. Ogg, C. L., Porter, W. L., and Willits, C. O., Ind. Eng. Chem., Anal. Ed., *17*, 394 (1945).
17. Schuette, H. A., and Baldinus, J. G., J. Am. Oil Chem. Soc., *26*, 651 (1949).
18. Siggia, S., "Quantitative Organic Analysis via Functional Groups," Wiley, New York (1949).
19. Smith, F. A., and Brown, J. B., Oil and Soap, *22*, 277-83 (1945).
20. Story-Maskelyne, N., J. Chem. Soc. (London), *22*, 87 (1869).
21. Swern, Daniel, and Knight, H. B., J. Am. Oil Chem. Soc., *26*, 366 (1949).
22. Warth, A. H., "The Chemistry and Technology of Waxes," Reinhold, New York (1947).

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Factors Affecting the Stability of Crude Oils of 16 Varieties of Peanuts

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MARKED differences have been noted in the stabilities of oil of raw peanuts and roasted peanut products. Crawford and Hilditch summarized (3) information reported on composition of groundnut oils by various workers during the past 30 years. They called attention to the extreme differences from about 65% to 40% in oleic acid content and from about 18% to nearly 40% in linoleic acid content of such oils and commented that these differences might be expected to influence the relative susceptibility of the oils to oxidative rancidity. Pickett and Holley have reported (17) a greater development of peroxides in Spanish peanuts than in either Runner or Virginia peanuts on aeration and heating of the nuts at 98°C. They noted that tocopherols and other substances which affect the stability of vegetable oils have been found in peanut oil and called attention to the findings of Jamieson *et al.* (10) that oil in Spanish peanuts contained slightly less olein and more linolein than that from Virginia peanuts. Higgins *et al.* reported (8) a wide variation in the linolein and olein contents of some selected strains of Spanish and Runner peanuts. Examination of their data shows that, as a group, runner type peanuts are lower in percentage of linolein than the bunch type of peanuts.

No information has been published in which composition and stability have been determined simultaneously for crude oils from known varieties of peanuts for the purpose of relating stability to composition. In the present work the oils of 16 varieties of raw shelled peanuts, including both the bunch and runner types, have been analyzed for initial peroxide value and stability, tocopherol content, and saturated, linoleic, and oleic glyceride contents in order to determine factors that may affect the stability of crude peanut oil.

Experimental

Analysis for Moisture and Oil Content. The moisture and oil contents of the peanuts were determined by method Ab 3-49 of "The Official and Tentative Methods of the American Oil Chemists' Society" (1). Results are shown in Table I.

Extraction of Oil from Peanuts. A 600-gram sample of each variety of peanuts with the seed coat intact was sliced in a Henry slicer[2] and extracted with *ca.* 1,200 ml. of commercial pentane (Skellysolve F)[2] at room temperature. The extracted seeds were dried at room temperature, reduced to a powder and reextracted with *ca.* 1,200 ml. of pentane. The oil was freed of solvent by heating the miscella under vacuum on a steam bath and subsequently by stripping with hydrogen under vacuum at temperatures of not more than 60°C. The extracted oils were stored under hydrogen in glass-stoppered bottles at —20°C.

TABLE I

Analysis of Peanuts

Sample No.	Variety[a]	Moisture	Oil	
			As is basis	Oven-dry basis
		%	%	%
1	Spanish 146[b]	6.75	47.72	51.17
2	Spanish 205[b]	6.03	49.96	53.17
3	Spanish P. I. 121070[b]	6.20	49.74	53.03
4	Spanish 18-38[b]	6.13	50.06	53.33
5	Spanish 13-10[b]	6.08	50.26	53.89
6	Improved Spanish 2B[b]	6.17	49.72	52.99
7	Virginia-Ga. Hybrid 119-24[c]	7.10	43.22	46.52
8	Virginia-Holland Station Runner[c]	6.99	44.00	47.31
9	Virginia Bunch, Large[b]	6.79	46.76	50.17
10	Virginia Jumbo J-11-L[c]	7.14	43.69	47.05
11	Virginia P. I. 124681[c]	7.00	45.71	49.15
12	Virginia-Holland Station Jumbo[c]	6.89	43.94	47.17
13	Dixie Runner[c]	5.88	49.46	52.55
14	Runner 230-118[c]	5.86	51.09	54.27
15	N. C. Runner 56-15[c]	6.10	49.04	52.23
16	Runner-Ga. Hybrid 199-22-A-2[c]	5.81	49.95	53.03

[a] Field and handling procedures were in conformity with practices generally followed.
[b] Bunch type.
[c] Runner type.

