I would also suggest that definite study be made and the findings recommended for adoption regarding each and all of the following items: (1) sampling tools; (2) removal of foreign material from the original sample by mechanical screening; (3) specifications for riffles for reducing a sample to proper size without having to rely upon the determinations of the samplers, in whom the human element of variability is always found to some extent; (4) specification of a definite, minimum amount of sample to be drawn per ton of peanuts delivered; (5) size of sample to be prepared for sending to chemists for analysis; and (6) elimination of all sampling by hand.

The results of such studies would certainly tend to improve the present methods of sampling and should lead to more accurate and representative samples being taken.

Norconidendrin: A New Antioxidant for Fats and Oils[1]

G. S. FISHER, LILLIAN KYAME, and W. G. BICKFORD
Southern Regional Research Laboratory[2]
New Orleans, Louisiana

IT has long been recognized that it is desirable, and in many cases essential, to improve the stability of animal and vegetable fats and oils to oxidative rancidity. Three methods have been used to improve the stability of fats, namely (1) careful control of processing conditions to retain the maximum amount of natural stability, (2) hydrogenation to reduce the degree of unsaturation of the components which are the most susceptible to oxidative attack, and (3) addition to the fat of antioxidants or synergists. Each of these methods possesses merit but the degree of improvement which can be obtained by the first two is limited by the nature of the fat and the ultimate properties required in the finished products. Therefore much effort has been expended to finding suitable antioxidants for edible fats and oils. The properties required of an effective antioxidant are that it should be (1) fat-soluble, (2) effective in low concentrations, (3) colorless or nearly so, (4) relatively odorless and tasteless, and (5) non-toxic in the concentrations used. It should also retain its effectiveness when the fat to which it has been added is incorporated in other products. Few such antioxidants have been found for use in food products, principal among which are the tocopherols, ascorbic and citric acids, gum guaiac, and nordihydroguaiaretic acid (NDGA). The two last-mentioned are derived from certain resinous woods and represent naturally-occurring polyphenols. Many resinous woods contain related polyphenols and the present report is concerned with an investigation of the antioxidant properties of one of these natural products, namely conidendrin, and particularly with norconidendrin, which is derived from conidendrin.

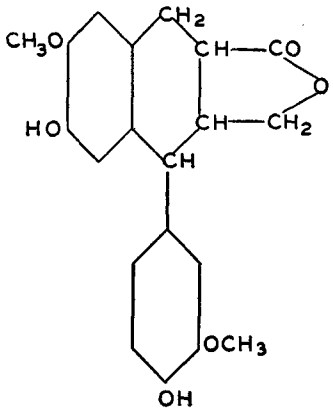
Conidendrin has been isolated from a number of coniferous woods including western hemlock (1). Its structure and that of nordihydroguaiaretic acid are indicated by the following formulas. According to Pearl (2) the sulfiite waste liquors produced during pulping of western hemlock offers an unlimited and readily available source of conidendrin in relatively pure form.

[1] Presented before the 38th Annual Meeting of the American Oil Chemists' Society, New Orleans, Louisiana, May 20-22, 1947.

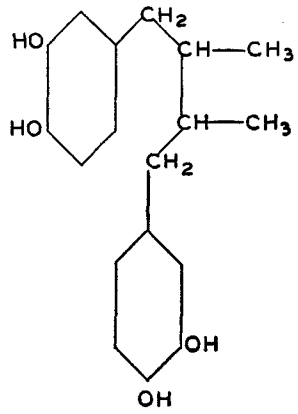
[2] One of the laboratories of the Bureau of Agriculture and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Experimental

Extraction of Conidendrin. Conidendrin was extracted from five-liter portions of sulfite waste liquor from western hemlock. Ether was used in earlier



CONIDENDRIN



NORDIHYDROGUAIARETIC ACID

extractions but subsequent extractions were made in an extractor modified for use with trichloroethylene. Mechanical stirring was used to increase the contact between the solvent-water phases. Solvent was passed through the apparatus illustrated in Figure 1 at the rate of 0.5 to 1 liter per hour for 5-10 hours. Most of the conidendrin was precipitated in the boiler either before or after cooling the extract to room temperature, after which it was removed by filtration. An additional quantity of conidendrin was obtained by reducing the various mother liquors to about one-third of their original volumes, cooling, and filtering. The total yield of crude product was about 0.75 g. per liter of waste liquor extracted.

