TABLE VIII
Percentage of Polyunsaturated Acids in Total Acids of Milk Fat

Dienes		Trienes	
Acid	%	Acid	%
18:2	2.11	18:3	0.50
18:2 c,t conj.[a]	0.63	18:3 conj.	0.01
18:2 t,t conj.[a]	0.09	20:3	0.11
20:2	0.05	22:3	0.02
22:2	0.01	......	......
Tetraenes		**Pentaenes**	
Acid	%	Acid	%
20:4	0.14	20:5	0.04
22:4	0.05	22:5	0.06

[a] c,t = *cis-trans* and *t,t* = *trans-trans*.

and subtracting from it the amount of conjugated *trans-trans* 18:2 (calculated from its separate peak by GLC); the remainder was considered the amount of conjugated *cis-trans* 18:2. The amount of conjugated *cis-trans* 18:2 was in turn subtracted from the total amount found by GLC for the unresolved pair. The difference was the amount of 18:3 in the fraction. Infrared spectrophotometry was always employed to confirm the presence of *cis-trans* isomers. Similarly, nonconjugated 20:3 was not separable from conjugated 18:3. In this instance, the conjugated triene was determined by ultraviolet spectrophotometry and the amount of 20:3 was found by difference. Indication by GLC for presence of conjugated 18:3 was shown in a previous publication (13).

The individual fatty acids in the various fractions were summated and computed to the original total methyl esters of the milk fat to give the data in Tables V, VI, VII, and VIII. The presence of acids having *cis, trans* and terminal double bonds was confirmed by infrared spectrophotometry, but no attempt was made to give relative proportions of the geometrical isomers. Also, positional isomers of 16:1 and 18:1 have been reported. In this study, no attempt was made to confirm their presence. In all, 64 different fatty acids were accounted for, 27 of which were present in less than 0.1% concentration in the milk fat and would account for only 1% of the total fatty acids. With the exception of 17:1 recently reported (3), the homologous series of odd-carbon chain length monounsaturated acids 15:1 to 23:1 had not previously been reported in cows' milk fat.

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Cocoa Butter-Like Fat from Cottonseed Oil: Preliminary Cost Study

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Abstract

This paper includes a preliminary cost study for producing cocoa butter-like fat from hydrogenated cottonseed oil and triolein at an annual rate of 8.4 million lb in a hypothetical plant, employing interesterification and fractional crystallization as used in pilot plant studies at the Southern Utilization Research and Development Division. Equipment costs, total plant cost, manufacturing costs, and general expenses are given. Operating cost is estimated at 36.9¢/lb of product. This includes 31.8¢ for manufacturing, 4.1¢ for general expenses, and 1¢ for refining of the recycled mixture of saturates and unsaturates.

Introduction

CLOSE TO 300 million lb of cocoa butter valued at 150 million dollars are used annually in the United States. Uses of cocoa butter include chocolate coatings, confectionery coatings from cocoa powder and fat other than cocoa butter, baking and cooking chocolate (sweetened and unsweetened), powdered cocoa in all types of packages, cocoa butter sales as such, chocolate sirups, molded and solid bar goods, and other products.

Available cocoa butter is frequently in short supply; and according to the candy industry more cocoa butter, or cocoa butter-like fat, could be used in manufacturing coatings for chocolates and candy bars, not as a substitute for cocoa butter but as a supplement to the natural fat (1). For example, typical formulations of sweet milk chocolate of the coating type consist of 5 parts of the nonfat portion and about 30 parts of the fat portion of the cocoa bean, and since the cocoa bean is approximately half fat, 10 parts of ground cocoa bean would contribute the necessary 5 parts of nonfat material but only 5 parts of the 30 parts of fat material needed.

