TABLE III

Urea Fractionation of Ester Distillates of Bodied-Oil Samples

Sample No.	1	2	3	4	5
Yield, %[a]					
Distillable esters	96.1	92.6	90.0	86.4	75.0
Adduct esters	....	81.7	80.0	76.9	54.6
Non-adduct esters	....	5.2	5.0	9.5	17.5
Cyclic[b] esters	....	6.4	6.5	8.2	19.4
Iodine value, Wijs 1 hr.					
Distillable esters	....	126.8	117.8	109.4	81.3
Adduct esters	....	128.6	119.1	113.2	78.7
Non-adduct esters	....	92.6	94.8	94.5	92.6
Refractive index at 20°C.					
Distilled esters	....	....	1.4649	1.4648	1.4705
Adduct esters	....	1.4625	1.4642	1.4645	1.4669
Non-adduct esters	....	1.4794	1.4798	1.4801	1.4802
Molecular weight					
Non-adduct esters	....	288.0	298.0	306.0	....

[a] Yields calculated on total ester basis.
[b] Cyclic esters = non-adduct of total mixed esters — nondistillable esters.

TABLE IV

Acetone-Soluble Portions of the Polymerized Safflower Oil

Sample No.	1	2	3	4
Yield, %	100.0	100.0	100.0	72.7
Iodine value, Wijs 1 hr	136.0	126.7	116.7	114.5
Refractive index at 20°C	1.4802	1.4828	1.4848	1.4854
Molecular weight	908.1	928.0	959.0	942.0
Dimeric acids[a] (A)	2.0	3.44	5.5	4.4
Non-distillable esters % of monomeric (B)	3.9	7.4	10.0	12.2
Intra-dimerization, % as acids (B-A)	1.9	3.96	4.5	7.8

[a] Dimeric acids calculated from eqn. $Y = 66.7\ (1-A_1/A_n)$.
Where A_1 = molecular weight of the original glyceride [Adams and Powers, J. Appl. Phys., 17, 325 (1946)].
A_n = molecular weight of the bodied glyceride.

was presumably a cyclized product of methyl linoleate as it has a mean molecular weight of 293.7 (theo. 295) and a mean unsaturation of approximately one double bond per mole of methyl ester corresponding to a hydrogen deficiency of 1.96 to 2.01.

REFERENCES

1. Mehta, T. N., and Sharma, S. A., J. Am. Oil Chemists' Soc., *33*, 38 (1956).
2. Wells, A. F., and Common, R. H., J. Sci. Food Agr., *4*, 233 (1953).
3. Paschke, R. F., and Wheeler, D. H., J. Am. Oil Chemists' Soc., *31*, 208 (1954).
4. Bradley, T. F., and Johnston, W. B., Ind. Eng. Chem., *32*, 802 (1940).
5. Benham, G. H., and Klee, L., J. Am. Oil Chemists' Soc., *27*, 127 (1950).
6. Joubert, F. J., and Sutton, D. A., J. Am. Oil Chemists' Soc., *29*, 287 (1952).
7. Paschke, R. F., Jackson, J. E., and Wheeler, D. H., Ind. Eng. Chem., *44*, 1113 (1952).

[Received August 21, 1956]

Determination of Ethylene Oxide in Fumigated Copra Products[1]

JAMES H. BENEDICT, Procter and Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio

THE MILLER AMENDMENT to the Federal Food, Drug, and Cosmetic Act (9, 10) requires the residue of an approved pesticide or fumigant remaining on a raw agricultural product to be below a limit established by the Food and Drug Administration. To obtain a limit or tolerance under the new law, information concerning the quantity of residue and the possible reaction products must be submitted to the Food and Drug Administration. Since raw copra is frequently fumigated with ethylene oxide, an analytical method was required for determining trace amounts of this material in the range of 0 to 50 p.p.m. in raw copra. In addition, examination of fumigated and unfumigated products is also required.

Analytical methods based upon the hydrolysis of ethylene oxide in concentrated salt solutions to yield ethylene chlorohydrins have been published by Lubatti (5, 6, 7) and others (1, 2, 4). These methods employ concentrated solutions of either NaCl, KCNS, $CaCl_2$, $MgBr_2$, or LiCl in standardized acids as a collecting and hydrolyzing solution.