The crude conidendrin was recrystallized from 95 per cent ethanol. Because of the poor solubility of conidendrin in hot alcohol, crystallization was carried out in small batches using the mother liquor from the

first batch as the solvent for the second batch, etc., until the concentration of the impurities in the mother liquor became too high for further satisfactory use. The final mother liquor was then reduced to a small volume and the conidendrin which separated was added to the next batch of crude product. The yield of purified conidendrin corresponded to 80 to 90 per cent of the original crude product.

Preparation of Norconidendrin. Norconidendrin was prepared by treating conidendrin with hydrobromic acid in acetic acid solution. Although the structure of norconidendrin has not been completely established it appears that the reaction results in partial or complete removal of the two methyl groups of conidendrin to yield the corresponding phenol.

The demethylation is carried out as follows: 5 g. of conidendrin once recrystallized from ethanol was dissolved in 25 ml. of glacial acetic acid. Five g. of 48 per cent hydrobromic acid was added to the solution and the mixture was refluxed for two hours after which 2.5 g. of the hydrobromic acid was added and the solution refluxed for an additional three hours. The dark brown reaction mixture was carefully neutralized with a saturated solution of sodium bicarbonate to which a small amount of sodium hydrosulfite had been added, after which the norconidendrin was extracted with several 50-ml. portions of ether. The ethereal extract was washed, dried, and the solvent removed by evaporation. The product (3.25 g.), a light-tan, glassy solid, when added in a concentration of 0.01 per cent to a peanut oil from which most of the natural antioxidants had been removed had an antioxidant index of 3 to 4. A more active product was obtained, however, when 1.1 g. of the crude norconidendrin was dispersed in 50 ml. of saturated sodium bicarbonate containing 5 ml. of ethanol and boiled for 10 minutes. After cooling the solution was filtered and 0.5 g. of sodium hydrosulfite was added to the filtrate, and the pH adjusted to 6.5 with dilute sulfuric acid after which it was again heated to boiling. The pale yellow solution was cooled, filtered to remove the precipitated sulfur, and extracted with ether. The aqueous layer was adjusted to pH 3 and re-extracted with ether after again filtering out the precipitated sulfur. The combined ethereal extracts were washed three times with saturated sodium sulfate solution to which a little hydrosulfite had been added, dried over anhydrous sodium sulfate, filtered, and the solvent removed under vacuum. The last traces of sulfur were removed by dissolving the norconidendrin in a minimum amount of acetone and filtering, after which the acetone was removed under vacuum. The final product consisted of 0.6 g. of a nearly colorless, fluffy solid.

Method of Testing Antioxidants. The antioxidant activity of the various products were compared by incorporating them, *per se* or together with other antioxidants and synergists, in several fats and determining their stability by the active oxygen method (3). The stability, designated as AOM in the following tables, is expressed as the number of hours required for the fat to reach 100 milliequivalents of peroxide per kilogram when aerated at 97.7° C. The effectiveness of the antioxidant is reported as antioxidant index or ratio of the AOM of the treated to the untreated fat.

The antioxidants were added to the fats in the form of 1-4 ml. of alcoholic solution. In each case 2 ml. of ethanol was added to the control. The fat and alcoholic solution of the antioxidant were thoroughly mixed and heated to *ca.* 97° C. in a water bath prior to determining the stability of the fat.