Methods of Oil Analysis. Iodine values were determined by the American Oil Chemists' Society's modification of the Wijs method (1). Thiocyanogen values were determined by the method described by Lambou and Dollear (12, 13).

The percentages of olein, linolein, and saturated constituents expressed as glycerides were calculated

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[2] The mention of a trade name in this article is for identification and implies no endorsement or recommendation by the Department of Agriculture for the product.

as prescribed in method Cd 2-38 of the "Official and Tentative Methods of the American Oil Chemists' Society" (1).

Method for Stability. Autoxidative stability was determined by the active oxygen method (2, 7, 11) using the procedure described by Moore and Bickford (14) and peroxide values are reported as milliequivalents of peroxide oxygen per kilogram of oil. Because there was considerable variation in the initial peroxide values of the oils, it seemed advisable to estimate the AOM keeping qualities of the oils by extrapolation of the peroxide accumulation curves to a point representing zero peroxide content to afford an approximate comparison on the same basis.

Methods of Tocopherol Analysis. Accuracy and precision in the analysis of tocopherol mixtures by the methods of Fisher (5) and Emmerie and Engel (4, 20) require a prior knowledge as to which of the four known tocopherols are present and also an approximation of the relative distribution of these tocopherols in their mixtures. This information is necessary because Fisher's method for determination of γ-tocopherol is inapplicable to oils containing β- or δ-tocopherols and also because in the calculation of the total tocopherol content the method of Emmerie and Engel requires the application of different constants depending upon the nature of the tocopherols present. In addition, the oils assayed by the above-mentioned methods may require treatment with sulfuric acid according to Parker and McFarlane (16) for the removal of interfering substances. While the above mentioned methods can also be used for the qualitative detection of the various tocopherols present in an oil, verification is obtained by the method of Quaife (19) which, although tedious, permits the identification as well as the assay of these tocopherols.

Tocopherol concentrates from six samples, two each of the oils from the Runner, Spanish, and Virginia peanuts, were obtained by distillation of 2 grams of each oil for 2 hours at a temperature of 215-220°C. and at a pressure of 1 micron (18). These samples were analyzed for non-α-tocopherols by the Quaife nitrosation method (19).

Analyses were made by the Emmerie and Engel method (4) for total tocopherols and by the Fisher nitric acid oxidation method (5) for γ-tocopherol on the 16 oils as prepared and also on those oils following treatment according to Parker and McFarlane.

The α-tocopherol contents were based upon the differences found between the total tocopherol contents and the γ-tocopherol contents of the oils which were treated with the Parker and McFarlane reagent.

Discussion of Tocopherol Analyses

The results of the nitrosation treatment of the tocopherol concentrates show that γ-tocopherol was the only non-α-tocopherol present in any of the six samples selected from three varieties.

Treatment of the oils by the method of Parker and McFarlane produced a lowering of the apparent total tocopherol content of only 0-7.5% as determined by the Emmerie and Engel method, which is within the limits of experimental error. It was further evident that on extension of the reaction time from 2½ to 10 minutes in the determination of total tocopherol content that δ-tocopherol was not present. Stern *et al.* (20) had shown that there is an increase of *ca.* 30% in the apparent tocopherol content of an alcohol solution of pure δ-tocopherol and very slight increases in the apparent tocopherol content of solutions of pure α-, β-, or γ-tocopherols on such an extension of the reaction time.

Under the conditions described by Fisher for the assay of γ-tocopherol (5) the red color formed when nitric acid reacts with β-tocopherol fades rapidly while the red color formed by reaction with γ-tocopherol increases slightly in intensity on standing. In all cases extension of the usual reaction times with Fisher reagents by 1 and 7 minutes resulted in slight gradual increases in the intensities of the colors formed indicating the absence of β-tocopherol. These results support conclusions of other workers (5, 21) that β-tocopherol does not occur in peanut oil.