Lubbati's method (7) was selected as the most promising. However the procedure as described was entirely too awkward and cumbersome for routine use. By using the techniques that Hollingsworth and Waling (3) employed to determine ethylene oxide in air, a completely revised method was developed for determining trace quantities in fumigated products. The method involves drawing air through the sample to sweep out ethylene oxide and then passing the gases through a magnesium bromide solution, where the oxide reacts to form ethylene bromohydrin. The two-step reaction is as follows:

a) $MgBr_2 + H_2SO_4 \longrightarrow MgSO_4 + 2\ HBr$

b) $HBr + CH_2{-}CH_2 \longrightarrow HO{-}CH_2{-}CH_2{-}Br$ (O bridging the $CH_2{-}CH_2$)

The decrease in acidity is proportional to the ethylene oxide content.

This paper will present the method in detail and some data obtained thereby.

Experimental

Apparatus Assembly. The arrangement of the apparatus is shown in Figure 1. The first air-washing tube is half filled with 40% sodium hydroxide solution. The sample flask is a 3-neck, 3-liter flask. The flow-meter may be any type capable of measuring 1.5 liters of air per minute. Only one meter is required; if several systems are set up, the air flow through the other systems may be regulated by comparison of the bubbling rates in the air-scrubbing tubes. A water aspirator is the preferable source of vacuum.

[1] Presented at the spring meeting of the American Oil Chemists' Society, Houston, Tex., April 23–25, 1956.

AERATION APPARATUS FOR ETHYLENE OXIDE

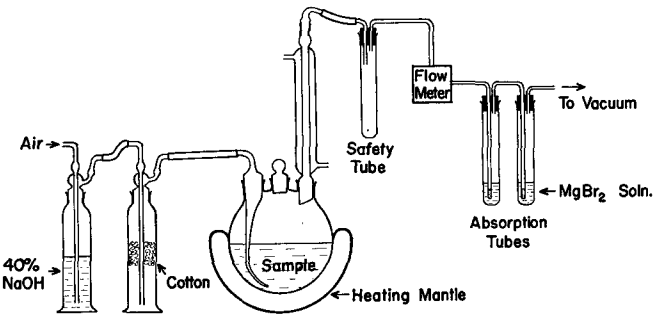


FIG. 1.

Procedure. Place 400 g. of sample in a 3-liter flask and attach to the apparatus assembly. Pipette 20 ml. of magnesium bromide solution (500 g. in one liter of 0.02 N sulfuric acid) into each absorption tube. Draw air at the rate of 1 to 1.5 liters per minute through the equipment for a period of one hour. This aeration is performed without heating.

After one hour add 2 liters of freshly boiled, hot distilled water to the sample in the flask. Intimate mixing of the sample with the hot water is absolutely essential. Apply enough heat to maintain the contents at the elevated temperature. Draw air continuously through this mixture for an additional 1.5 hrs.; then disconnect the equipment. Add three drops of 0.1% bromcresol green indicator to each tube, and titrate with 0.02 N sodium hydroxide solution. When the solution turns green, stopper the tube with a clean rubber stopper and shake to rinse down the walls of the tube. Continue the titration dropwise to the first appearance of a definite blue end-point. Compare the color with a blank titrated to the same end-point. A magnetic stirrer provides efficient stirring during the titration.

To determine reagent blanks, pipette exactly 20 ml. of magnesium bromide solution into large test tubes. Add 3 ml. of distilled water and titrate as described above.

Results and Discussion

The method was tested by pipetting known quantities of ethylene oxide in water into unfumigated samples and analyzing for ethylene oxide. The amount of ethylene oxide added was determined by placing a comparable aliquot in 20 ml. of magnesium bromide solution and, after one hour, titrating in the same manner as the absorbing tubes. The data are presented in Table I. Each value is the average of duplicate determinations. The average difference between duplicates was 9% relative, which amounts to less than 0.1 p.p.m. at the one p.p.m. level. It is seen that the recoveries were greater than 90% in nearly all cases.