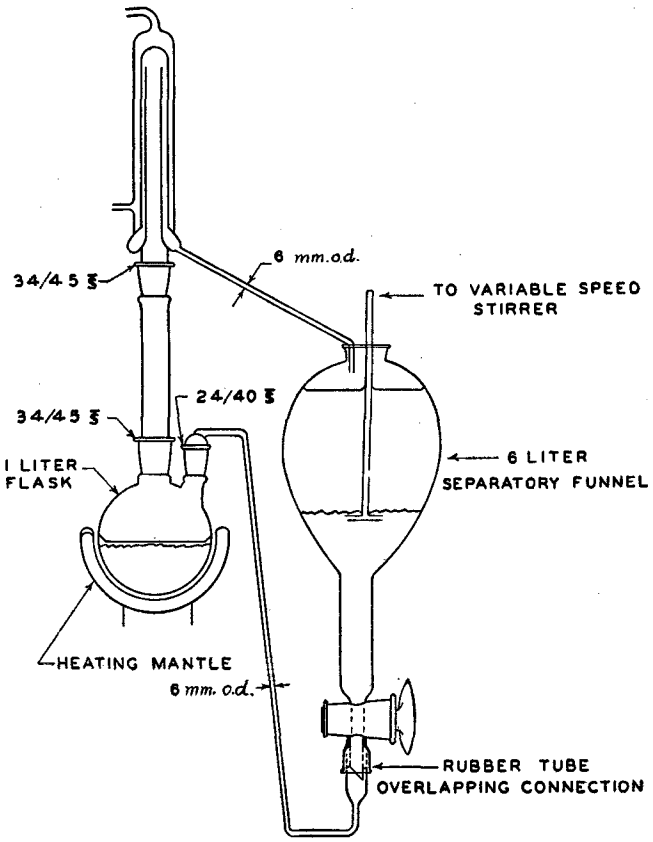


FIG. 1. Extractor used for recovery of conidendrin from sulfite waste liquor.

The fats used included hydrogenated and unhydrogenated oils and a peanut oil from which as much of the natural antioxidants as possible had been removed by adsorption on alumina and carbon (4), (tocopherol 0.001%) prior to deodorization.

TABLE 1.

Antioxidant Activity of Norconidendrin at Various Concentrations.

Antioxidant added %	0-409 Cottonseed oil		0-317 Peanut oil		GO-317 Antioxidant-free peanut oil	
	AOM hrs.	Index	AOM hrs.	Index	AOM hrs.	Index
....	9.3	1.0	9.3	1.0	3.0	1.0
0.001.....	12.5	1.3	10.5	1.1	4.2	1.4
0.01.....	14.5	1.5	20.0	2.2	18.2	6.1
0.025.....	17.0	1.8	30.5	3.3	.....	.....
0.05.....	18.0	1.9	50.0	5.4	47.7	15.9
0.10.....	24.5	2.5	58.0	6.2	64.7	21.6

Results and Discussion

Conidendrin and norconidendrin (NC) were added in 0.05 per cent concentration to hydrogenated cottonseed, peanut, and antioxidant-free peanut oils having AOM values of 160, 15, and 3 hours, respectively. No improvement in these values was observed by the addition of conidendrin, whereas addition of norconidendrin increased them to 600, 57, and 50 hours, respectively.

The effect of the addition of norconidendrin in concentrations of 0.001 to 0.10 per cent to refined cottonseed and peanut oils and an antioxidant-free peanut

oil are shown in Table 1. From these data it is evident that the antioxidant activity increased with increased concentration of norconidendrin.

It is also apparent that norconidendrin possesses a relatively low activity in cottonseed oil compared with that observed with the two peanut oils. The data given in Table 2 indicate that norconidendrin possesses a similarly low activity in soybean and rice bran oils.

TABLE 2.

Relative Antioxidant Activity of Norconidendrin in Various Refined Oils.