Increased domestic consumption of candy brought about by rising disposable income, gives further emphasis to the need for an additional supply of cocoa butter-like fat. At the same time, increased availability of cocoa butter-like fat would increase the utilization of cocoa powder, a by-product of the cocoa bean crushing and pressing operation. Consequently, candy manufacturers have expressed an intense in-

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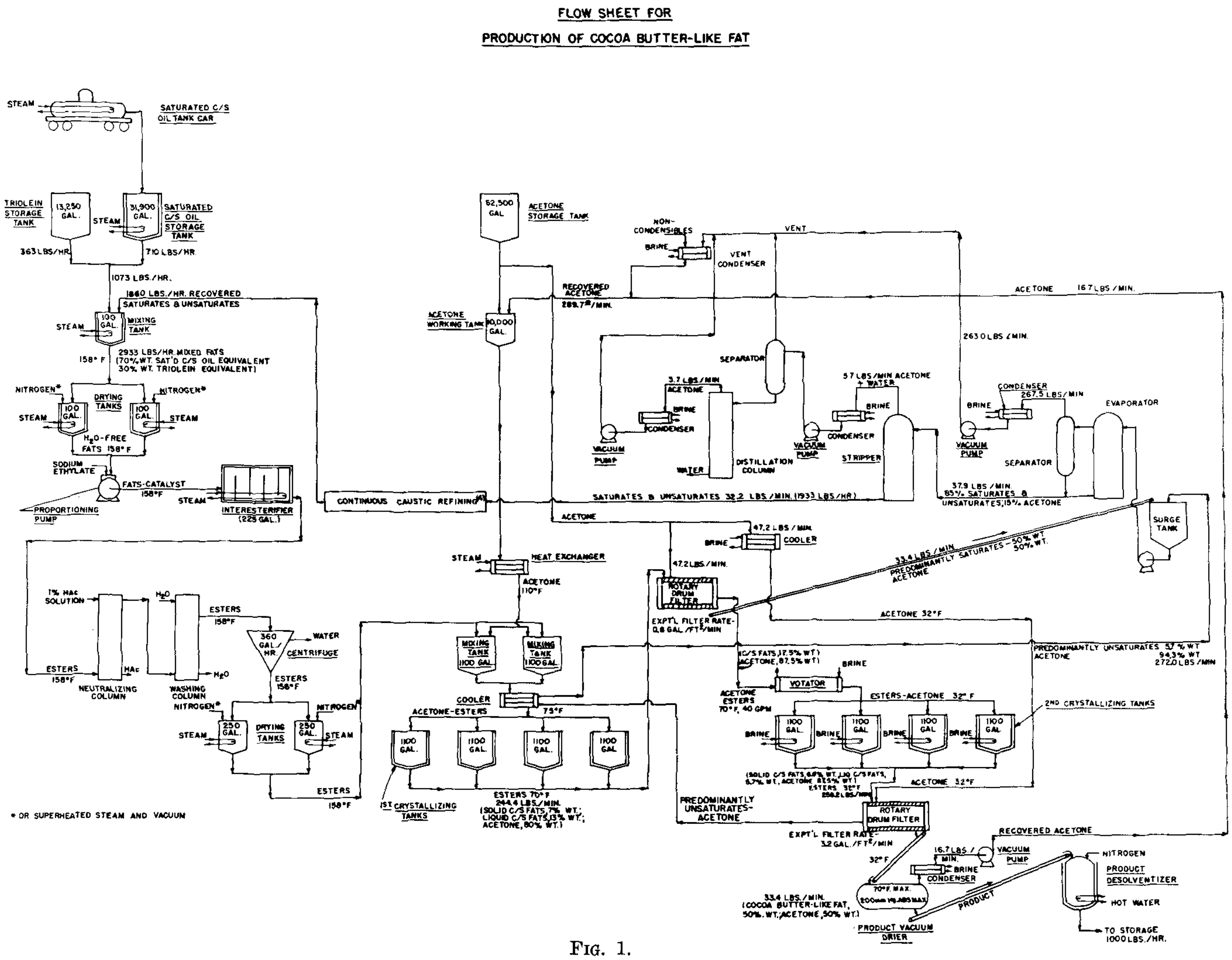

FIG. 1.

terest in obtaining a cocoa butter-like fat having all the desirable attributes of cocoa butter, at a stable price of about 30¢/lb.

