allow them to be dried directly to the optimum moisture for solvent extraction.

Summary

A new method for the removal of skins from peanut kernels by water-treatment, drying, and blanching in a standard split-nut blancher has been developed on a pilot-plant scale. Optimum conditions for approximately 98% skin removal from U. S. No. 1 shelled Spanish peanuts by this method are water-treatment at room temperature, to gain not less than 20%, drying with forced circulated air at 120° to 125°F. to approximately 4.5% moisture in the peanuts, and blanching. The lipids and protein losses resulting from the water-washing action on the kernels were relatively low and less than those losses obtained by lye treatment of the kernels. The method however did not give satisfactory results with either shelled U. S. No. 2 or oil mill stock kernels.

Meal prepared by hexane extraction of de-skinned (98%) water-treated U. S. No. 1 kernels had color and flavor characteristics superior to other hexane solvent-extracted peanut meals for food utilization. Protein prepared from this meal had a light color equal to that produced from peanut kernels treated with 0.5% lye solution.

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Pyrogallol Derivatives as Antioxidants for Carotene

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PYROGALLOL and esters of gallic acid have been shown to possess marked ability to prolong the induction period of autoxidizing fats and oils (1) and under certain conditions similarly to protect carotene (2). In connection with studies at our laboratory on the stability of carotene in dehydrated alfalfa meal, a series of compounds related to or derived from pyrogallol was prepared (3), and their ability to stabilize carotene in different media was measured. As far as possible the compounds tested were chosen to permit observation of change in activity with systematic change in structure. The present report deals with the results of these stability tests.

Experimental

Stability of Oil Solution. The effectiveness of the antioxidants for the protection of carotene in oil solution was first determined. The substrates used for testing the antioxidants included a highly refined medicinal mineral oil, a good-quality steam-rendered lard, and a commercially refined coconut oil.

The details of the stability test for carotene in oil solution have been published previously (4). It consists of a determination of the time required for breakdown of 20% of the carotene in the oil solution stored as a thin layer at 75°C. under specified conditions. As in previous work (2), the antioxidant compounds which had been highly purified were incorporated on an equivalent molecular basis rather than on a weight basis in order to facilitate the comparative evalution of the antioxidants in the oil solution.

[1]Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Report of a study made under the Research and Marketing Act of 1946.

Stability in Alfalfa Meal. To test the effect of the antioxidants on the stability of carotene in alfalfa meal, a rapid, simple method of incorporating the antioxidant was employed. This involved spraying a Cellosolve (ethylene glycol monoethyl ether) solution of the antioxidant on a 200-g. sample of meal while it was being tumbled at 12 r.p.m. in a rotary mixer. Samples were then stored for 2 weeks at 65°C. Results so obtained were comparable to about 8 months' storage at 25°C. Details of this technique have been described fully in an earlier report (5).

Results

PYROGALLOL DERIVATIVES IN MINERAL OIL SOLUTION.

Alkyl Substitution. The results showed that pyrogallol is a very effective antioxidant for carotene in mineral oil solution (Table I). The addition of one alkyl group to pyrogallol as in 4-ethyl pyrogallol produced a moderate increase in antioxidant effectiveness. The addition of a second alkyl group as in 4,6-diethyl pyrogallol was less effective. Furthermore, if tertiary butyl groups were introduced in the 4 and 6 positions, the activity was decreased below that of the parent compound. Substitution of a triphenylmethyl group in the 5 position greatly enhanced the activity when compared to pyrogallol.

Acyl Substitution. With the exception of 4-acetyl pyrogallol, an acyl group in the 4 position increases the activity to about the same extent, independently of the size of the group. If an alkyl group is substituted in the 6 position of 4-acetyl pyrogallol, the antioxidant activity is markedly increased. Substitution of a benzoyl group in the 4 position of pyrogallol

TABLE I

Comparison of Antioxidants for Carotene in Oil Solution at 75°C. (Time required for loss of 20% of the carotene)