Oil	No antioxidant. AOM hrs.	Antioxidant index	
		0.01% antioxidant	0.025% antioxidant
Cottonseed	10.0	1.6	1.9
Peanut, 0-317	9.3	2.2	3.3
Peanut, 0-406	16.0	2.3	2.6
Soybean	8.0	1.9	2.4
Rice bran	22.5	1.4	1.7

The antioxidant activity of norconidendrin, nordihydroguaiaretic acid, catechol, and hydroquinone in cottonseed and peanut oils are compared in Table 3. The data in this table demonstrate that all of the polyphenolic antioxidants tested are appreciably less effective in cottonseed than in peanut oil.

TABLE 3.

Comparison of Activity of Norconidendrin and Other Antioxidants in Cottonseed and Peanut Oils.

Antioxidant	Conc. %	Cottonseed oil 0-409		Peanut oil 0-406	
		AOM hrs.	Index	AOM hrs.	Index
None	.....	9.3	1.0	16.0	1.0
Norconidendrin	0.01	14.5	1.5	36.0	2.3
NDGA	0.01	12.0	1.3	35.3	2.2
Norconidendrin	0.025	15.0	1.6	42.0	2.6
NDGA	0.025	12.8	1.4	46.0	2.9
Catechol	0.025	11.0	1.2	37.5	2.3
Hydroquinone	0.025	22.5	2.4	59.0	3.7

Data showing the comparative effect of additions of 0.01 per cent of norconidendrin in stabilizing cottonseed and peanut oils in the presence and absence of other antioxidants and inhibitors are given in Table 4. Examination of these data indicate that the acid-type inhibitors or synergists when used alone were more effective in improving the stability of refined cottonseed and peanut oils than were either of the polyphenolic inhibitors, but in all cases combinations of the two were superior to any one alone. In the case of the antioxidant-free peanut oil, the acid-type synergists were entirely ineffective. whereas the polyphenolic antioxidants were highly effective and combinations of antioxidants and synergists were markedly so.

Since it is often advantageous to add an antioxidant to a refined oil prior to deodorization, a comparison was made of the stability of cottonseed and peanut oils to which norconidendrin had been added prior to and after deodorization. Small samples (20 g.) of cottonseed and peanut oils, treated as indicated in Table 5, were deodorized for two hours at 200° C. (392° F.). The antioxidant was added in the form of its alcoholic solution and a corresponding amount of alcohol was added to the control oil. The data in Table 5 indicate that norconidendrin has approximately the same effectiveness in these oils whether added before or after deodorization. The deodorized oils were bland and unchanged in color as a result of the addition of norconidendrin prior to deodorization.

TABLE 5.

Comparative Stabilities of Redeodorized Cottonseed and Peanut Oils Containing Norconidendrin (0.01%) and Norconidendrin (0.01%) Plus Ascorbic Acid (0.005%).

Antioxidant	Redeodorized	Cottonseed oil		Peanut oil	
		AOM hrs.	Index	AOM hrs.	Index
None	No	10.0	1.0	9.3	1.0
None	Yes	9.0	1.0	6.7	1.0
Norconidendrin	No	16.0	1.6	20.0	2.2
Norconidendrin	Yes	17.5	1.9	18.5	2.8
NC + ascorbic acid	No	23.0	2.3	37.5	4.0
NC + ascorbic acid	Yes	21.5	2.4	26.0	3.9

The effectiveness of norconidendrin in hydrogenated cottonseed and peanut oils is shown in Table 6.

Since it has been shown by various workers that NDGA and gum guaiac are relatively active antioxidants for lard, it was of interest to compare the activity of the structurally related norconidendrin in this substrate. It was tested alone and in combination with other antioxidants in a commercial sample of prime steam lard and the results are given in Table 7.

TABLE 7.

The Antioxidant Activity of Norconidendrin in Lard With and Without Other Added Antioxidants.