At the Southern Utilization Research and Development Division, low-melting film-forming coating materials have been prepared from hydrogenated cottonseed oil and triolein, the triglyceride of oleic acid which is a natural constituent of most fats and oils. These coating materials have melting points close to that of body temperature, are edible and digestible, and some closely resemble cocoa butter in melting characteristics. Cocoa butter-like fat has been prepared in the laboratory (2), and later in the pilot plant (3) as a major step toward commercialization of the developed process. Approximately 75 million lb of surplus cottonseed oil would be consumed in manufacturing a cocoa butter-like fat that would supply only 10 of the 30% of fat in chocolate and chocolate type coatings.

This paper is a preliminary cost study for producing cocoa butter-like fat from hydrogenated cottonseed oil and triolein at an annual rate of 8.4 million lb in a hypothetical plant, employing essentially the unit operations and conditions of the pilot plant studies at the Southern Division. The hypothetical plant has an hourly processing capacity of 2,933 lb of raw materials for producing 1,000 lb of fat product.

Laboratory and pilot plant research under way holds promise for further process improvement, both technologically and economically.

Process

The process is illustrated in Figure 1 which is a flow sheet-material balance. Two fats are interesterified in the presence of alkaline catalyst, and esters formed are crystallized from acetone at two temperatures. The first crystallization, at room temperature, yields a predominantly saturated triglyceride fraction, and the second crystallization at 32F yields the cocoa butter-like product. It is a continuous process with the exception of the fats-drying, ester-drying, acetone-ester mixing, and crystallization operations, for which multiple tank arrangements are used. The initial feed consists of 70% hydrogenated cottonseed oil and 30% triolein, which gives a high yield of monounsaturated glycerides (3). Makeup is in the proportion of 65% hydrogenated cottonseed oil and 35% triolein. Hydrogenated cottonseed oil used had an Iodine Value of 1.5. A typical analysis of commercial triolein used is as follows:

FFA, as oleic acid	0.02%
Iodine Value	84.6
Saponification Value	196.0
Hydroxyl Value	3.0
Moisture	0.1%
Color	21 Yellow/2.1 Red
Trans isomers, as elaidic acid	6.8%
Capric	0.3
Lauric	0.4
Myristic	2.3
Myristoleic	1.0
Palmitic	4.0
Palmitoleic	5.4
Stearic	0.7
Oleic	71.8
Linoleic	14.1

The saturated cottonseed oil, triolein, and recovered saturates and unsaturates are then heated to 158F, mixed in the mixing tank for 5 min and pumped into drying tanks where traces of moisture are removed by nitrogen sparging under vacuum for 15 min at 158F. Catalyst, dry sodium ethoxide (ethylate), is added to the dried liquid mixture by a proportioning pump in an amount equal to 0.13 lb of sodium equivalent per 100 lb, and the resulting catalyst-fatty mixture is interesterified for a minimum of 30 min at 158F. The esters formed are neutralized with 1% acetic acid for 20 min and water washed for 20 min, both in continuous countercurrent washers; centrifuged to remove water; and dried by nitrogen sparging for 30 min; all at 158F. Then they are mixed for 15 min with 4 times their weight of acetone, which has been preheated to 110F; the mixture is cooled to and held at 70F in the first crystallization tanks for 1 hr, for crystallization of the predominantly saturated triglyceride fraction. The crystals are washed with acetone, filtered, and conveyed to the evaporator surge tank where they are reintroduced into the system. The filtrate is chilled with brine to 32F in a continuous crystallizer and held in the second crystallization tanks at that temperature for 1 hr, for crystallization of the monounsaturated glycerides (cocoa butter-like fat). The product is washed with acetone which has been chilled to 32F, is filtered, vacuum dried at 70F, remelted at about 100F, and sparged with nitrogen to remove any trace of acetone and, while yet a liquid, is pumped either into tank cars for shipment or into pans in which it solidifies into slab form. The desolventized product has acceptable edible quality without further deodorization provided the starting materials are of good quality. The crystals from the first crystallization and filtration are dissolved in the second filtrate, and 99% of the acetone is recovered from the solution for reuse by evaporation, stripping, and fractionation. After evaporating and stripping, the saturates and unsaturates are refined to remove small amounts of free fatty acids present, and recycled into the mixing tank. Further development work shows promise of the elimination of the refining operation, the use of nitrogen, and for other process improvements.