Decreases of 5-35% in the apparent γ-tocopherol contents as determined by the Fisher method were observed on the samples that received the Parker and McFarlane treatment. It has been established that such treatment of substrates containing known quantities of pure γ-tocopherol does not result in loss of tocopherol. Fisher reported (5) that refined peanut oils show no decrease in total or γ-tocopherols on treatment with the Parker and McFarlane reagent. These results are reported to call attention to the necessity for treating crude peanut oils with this reagent prior to use of the Fisher method.

Results and Conclusions

Data on the characteristics, fatty acid composition, contents of α- and γ-tocopherols, together with the determined and extrapolated AOM keeping qualities of the crude oils from the different varieties of peanuts are presented in Table II. The relationship of fatty acid composition and content of antioxidants to the stabilities of the various oils is considered below.

There appears to be a correlation between the linoleic acid contents and stabilities of the oils included in this study. Oils of the Spanish, Virginia, and Runner peanuts had average linoleic acid contents of 34.2, 29.6, and 22.0% and average extrapolated stabilities of 31, 36, and 43 AOM hours, respectively. From the data in Table II and from these averages it will be seen that the oils from Runner peanuts contain less linoleic acid and have a correspondingly higher order of stability than oils of either the Spanish or Virginia peanuts. Furthermore, in general, oils of the Virginia peanuts contain less linoleic acid and are more stable than oils of the Spanish peanuts. In addition, a trend toward increasing stability with decreasing linoleic acid content is discernible among the individual oils. Fisher and co-workers (6) have previously observed a similar phenomenon with regard to the relationship between linoleic acid contents and stabilities of various refined vegetable oils.

Antioxidants. α-, β-, γ-, and δ-tocopherols, the usual antioxidants in vegetable oils, show increasing antioxygenic activity in the order named (15). Only α- and γ-tocopherols occur in the oils under consideration, and in all cases the ratio of α- to γ-tocopherols is approximately one. Therefore only the relation of total tocopherol contents to the stabilities of the oils needs to be considered.

Although the higher tocopherol contents of the oils of Runner peanuts may be a factor contributing to the high order of stability of these oils, in general,

TABLE II

Analysis, Composition, and Stability of Peanut Oils

Sample No.	Initial peroxide value[a]	Stability–AOM hours		Thiocyanogen value	Iodine value	Fatty acid composition			Tocopherol content		
		Test[b]	Extrapolated[c]			Linolein	Olein	Saturated glycerides	Total[d]	α	γ[e]
						%	%	%	%	%	%
1S	5	26.5	29	71.5	101.6	37.0	43.5	19.5	0.039	0.021	0.018
2S	2	30.0	32	71.3	98.2	33.1	47.6	19.3	0.041	0.024	0.019
3S	7	28.0	32	70.7	98.5	34.1	45.7	20.2	0.038	0.023	0.015
4S	4	26.0	29	70.7	98.9	34.6	45.2	20.2	0.043	0.026	0.017
5S	2	30.0	32	70.3	98.4	34.5	44.9	20.6	0.041	0.025	0.016
6S	4	30.5	34	72.0	98.0	31.9	49.7	18.4	0.039	0.024	0.015
7V	5	28.5	32	74.9	101.3	32.4	52.5	15.1	0.046	0.026	0.020
8V	3	32.5	36	75.5	99.1	28.9	57.0	14.1	0.044	0.025	0.019
9V	7	30.0	36	73.8	95.4	26.4	57.7	15.9	0.043	0.023	0.020
10V	5	30.5	35	73.8	98.3	30.0	53.8	16.2	0.041	0.025	0.016
11V	2	41.0	44	73.4	97.6	29.6	53.7	16.7	0.041	0.025	0.016
12V	3	31.0	36	73.3	98.1	30.4	52.9	16.7	0.041	0.026	0.015
13R	2	48.0	49	73.8	90.2	19.9	64.7	15.4	0.048	0.030	0.018
14R	3	36.5	44	74.4	91.8	21.2	64.2	14.6	0.048	0.029	0.019
15R	4	32.5	38	74.5	94.1	23.9	61.3	14.8	0.052	0.029	0.023
16R	4	36.5	41	73.9	92.8	23.0	61.5	15.5	0.053	0.030	0.023

[a] Milliequivalents of peroxide per kilogram of oil.
[b] Time required by oil to attain a peroxide content of 100 milliequivalents per kilogram of oil during aeration at 97.8°C. with an air flow of 2.33 ml./sec.
[c] Obtained by extrapolation of peroxide accumulation curves to a peroxide value of zero.
[d] Determined by the Parker and McFarlane modification of the Emmerie and Engel method using a 2½-min. reaction time.
[e] Determined by Fisher method using Parker and McFarlane treatment.
R—Runner peanuts.
S—Spanish peanuts.
V—Virginia peanuts.

variations in total tocopherol contents are probably not large enough to be considered significant.