TABLE I

Recovery of Ethylene Oxide

p.p.m. added	% Ethylene Oxide Recovered		
	Copra	CNO	Meal
0.6	116	80	93
1.7	109	103	109
2.3	97	96	....
3.2	93	104	81
4.2	....	....	92
7.0	80	....	90
9.7	....	89	....
30.9	92	....	....
66.0	95	....	....
111.0	94	....	....

Contrary to prevalent conceptions, ethylene oxide is quite stable in a neutral or alkaline solution (7, 8). We have observed that only one-third of the ethylene oxide hydrolyses upon standing one week in distilled water at room temperature. Ethylene oxide appears to be quite stable in coconut oil at room temperature. When added to coconut oil at the 2-p.p.m. level, no change in the ethylene oxide content was noted after standing one month at room temperature (23–27°C.).

Samples of unfumigated raw copra, copra meal, and coconut oil (CNO) were examined for ethylene oxide content. In all cases no detectable amount was found. This demonstrates the absence of any interfering substances in the copra or meal. Volatile amines or acids will interfere. In the case of coconut oil containing free fatty acids the addition of NaOH to the sample before aerating prevents the volatilization of these acids.

Fumigated copra, copra meal, and coconut oil were analyzed, and some of the data are presented in Table II. Traces of ethylene oxide were found in all of the raw copra samples examined, but in no instance did the level exceed 4.5 p.p.m. Only half of the coconut oil samples showed detectable quantities of ethylene oxide, and all were below 1.5 p.p.m. No ethylene oxide was found in most of the copra-meal samples. It was also determined that deodorization of coconut oil, as commercially practiced, would completely remove any ethylene oxide that might be present in the oil. In one case 75 p.p.m. of added ethylene oxide were completely removed by deodorization.

TABLE II

Ethylene Oxide Found in Fumigated Products

Sample No.	p.p.m. Ethylene Oxide in		
	Copra	CNO	Meal
1	3.6	NF	NF
2	1.4	NF	NF
3	2.1	0.7	NF
4	4.1	1.2	2.9
5	0.6	NF	NF
6	0.4	NF	NF
7	0.6	0.6	NF
8	4.2	0.9	2.7
9	0.6	NF	NF
10	0.3	0.3	NF

NF — None found (less than 0.3 p.p.m.).

This method is suitable for routine-control analyses on many products in addition to copra products. Cottonseed flour, soybean meal, and spices have been examined successfully with only minor variations in the procedure.

Summary

A method is presented for the determining of trace amounts of ethylene oxide in raw copra, copra meal, and coconut oil. The lower limit of detection is 0.3 p.p.m. with an average deviation of 0.2 p.p.m in the range 0 to 5 p.p.m. The recoveries of added known quantities of ethylene oxide were greater than 90% in nearly all cases.

Fumigated raw copra was found to contain small residues of ethylene oxide, but in no instance did the level exceed 4.5 p.p.m. Only half of the coconut oil samples from fumigated copra showed detectable quantities, and all were below 1.5 p.p.m. Nearly all of the meal samples were "none found."

The method should be applicable to all types of edible products.

REFERENCES
1. Burns-Brown, W., J. Soc. Chem. Ind., *55*, 321 (1936).
2. Burns-Brown, W., J. Soc. Chem. Ind., *56*, 116 (1937).
3. Hollingsworth, R. L., and Waling, B. F., Am. Ind. Hyg. Assoc. Quart., *16*, 52 (1955).
4. Kerchow, W. F., Z. Anal. Chem., *108*, 240 (1937).
5. Lubatti, O. F., J. Soc. Chem. Ind., *51*, 361 (1932).
6. Lubatti, O. F., J. Soc. Chem. Ind., *54*, 424 (1935).
7. Lubatti, O. F., J. Soc. Chem. Ind., *63*, 133 (1944).
8. Phillips, C. R., and Kaye, S., Am. J. Hyg., *50*, 270 (1949).
9. Public Law No. 518, 83rd Congress.
10. Rankin, W. B., J. Agr. Food Chem., *4*, 214 (1956).

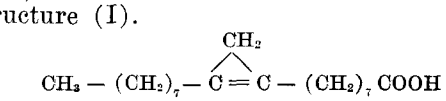
[Received January 22, 1957]

Composition of the Seed Oil of Sterculia foetida, Linn.