Antioxidant	AOM hrs.	Index
None	3	1.0
Norconidendrin (0.01%)	22	7.3
NDGA (0.01%)	25	8.3
NC (0.01%) + NDGA (0.01%)	34	11.3
NC (0.005%) + NDGA (0.005%)	28	9.3
Alpha-Tocopherol (0.05%)	14	4.7
Gamma-Tocopherol (0.05%)	29	9.7
NC (0.01%) + alpha-tocopherol (0.05%)	20	6.7
NC (0.01%) + gamma-tocopherol (0.05%)	41	13.7
NDGA (0.01%) + alpha-tocopherol (0.05%)	20	6.7
NDGA (0.01%) + gamma-tocopherol (0.05%)	43	14.1

On the basis of these data norconidendrin appears to possess approximately the same antioxidant activity as NDGA in lard. The combination of norconidendrin

TABLE 4.

Comparison of Activity of Norconidendrin (0.01%) With and Without Other Added Antioxidants or Synergists.

Antioxidant	Cottonseed oil 0-409		Peanut oil 0-317		Antioxidant-free peanut oil. GO-317	
	AOM hrs.	Index	AOM hrs.	Index	AOM hrs.	Index
None	9.3	1.0	9.3	1.0	3.0	1.0
Norconidendrin (0.01%)	14.5	1.5	20.0	2.2	18.2	6.1
Citric acid (0.005%)	18.0	1.9	15.0	1.6	4.2	1.4
NC + citric acid (0.005%)	23.2	2.5	32.0	3.4	27.0	9.0
Ascorbic acid (0.005%)	21.5	2.3	23.0	2.5	3.6	1.2
NC + ascorbic acid (0.005%)	26.0	2.7	37.5	4.0	26.0	8.7
H_3PO_4 (0.001%)	18.0	1.9	14.0	1.5	4.0	1.3
NC + H_3PO_4 (0.001%)	24.0	2.6	28.5	3.1	23.7	7.9
α-Tocopherol (0.05%)	10.0	1.1	9.5	1.1	11.5	3.8
NC + α-tocopherol (0.05%)	14.0	1.5	18.5	2.0	14.5	4.8
Nordihydroguaiaretic acid (0.01%)	12.0	1.3	18.5	2.0	12.8	4.3
NDGA + citric acid (0.005%)	28.5	3.1	44.0	4.1	28.5	9.5

TABLE 6.

Activity of Norconidendrin in Hydrogenated Oils

Antioxidant Type	Conc. %	Hydrogenated peanut oil[1] HO-406 W		Hydrogenated peanut oil[2] HO-406-R		Hydrogenated cottonseed oil[3] CO-60 C	
		AOM hrs.	Index	AOM hrs.	Index	AOM hrs.	Index
None	.....	110	1.0	228	1.0	149	1.0
Norconidendrin	0.01	221	2.0	400	1.8	205	1.4
Norconidendrin	0.025	332	3.0	435	1.9	292	2.0
Nordihydroguaiaretic acid	0.01	236	2.1	476	2.1	260	1.7

[1] Iodine value 66.8. [2] Iodine value 67.4. [3] Iodine value 58.1.

and NDGA in a total concentration of 0.01 per cent is slightly more effective than either antioxidant alone in 0.01 per cent concentration. Combinations of the polyphenolic antioxidants and γ-tocopherol are more effective and combinations of the polyphenolic antioxidants and α-tocopherol are slightly less effective than the polyphenol alone.

Summary and Conclusions

The preparation of norconidendrin from western hemlock sulfite waste liquor has been described. Norconidendrin has been shown to possess antioxidant activity in both hydrogenated and unhydrogenated cottonseed and peanut oils, in a peanut oil essentially free of natural antioxidants, and in lard. Its activity in these products is comparable with that of other polyphenolic antioxidants. Norconidendrin, as well as the other polyphenols tested, exhibited greater antioxidant activity in the particular peanut oils used than in several other vegetable oils and still greater activity in substrates which contained only small amounts of natural antioxidants. The effectiveness of norconidendrin was found to be appreciably enhanced by the addition of acid-type synergists. It may be added either before or after deodorization with approximately equal effectiveness. When added before deodorization, it contributes no odor, color, or flavor to the finished oil.