The high stability of oil number 11 cannot be explained on the basis of either fatty acid composition or tocopherol content. It appears therefore that some non-tocopherol antioxidant is present. In this connection it may be noted that Hilditch and Paul (9) isolated from defatted peanut meal a non-tocopherol material which had antioxygenic properties. In addition, Fisher and co-workers (6) have reported that a freshly refined, bleached, and deodorized peanut oil having a linoleic acid content of 32.8%, and α-tocopherol content of 0.023% and a γ-tocopherol content of 0.023% had a stability of 16.5 AOM hours. Of the crude oils included in the present study, samples 2 and 7 had linoleic acid contents of 33.1 and 32.4%, α-tocopherol contents of 0.024 and 0.026%, γ-tocopherol contents of 0.019 and 0.020%, respectively, each had a stability of 32 AOM hours. While the compositions of these two series of oils are practically identical, there is a twofold difference in stabilities. On the basis of this and other similar observations it may be inferred that crude peanut oils contain some powerful antioxidants and/or synergists, which are partially or wholly removed during refining operations. Further work is in progress to determine what effect, if any, other minor components of crude oils may have on their relative stabilities.

Rancidity has long been recognized as a troublesome factor in the marketing of roasted peanut products, and workers have reported (17) that roasted Spanish peanuts display a greater susceptibility to development of rancidity than roasted Virginia or Runner peanuts. Fisher and co-workers (6) have reported that there is a reciprocal relationship between the linolein contents and the stabilities of various hydrogenated peanut oils. The present work directs attention to an analogous relationship between the composition and stability of crude peanut oils and to the appreciable differences in linolein contents and stabilities of the crude oils of Spanish, Virginia, and Runner peanuts.

It is suggested on the basis of the work reported that products made from peanuts containing oils of relatively low linolein content and of high stability would have an increased shelf-life.

Furthermore information developed in this work points to the desirability of obtaining further information regarding composition of peanuts and stability of oil. A possible solution to the problem of extending the usefulness of peanut products through increased stability is to devote more attention to the relationship between composition and quality of products. Varieties have been shown to have significant differences in composition, and undoubtedly different conditions of growth, handling, or storage of any given variety are reflected in changes in composition.

Summary

The relation between fatty acid compositions, tocopherol contents, and autoxidative stabilities of a series of 16 crude oils from different varieties of peanuts has been investigated. It was found that the relative linoleic acid content of the oils is one of the major factors affecting the variations in the stabilities of the oils tested. With the exception of the oils from Runner peanuts the tocopherol compositions of the oils were not found to vary significantly, either in the nature and distribution of individual tocopherols, or in total tocopherol contents. The enhanced stability of the oils from the Runner peanuts may be due in part to the higher tocopherol contents of these oils. There is some evidence that crude peanut oils contain some non-tocopherol antioxidant and/or synergist.

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REFERENCES

1. American Oil Chemists' Society, Official and Tentative Methods, rev. to January, 1951.
2. Committee on Analysis of Commercial Fats and Oils, Ind. Eng. Chem., Anal. Ed., *17*, 336-340 (1945).
3. Crawford, R. V., and Hilditch, T. P., J. Sci. Food and Agriculture, *1*, 372-379 (1950).
4. Emmerie, A., and Engel, Chr., Rec. trav. chim., *57*, 1351-1355 (1938).

5. Fisher, G. S., Ind. and Eng. Chem., Anal. Ed., *17*, 224-227 (1945).

6. Fisher, G. S., Bickford, W. G., and Dollear, F. G., J. Am. Oil Chem. Soc., *24*, 379-382 (1947).

7. Fore, S. P., Moore, R. N., and Bickford, W. G., J. Am. Oil Chem. Soc., *28*, 73-74 (1951).

8. Higgins, B. B., Holley, K. T., Pickett, T. A., and Wheeler, C. D., Georgia Experiment Station, Bulletin 213, June, 1941.