J. P. VARMA, SHARDA DASGUPTA, BHOLA NATH, and J. S. AGGARWAL,
National Chemical Laboratory, Poona, India

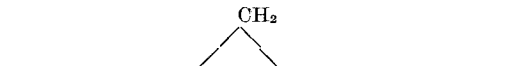
Sterculia foetida, Linn, which is called Java olives in English and Jangli Badam in Hindi *(N. O. Sterculiaceae)*, is a large evergreen tree found usually in the western and southern parts of India, Burma, and Ceylon and occasionally (17, 7) in east tropical Africa, Borneo, Java, Sumatra, Indo-China, Malaya, and North Australia. The seed kernels contain 53–55% of a pale yellow oil which polymerizes rapidly at 240–250°C. and even to some extent at lower temperatures (14).

From the oxidation products of the mixed methyl esters of this oil Hilditch, Meara, and Zaky (6) deduced the presence of 70% of a new C_{19}-acid, 12-methyl-9:11 octadecadienoic acid. Later Nunn (9) fractionated the mixed acids with urea and isolated this acid, which he named sterculic acid and assigned the structure (I).



(I)

Recently pure sterculic acid has been isolated in this Laboratory from the total fatty acids of the oil by low-temperature, fractional crystallization. On the basis of physical constants, spectroscopic data, and degradative and synthetic studies, it has been given the structure (II) (15, 13, 16).



(II)

The availability of the pure acid prompted further studies on the composition of the oil. In the absence of a suitable method for the estimation of sterculic acid, an infrared technique has been evolved in this Laboratory. The 9.92μ band charcateristic of a cyclopropane ring (2) has been employed for the estimation of sterculic acid.

Extraction and Saponification of the Oil. The seeds of *Sterculia foetida* were obtained from the Government Botanical Gardens, Poona, and decorticated. The kernels were finely crushed and exhaustively extracted with petroleum ether (b.p. 40–60°C.) at 15°C. Oil was recovered from a portion of the extract and found to have the following characteristics:

Specific gravity (40°C.)	0.9239
refractive index (40°C.)	1.4662
acid value	5.7
saponification value	177.5
iodine value (Wijs)	74.0

In order to avoid polymerization of the oil, the remainder of the extract was hydrolyzed by being stirred with an excess of methanolic caustic potash for about 18 hrs. at 25–28°C. The solvent was distilled off under reduced pressure, and the soap was dissolved in water. After removal of the unsaponifiable matter, according to the method of the Society of Public Analysts (11), the total fatty acids were isolated and analyzed.

Estimation of Sterculic Acid. The presence of the 9.92μ absorption band, characteristic of a cyclopropane ring, has been used in these experiments for estimating sterculic acid. The measurements were made with a Grubb Parsons, single-beam, infrared spectrometer with a sodium chloride prism, a fixed slit width of 0.25 mm., and a 0.1-mm. sodium chloride cell. Optical densities at various concentrations of sterculic acid in carbon disulphide solution are given below:

Conc. g/liter	optical density
54	0.10
82	0.15
113	0.21
200	0.37
250	0.46
300	0.56

The "base line" technique (4) was adopted in measuring the absorption peaks. The specific extinction coefficient of sterculic acid was calculated according to the formula

$$A = Ect.$$

where A = optical density; C = Conc. in g. per liter; E = specific extinction coefficient; and t = thickness in cm. The mean specific extinction coefficient comes to be 0.185.

The accuracy of the method was tested by examining known mixtures of sterculic and linoleic acids. The results recorded below show a good agreement with the known weights of sterculic acid in the mixtures.

Added	Found
79.1	79.8
60.3	59.8
50.9	50.5
19.0	18.7

In six replicate analyses the sterculic acid content of sterculia oil was found to be between 71.5–72.0% (average 71.8%) of the total fatty acids.

Estimation of Polyethenoid Acids. When sterculic acid is isomerized according to the method recommended by Hilditch, Morton, and Riley (5) for linoleic acid, the $E^{1\%}_{1cm.}$ value at 234 mμ is 66.1.

After the mixed acids of sterculia oil were isomerized with a potassium hydroxide-glycol reagent at