Ethyl esters formed by the catalyst in varying amounts do not crystallize, but remain in the low melting fraction. On refining of this fraction for reuse, they react with caustic more readily than do the triglycerides and are thereby removed. These monoesters could also be removed in a deodorization step.

Plant

The hypothetical plant is equipped with an acetone storage tank having a capacity for enough acetone to completely fill that part of the processing system involving its use plus five times the expected solvent loss during one month's operation. Hydrogenated cottonseed oil and triolein storage tanks are provided with capacities for a two-week supply of these raw materials. Surfaces of process equipment and piping coming into contact with the mixed fatty materials are made of 304 or 316 stainless steel, whichever was quoted by equipment manufacturers. A moderate amount of instrumentation is allowed, and auxiliary facilities include a steam boiler and an ammonia (or dichlorodifluoromethane) refrigeration system. A manufacturing building is provided. Refining equipment costs are not included in total plant cost.

TABLE I

Equipment Costs

No.	Name	Description	1960 Cost	
			Purchased	Installed
		TANKS		
1	Acetone Storage	62,500 gal, steel	$ 3,950	$ 5,450
1	Acetone Work	10,000 gal, steel	1,860	2,420
1	Triolein Storage	13,250 gal, steel	2,200	2,860
1	Sat. C/S Oil Storage	31,900 gal, steel, with coil	4,130	5,370
1	Mixing	100 gal, 304ss, with jacket, coil, and agitator	1.490	1,940
2	Drying	100 gal, 304ss, with jacket and coil	3,170	4,120
2	Drying	250 gal, 304ss, with jacket and coil	3,200	4,160
2	Mixing	1100 gal, 304ss, with agitator	5,330	6,930
8	Crystallization	1100 gal, 304ss, with jacket and agitator, 4 with coils	21,860	28,420
1	Surge	1350 gal, 304ss, with agitator	3,000	3,900
		Total—Tanks	$50,190	$ 65,570
		HEAT EXCHANGERS		
1	Evaporator Condenser	316ss, 440 ft²	$ 7,100	$ 8,880
1	Evaporator After Cooler	316ss, 23 ft²	450	560
1	Rectification Column Condenser-Cooler	316ss, 11 ft²	300	380
1	Acetone Cooler	316ss, 16 ft²	415	520
1	Acetone-Ester Cooler	316ss, 124 ft²	1,590	1,990
1	Acetone Preheater	316ss, 7.4 ft²	300	380
		Total—Heat Exchangers	$ 10,155	$ 12,710
		MAJOR UNITS		
1	Interesterifier	ss, with Jacket	$ 850	$ 1,100
1	Neutralizing Column	240 gal, 304ss	5,110	6,390
1	Washing Column	240 gal, 304ss	5,110	6,390
1	Centrifuge	Continuous, ss, 360 gph with accessories	4,130	5,160
1	Filter	37.6 ft², 304ss, rotary drum, totally enclosed with accessories	16,520	22,300
1	Crystallizer	Continuous, 316ss, jacketed	26,670	37,340
1	Filter	18.8 ft², 304ss, rotary drum, totally enclosed with accessories	14,460	19,520
1	Product Dryer	Rotary vacuum, 304ss, with condenser and vacuum pump	24,700	35,820
1	Evaporator	Long tube, vertical, rising film, 304ss	13,430	16,790
1	Stripping Column	ss, with condenser	13.360	18,040
1	Product Desolventizer	250 gal, 304ss, with jacket and coil	1,605	2,090
1	Acetone-Water Rectification Column	Steel, plate	4,460	6,020
3	Conveyors	Belt, enclosed	4,380	5,910
		Total—Major Units	$134,785	$182,870
		PUMPS		
3	Vacuum	Bronze, with motors	$ 1,300	$ 1,560
12	Transport	ss. with motors, centrifugal and positive displacement	8,695	10,430
		Total—Pumps	$ 9,995	$ 11,990
		Total—Process	$205,125	$273,140
		AUXILIARY FACILITIES		
1	Refrigeration System	Ammonia or Freon, 425 tons		$212,500
1	Steam Boiler	60 psig, 6535 #/hr		32,675
		Total—Auxiliaries		$245,175