9. Hilditch, T. P., and Paul, S., J. Soc. Chem. Ind., *58*, 21-24 (1939).

10. Jamieson, G. S., Baughman, W. F., and Brauns, D. H., J. Am. Chem. Soc., *43*, 1372 (1921).

11. King, A. E., Roschen, H. L., and Irwin, W. H., Oil and Soap, *10*, 105-109 (1933).

12. Lambou, M. G. and Dollear, F. G., Oil and Soap, *22*, 226-232 (1945).

13. Lambou, M. G., and Dollear, F. G., Oil and Soap, *23*, 97-101 (1946).

14. Moore, R. N., and Bickford, W. G., J. Am. Oil Chem. Soc., *29*, 1-4 (1952).

15. Olcott, H. S., and Emerson, O. H., J. Am. Chem. Soc., *59*, 1008-1009 (1937).

16. Parker, W. E., and McFarlane, W. D., Can. J. Research, *18B*, 405-409 (1940).

17. Pickett, T. A., and Holley, K. T., J. Am. Oil Chem. Soc., *28*, 478-479 (1951).

18. Quaife, M. L., and Harris, P. L., Ind. and Eng. Chem., Anal. Ed., *18*, 707-708 (1946).

19. Quaife, M. L., J. of Biol. Chem., *175*, 605-617 (1948).

20. Stern, M. H., and Baxter, J. G., Ind. and Eng. Chem., Anal. Ed., *19*, 902-905 (1947).

21. Weisler, Leonard, Robeson, Charles D., and Baxter, James G., Anal. Chem., *19*, 906-909 (1947).

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Report of Cellulose Yield Committee, 1952-53

DURING the past year three sets of second-cut linters were sent out for yield analyses. High, medium, and low yield linters were used. The following table gives the averages of the analyses for each mill and overall average for all mills.

Lab. No.	No. of tests	A Linter	B Linter	C Fiber	Overall avg. for the year
1	3	79.4	75.1	71.1	75.2
2	3	78.5	74.4	70.3	74.4
3	3	79.0	75.1	70.9	75.0
4	3	79.0	75.0	70.9	74.9
5	3	78.9	74.6	70.9	74.8
6	3	79.7	75.0	71.2	75.3
7	3	78.8	74.5	70.5	74.5
8	3	80.0	75.6	71.3	75.6
9	3	78.9	74.6	70.9	74.8
10	3	78.5	74.5	70.7	74.6
11	3	79.2	74.0	69.7	74.3
Average		79.1	74.8	70.8	74.9

On the average the checks were very good. At times some of the laboratories were off but were quickly corrected after results were returned to them.

Recommendations. It is recommended samples still be sent out for check analyses. We believe that sending out these samples periodically is the best way to show the laboratories that their equipment is in good working shape.

E. C. AINSLIE
W. S. HUDE
R. E. KNIPPLE
P. D. CRETIEN
E. H. TENENT
L. N. Rogers, chairman

Report of the Referee Board, 1952-53

FOR the year ending May 31, 1953, 36 Referee Chemists were appointed. Thirty-two were renewals, and 26 were given certificates on cottonsed, oil cake and meal, and fatty oils. Ten held restricted certificates either from choice of application or by the discretion of the Board. The chemists are located in 10 states and 23 cities and represent 20 different laboratory organizations.

The established policies of other Boards have been closely followed, but two new suggestions were adopted also, *viz:*

1. When possible, we urge any prospective new applicants to meet with the Board at the Spring Meeting. This may be formal or informal as desired, but it will greatly aid the Board in its decisions.
2. The laboratory of new applicants will be regularly inspected either by a member of the Referee Board or by some qualified member of the Society.

The Board again strongly urges any prospective applicants to participate in the Smalley Check Sample Program and to compete and report their results according to schedule. Performance on the check sample work has considerable bearing on our decisions.

Many inquiries were received during the year, relative to certification, and were handled as expeditiously as possible.

R. R. KING
J. R. MAYS JR.
A. S. RICHARDSON
E. M. JAMES
R. W. BATES, chairman