Practical applications of norconidendrin in preserving food products should be postponed until toxicity studies have been conducted.

LITERATURE CITED

1. Brauns, F. E., J. Org. Chem., *10*, 216-218 (1945).

2. Pearl, I. A., *ibid.*, *10*, 219-221 (1945).

3. "Report of the Committee on Analysis of Commercial Fats and Oils," Oil & Soap, *22*, 101-107 (1945).

4. Swift, C. E., Mann, G. E., and Fisher, G. S., Oil & Soap *21*, 317-320 (1944).

Abstracts

Oils and Fats

Edited by
M. M. PISKUR and SARAH HICKS

PROCESSING CHICKEN FAT. Anon. *U. S. Egg, Poultry Mag. 53,* No. 8, 7-9, 29 (1947). The fat is heated to 180°, drawn off into a vacuum rendering tank where it is homogenized under pressure. The moisture is drawn off in 8-13 minutes and the fat is siphoned to 30-lb. cans to cool. It is packed in 13-oz. glass jars. It is claimed that a product of enhanced stability is obtained.

PROTEIN AND FAT PRODUCTION WITH YEAST ON SULFITE RESIDUES. E. Schmidt. *Die Chemie 59A,* 16-20 (1947).

BY-PRODUCTS OF PARAFFIN OXIDATION. L. Mannes. *Die Chemie 57,* 6-11 (1944). A review from 71 references.

THE EMULSIFIERS. Francine Appell. *Chim. & Ind. 57,* 241-9 (1947). This is a bibliography and review on the subject, containing diagrams of equipment and methods.

ADSORPTION IN FAT EMULSIONS. A. E. Sandelin. *Finska Kemistsamfundets Medd. 54,* 53-67 (1945). To throw light on the behavior of milk as an emulsion, butterfat was emulsified in aq. solns. of 7 emulsifying agents. Each emulsion was skimmed with a separator and the "cream" churned. Titrations showed that the fat globules carry more acid than alkali into the "cream" and "butter" from solutions of Na and K oleate, Na abietate, gum arabic, and saponin; this indicates hydrolytic adsorption with anions predominating in the protective layer. The reverse is true in solutions of Na caseinate and egg albumin. The titrimetric data, combined with microscopic determination of the total surface of the droplets lead to a thickness of 4.0-5.0 μ for the adsorbed layer in emulsions containing 0.05-0.1% Na oleate and 3.7-28.7% fat. Breaking of fat emulsions by agitation may be due to discharge of adsorbed ions by frictional electricity. If foam is formed, breaking is assisted by passage of the emulsifying agent into the foam. (*Chem. Abs. 41,* 3878.)

LEATHER TREATING AGENTS. H. Herfeld. *Die Chemie 58,* 69 (1945). Leather blacks, creams, fats, and impregnating agents are discussed.

ADSORPTION IN THE FAT FIELD. V. SEPARATION OF CIS-TRANS-ISOMERS. H. P. Kaufmann and W. Wolf. *Fette u. Seifen 50,* 519-21 (1943).

FAT CHEMISTRY PROCESSES AND THEIR ECONOMY. VI. MANUFACTURE OF GLYCERIDES AND OTHER ESTERS FROM FAT ACIDS. K. Linder. *Fette u. Seifen 50,* 396-8 (1943). Recent patented fat derivatives are reviewed.

SYNTHESIS OF ALIPHATIC COMPOUNDS. Th. A. Lennartz. *Die Chemie 59A,* 10-16 (1947). A portion of this review deals with fat acids and glycerides.

PHENOMENA OF TRANSESTERIFICATION BETWEEN TRIGLYCERIDES. II. TRIOLEIN-TRISTEARIN AND TRIOLEIN-DILAUROMYRISTIN TRANSESTERIFICATION IN THE PRESENCE OF SODIUM METHYLATE. M. Naudet and P.