Costs

Equipment costs, total plant cost, manufacturing costs, and general expenses are given in Tables I, II, and III, respectively.

Investment Cost. Most of the purchased equipment costs in Table I are those provided by equipment manufacturers. Installed equipment costs were estimated from the purchased costs using factors recommended by Aries (5) and Peters (6).

Process piping, instrumentation, outside lines, engineering and construction, and contingencies costs were estimated as indicated in Table II.

TABLE II

Total Plant Cost (Excluding Refining)

Annual production	8,400,000 lb
Operation	
Hours per day	24
Days per year	350
Production rate	1,000 lb/hr
Investment cost	
a) Installed equipment cost (see Table I)	$ 273,140
b) Process piping, 30% of a)	81.940
c) Instrumentation, 5% of a)	13,660
d) Insulation	23,670
e) Outside lines, 5% of a)	13,660
f) Auxiliary facilities (see Table I)	245,180
g) Buildings	30,600
h) Total physical plant cost	681,850
i) Engineering and construction, 30% of h)	204,560
j) Contingencies, 20% of h)	136,370
k) Total plant cost	$1,022,780

Building costs are for a single story manufacturing building with 12-in solid brick wall, of mill construction with wood-plank roof, and estimated at $15/ft^2 of floor area. Insulation cost was estimated at 8% of the installed equipment cost of those equipment units in the refrigeration cycle, which includes not only the compressor system but the coolers and condensers to which brine is supplied. Installed auxiliary facilities costs were estimated on the basis of $500/ton for refrigeration, and $5/lb/hr for steam. It is believed that a substantially shortened crystallization time can significantly reduce equipment and investment costs by eliminating the need for 8 crystallization tanks. At the same time, operating labor to attend these tanks would be reduced. Crystallization time is being investigated further including the possibility of using a crystal promoter. A reduction in the 4:1 acetone to interesterified oil weight ratio would reduce equipment sizes and costs throughout the system. Also, as additional data are obtained and the process is developed further, enabling a more extensive establishment and application of optimum conditions, engineering and construction and contingencies costs can be reduced accordingly.

Working Capital was estimated to be $1,029,840 and includes allowances for raw material inventory, inprocess inventory, product inventory, extended credit, and funds available for the payment of wages and other expenses (5).

TABLE III

Manufacturing Costs and General Expenses

k) Total plant cost	$1,022,780	
	Annual	Unit, cents per lb of product
Manufacturing cost		
Direct		
l) Raw materials	$1,827,840	21.8
m) Labor	172,000	2.1
n) Supervision, 20% of m)	34,400	0.4
o) Maintenance, 6.5% of (k–1.5f)	42,580	0.5
p) Plant supplies, 15% of o)	6,390	0.1
q) Utilities	178,040	2.1
r) Total direct	2,261,250	27.0
Indirect		
s) Payroll overhead, 15% of (m+n)	30,960	0.3
t) General plant overhead, 50% of (m+n+o+p)	127,690	1.5
u) Control lab, 15% of m excl. packaging	25,800	0.3
v) Packaging	5,290	0.1
w) Total indirect	$ 189,740	2.2
Fixed		
x) Insurance, 2% of (k—1.5f)	13,100	0.16
y) Property tax, 2% of (k–1.5f)	13,100	0.16
z) Depreciation, 10% of (k–1.5f)	65,500	0.8
aa) Total fixed	$ 91,700	1.1
ab) Contingencies, 5% (r+w+aa)	127,130	1.5
ac) Total manufacturing cost	$2,669,820	31.8
General Expenses		
ad) Gen. admin. and office overhead, 3% of (ac)	80,090	1.0
ae) Financing, 6% of (k—1.5f+working capital)	101,090	1.2
af) Sales, 6% of ac)	160,180	1.9
ag) Total general expenses	$ 341,360	4.1
TOTAL COST (excluding refining)	$3,011,180	35.9
Refining cost	84,000	1.0
TOTAL COST (including refining)	$3,095,180	36.9