Compound	Mineral Oil	Lard	Coconut Oil
	Hours	*Hours*	*Hours*
Control	2	3½	½
Pyrogallol	155	136	74
Pyrogallol trimethylether	2		
Pyrogallol tribenzylether	2		
Pyrogallol triacetate	15		
Pyrogallol 1,3-dimethylether	89		
Dihydrocoerulignone	141		
Purpurogallin	163		
Gallic acid	7		
Tannic acid	5		
Ethyl gallate	165		
Lauryl gallate	138		
Gallic acid tribenzylether	4		
4-Ethyl pyrogallol	185	75	97
4,6-Diethylpyrogallol	162	39	75
4,6-Di-t-butylpyrogallol	82		
5-Triphenylmethylpyrogallol	218	45	30
4-Acetopyrogallol	160	34	4
4-Propiopyrogallol	220	28	4
4-n-Butyropyrogallol	204		
4-n-Valeropyrogallol	226		
4-iso-Valerylpyrogallol	225		
4-(Diethylacetyl)pyrogallol	226	25	4
4-Benzoyl pyrogallol	240	40	5
4-Ethyl-6-acetopyrogallol	192	25	4
4-t-Butyl-6-acetopyrogallol	235	34	6
4-t-Butyl-6-valeropyrogallol	202		
5-Amino pyrogallol tribenzylether	240	9	3
5-Nitro pyrogallol	135		
5-Nitro pyrogallol tribenzylether	4		
3,4,5-Tribenzyloxy benzyl alcohol	5		

also greatly increases the antioxidant potency of the compound.

Conversion of two of the hydroxyl groups of pyrogallol to methyl ethers reduces the activity approximately by half whereas conversion of all three hydroxyl groups to methyl or benzyl ethers destroys the antioxidant activity completely. An exception is 5-aminopyrogallol tribenzyl ether. This compound would be expected to possess some antioxidant activity because of the para-amino phenol configuration; however there is no ready explanation for the very large activity observed. Dihydrocoerulignone, a derivative of 4,4'-dihydroxybiphenyl which is actually a vinylogue of hydroquinone, possesses activity characteristic of such a structure. Purpurogallin, which is similar in structure to acetopyrogallol, shows approximately the same activity.

The presence of a carboxyl group on the pyrogallol nucleus destroys essentially all the activity. However if the carboxyl group is esterified, the rather considerable activity charactersitic of the well-known gallic acid esters is obtained.

Pyrogallol Derivatives in Lard and Coconut Oil. Only those compounds which indicated antioxidant activity greater than pyrogallol were tested in media other than mineral oil. Pyrogallol was almost as effective in lard as in mineral oil. However all substituted pyrogallols showed decreased activity when compared to pyrogallol. The most active of those studied was 4-ethyl pyrogallol. No consistent relationship between structure and activity is apparent from the date.

Pyrogallol was only half as effective in coconut oil as in mineral oil while 4-ethyl pyrogallol displayed somewhat greater activity. 4,6-Diethyl pyrogallol displayed about the same activity as the parent compound. All other compounds showed decreased activity. Substitution of an acyl group in the pyrogallol molecule essentially destroyed all activity.

Pyrogallol Derivatives for Carotene in Alfalfa Meal. Neither pyrogallol itself nor any of its derivatives were effective antioxidants for carotene in alfalfa meal (Table II). Most of the acyl derivatives were pro-oxidants for the carotene to some extent. The best pyrogallol derivative was 4-ethyl pyrogallol, which produces a definite enhancement of carotene stability, although not of the same order of magnitude as 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline, which is very effective (5). Data on this latter compound are included in Table II for comparative purposes.

Discussion

There exists no easily apparent explanation for the diversity of results in different media. However it may be pointed out that any antioxidant is effective only in a competitive way. Its principal function is to react with one or more of the intermediate products of autoxidation to stop the chain-sustaining reactions and prolong the induction period. The complex media of lard or coconut oil and carotene contain a number of substances which are subject to autoxidation either selectively or concurrently. In addition, the individual stability of these components is affected markedly by the presence of others. Whether an antioxidant will afford the same order of magnitude of protection in different media appears at this time difficult to predict. It has been observed, in fact, that under different conditions an antioxidant may not only lose all activity but may even appear to act as a pro-oxidant. Finally it should be noted that the solubility of an antioxidant in the media in which its activity is being observed is beyond question an important factor. Thus in a heterogeneous mixture such as alfalfa the antioxidant must be soluble in that phase which it is designed to protect, a fact which may account for the complete lack of activity of most of the pyrogallol derivatives toward carotene in alfalfa.

TABLE II

Comparison of Antioxidants for Carotene in Alfalfa Meal at 65°C.