Manufacturing Costs, exclusive of refining costs, and general expenses were calculated for operating the hypothetical plant for 24 hr per day, 350 days per year, at its capacity. Table III shows that manufacturing cost at plant capacity is 31.8¢/lb of product, and general expenses an additional 4.1¢, totalling 35.9¢/lb of cocoa butter-like fat. Refining cost is an additional 1¢/lb of product. Raw materials cost is the largest manufacturing cost, amounting to more than half of the total. Raw materials cost for producing 100 lb of cocoa butter-like fat is given in Table IV. September 1960 market prices were used except for hydrogenated cottonseed oil for which the August-December 1960 average price was used; however individual contract prices could be less.

One manufacturer of nitrogen has recommended, on the basis of the monthly requirement of nitrogen, that it be purchased rather than produced at the plant site. The method of supply suggested is liquid deliveries. Recovery of 99% of acetone is assumed. Sodium ethoxide must be evaporated to dryness before introduction into the process.

Labor costs were estimated on the basis of one foreman at $3.87/hr base salary, and four operators, each at $2.85/hr base salary. Overtime and night differential were added whenever applicable. Utilities costs include those for steam, electricity, and refrigeration. Rates used were 70¢/1,000 lb of steam, 90¢/ton-day of refrigeration, and those prescribed for demand and energy charges as listed in a local electric schedule for commercial and industrial purposes. The reported cost of 36.9¢/lb of product in Table III is for shipment in tank cars; however if shipment in 10-lb slabs is specified the cost becomes 38.0¢/lb of product, or 1.1¢/lb higher. The slabs would be individually wrapped in paper and packaged 5 to the carton, requiring the full time services of one packager. Sales cost was estimated on the basis of 6% of manufacturing cost because established channels of distribution of cocoa butter would be used and the product is a "pull" item, that is, one wanted and asked for by the user at the right price.

Conclusion

This preliminary cost study of semicontinuous operations in a hypothetical plant shows that cocoa butter-like fat could be produced from cottonseed oil by interesterification and fractional crystallization for 36.9¢/lb at an annual production rate of 8.4 million lb. The process holds promise for improvement both technologically and economically. Surplus do-

TABLE IV

Chemicals Cost per 100 lb of Product

Raw material	Quantity	Unit price	Cost $/100 lb product
Hydrogenated C/S oil	71.0[a]	13¢/lb	$9.23
Triolein	36.3[a]	25¢/lb	9.08
Nitrogen gas	320 cu ft	35¢/100 cu ft[b]	1.12
Sodium ethoxide	1.1 lb	11¢/lb[c]	.69
Acetic acid	1.4 lb	10¢/lb	.14
Acetone	18.8 lb	8¢/lb	1.50
			$21,76

[a] 2.5% losses of fats in system experienced in pilot plant.

[b] Liquid nitrogen delivery.

[c] Price of 17–18% solution.

mestic cottonseed oil can be converted into cocoa butter-like fat needed by the candy industry in the United States, not as a substitute for cocoa butter, but as a supplement to the natural fat. Increased domestic consumption of candy brought about by rising disposable income, gives additional emphasis to the need for this product.

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The Antioxidant Activity of 3,5-Di-tert-butyl-4-hydroxybenzyl Derivatives[1]

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Abstract

Various electron donating groups such as alkoxyl, alkylthio, and alkylamino groups were used to replace a hydrogen atom of the para-methyl group of 2,6-di-tert-butyl-4-methylphenol, BHT. The antioxidant activity of these 3,5-di-tert-butyl-4-hydroxybenzyl derivatives in stripped corn oil at 79.5° ±1.0C was measured on the basis of the length of the induction period. A modified peroxide determination was devised and used in the present study. The overall average of the per cent accuracy, based on the standard error, was 2.5%.

The results indicated that the tertiary methyl and ethylamine derivatives had the strongest potency among all compounds tested. Both amine derivatives were able to prolong the induction period of the corn oil twice as much as BHT. The alkoxyl derivatives were as effective as BHT. The alkylthio derivatives showed stronger activity than either BHT or the alkoxyl derivatives. The secondary alkylamine derivatives, except the n-hexadecylamine derivative, demonstrated nearly the same degree of potency as BHT. However, the n-hexadecylamine derivative exhibited far stronger activity than either the three lower alkylamine derivatives or BHT. In all three homologous series, the methyl derivatives showed significantly lower activity than the ethyl or n-propyl derivatives. Differences between the ethyl and n-propyl derivatives were not significant. 3,5-Di-tert-butyl-4-hydroxybenzylpyridinium bromide acted as a prooxidant. An attempt has been made to explain the variation in activity of these derivatives in terms of the inductive effect exerted by the nucleophilic substituents and/or in terms of the structural features of the derivatives.

IT HAS BEEN SHOWN (1) that tert-butyl groups in the ortho-positions and an alkyl group at the para-position resulted in the most effective antioxidant activity in the alkyl phenolic type of antioxidants of which 2,6-di-tert-butyl-4-methylphenol (BHT) is one of the best known to date. Among 2,6-di-tert-butyl-4-alkylphenols, a variation of the alkyl chain from a methyl to n-butyl group did not cause any significant modification in antioxidant activity (2). It has been reported that an electron donating group at the para-position of the alkylphenols would enhance antioxidant activity (3). On the other hand, an electron withdrawing group at the same position has been reported to retard or completely eliminate antioxidant activity (3,4). Furthermore, it has been observed that the removal of such an electron withdrawing group at the para-position of 3,5-di-tert-butyl-4-hydroxybenzaldehyde resulted in the recovery of antioxidant activity. 3,5-Di-tert-butyl-4-hydroxybenzaldehyde regained antioxidant activity when it was converted into 3,5-di-tert-butyl-4-hydroxybenzaldehyde isonicotinoylhydrazone (4).

In the present study a hydrogen atom on the para methyl group of 2,6-di-tert-butyl-4-methylphenol (BHT) was replaced with various electron donating groups such as the alkoxyl, alkylthio, and alkylamino groups. We have assumed that replacement of a hydrogen atom of the para-methyl group of BHT with a strong electron donating group would enhance the functional activity of the compound. The antioxidant activity was measured and compared on the basis of the length of induction periods of substrates (stripped corn oil) containing the 3,5-di-tert-butyl-4-hydroxybenzyl derivatives. Efforts were made to correlate the variation in antioxidant potency with the inductive effect of the substituent groups and/or with structural features of the benzyl derivatives.

Experimental

The Synthesis of Test Compounds. 3,5-Di-tert-butyl-4-hydroxylbenzyl bromide (III) was prepared directly from 2,6-di-tert-butyl-4-methylphenol (BHT) as described by Schmid and Karrer (5) and Dauben (6) (Fig. 1). The benzyl bromide was also obtained through rearrangement of 2,6-di-tert-butyl-4-methyl-4-bromo-2,5-cyclohexadienone (II) (7,8). The synthesis of 3,5-di-tert-butyl-4-hydroxy-benzylmethyl (V), ethyl (VI), and n-propyl (VII) ethers was achieved by alkylation of 3,5-di-tert-butyl-4-hydroxybenzyl alcohol (IV) with sodium alkoxide. The methyl derivative was also prepared by direct reaction of 2,6-di-tert-butyl-4-methyl-4-bromo-2,5-cyclohexadienone (II) with sodium methoxide. 3,5-Di-tert-

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