Compound	Carotene remaining after 2 weeks
	%
Control	23
6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline	63
Pyrogallol	25
Pyrogallol tribenzylether	26
Dihydrocoerulignone	23
Purpurogallin	24
Gallic acid	27
Ethyl gallate	28
Propyl gallate	26
4-Ethyl pyrogallol	35
4,6-Diethylpyrogallol	28
4,6-Di-t-butylpyrogallol	20
5-Triphenylmethylpyrogallol	20
4-Acetopyrogallol	21
4-Propiopyrogallol	21
4-n-Butyropyrogallol	19
4-iso-Valerylpyrogallol	19
4-Ethyl-6-acetopyrogallol	19
4-t-Butyl-6-acetopyrogallol	17
5-Amino pyrogallol tribenzylether	28
5-Amino pyrogallol 1,3-dimethylether	25
4,6-Diamino pyrogallol hydrochloride	25
5-Nitro pyrogallol	25
5-Nitro pyrogallol tribenzyl ether	25
4-(beta-dimethyl amino propio) pyrogallol	23

Conclusions

Certain derivatives of pyrogallol have been shown to possess marked activity as antioxidants for carotene in some systems while they are of little value in others. Thus all the derivatives which are more effective than pyrogallol in protecting carotene in mineral oil are very much less effective than pyrogallol in lard and, with two exceptions, are also less effective in coconut oil. Neither pyrogallol nor any of its de-

rivatives tested were effective antioxidants for carotene in alfalfa meal. Insufficient data are available to permit conclusions regarding relationships between changes in antioxidant activity and minor structural variations.

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Relation Between Fatty Acid Composition and Iodine Value of Cottonseed Oil[1,2]

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THOUGH it is well known that the iodine value of a vegetable oil of a given species of a plant is influenced by the genetical characteristics of the variety and the environment under which the oil is elaborated and that the iodine value is related to the amounts of the several unsaturated fatty acids present, no systematic investigation of this relationship for cottonseed oils has been found in the literature. Such relationships have been investigated for soybean oils (8) and linseed oils (6). Grindley (4) reported data on the fatty acid composition and the iodine value for a few cottonseed oils obtained from seed taken at various stages of maturity. Bailey (2) cited that the fatty acid composition of cottonseed oils will seldom fall outside the limits of 44 to 53% linoleic, 22 to 28% oleic, and 23 to 28% saturated acids.

The purpose of this paper is to report compositional data on 48 cottonseed oils, varying more widely in iodine value than oils heretofore available in one laboratory for investigation, and to correlate the percentages of the fatty acids present with the iodine values, providing a basis for approximating the fatty acid composition of a cottonseed oil from its iodine value.

The oils investigated were obtained from 48 lots of cottonseed selected from 312 samples whose oils had previously been analyzed for iodine value. They were selected to give an even distribution in iodine values between limits of 89.8 and 117.0 and, as shown in Table I, represent a random distribution of samples with respect to 8 varieties, 13 stations, and 3 years. The seed were from experimental growths of the Division of Cotton and Other Fiber Crops and Diseases of the Bureau of Plant Industry, Soils, and Agricultural Engineering. The seed cottons were picked from freshly opened bolls and dried. Hence the seed were subjected to little if any field damage as is shown by the analyses of the oils for free fatty acids. On receipt of the ginned seed they were stored in sealed containers at 0°F. Storage at this temperature and at less than 8% moisture has been shown previously to preserve cottonseed with no significant change in chemical composition (10).

The oils were extracted from approximately 140 g. of freshly separated and ground meats (2 mm. mesh) in large Butt-type tubes by cold percolation with successive 125, 50, 50, and 50 ml. portions of commercial pentane (Skellysolve F[4]). The solvent was removed under an atmosphere of nitrogen by heating on a steam bath and subsequently under vacuum in an oven at a low temperature. The solvent-free oils were stored under nitrogen in stoppered bottles in a refrigerator.

The oils were analyzed for iodine and thiocyanogen values by the American Oil Chemists' Society method Cd 1-25 (1) and the Lambou and Dollear method (5), respectively. Unsaponifiable matter was determined by the method of the Society of Public Analysts (9) and free fatty acids by a procedure originally designed for small cottonseed samples (10). The percentages of the fatty acids present in the oils were calculated by substituting the iodine and thiocyanogen values found in the equations specified in the American Oil Chemists' Society method Cd 2-38 (1). The results are expressed in Table I as hypothetical pure triglycerides of linoleic, oleic, and saturated acids. Average results of closely agreeing duplicates are reported in each instance.

Results

The free fatty acid contents of the oils, expressed as oleic acid were low, averaging 0.22% and ranging from 0.10 to 1.88%. This indicates that the seed had been collected and preserved with little or no deterioration.

The unsaponifiable matter averaged 0.65%, varying from 0.57 to 0.77%. The values are within the range of those found for authentic samples of commercial cottonseed oils reported in A.O.C.S. Table I 2-46 (1).

The iodine and thiocyanogen values ranged from 89.8 to 117.0 and from 62.2 to 71.1, respectively. The oils were uniformly distributed between the limits of these absorption values.

[1] Report of a study made under the Research and Marketing Act of 1946.

[2] Presented at the spring meeting of the American Oil Chemists' Society, New Orleans, La., May 1-3, 1951.

[3] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[4] The mention of firms' names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.