Fire Record of Oil-Extraction Plants, and g) How to Get the Facts on Accidents. The foregoing were sent to "All Members of the A.O.C.S. Technical Safety Committee" in letters from the chairman dated May 16, September 11, and October 19, 1956, and January 2, January 3, March 8, and April 5, 1957.

A. Ernest MacGee, chairman

Cyclization During Heat Bodying of Safflower Oil at 300°C.

T. N. MEHTA and S. A. SHARMA, Laxminarayan Institute of Technology, Nagpur University, Nagpur, India

IT WAS CONCLUDED in previous work (1) on heat-bodying of linseed oil that cyclization of linolenic acid took place to an extent of 17% during the initial stages of polymerization because the isolated cyclic product was found to contain an average of two double bonds. Wells and Common (2) also affirmed that the cyclic products obtained from the polymerization of linseed oil were derived from linolenic acid. Therefore it is presumed that oils containing only linoleic acid (but not linolenic) may not result in cyclic products during the polymerization.

However it was pointed out by Paschke and Wheeler (3) that methyl linoleate also cyclized during heat-bodying. They observed that after prolonged polymerization 60% of the monomer was monoethenoid and did not hydrogenate to methyl stearate. The product was thought to be the cyclic monoethenoid isomer of methyl linoleate although it was found to contain slightly higher unsaturation than corresponded to one double bond per mole of esters.

Indian safflower oil was chosen to study the cyclization of linoleic acid during heat-bodying at 300°C. as the oil contains mainly the di-ethenoid acid with very little or no linolenic acid. The methyl esters of the bodied oil samples were distilled, and the distillates were fractionated with urea to separate the cyclic products present, if any. The esters of the acetone-soluble oil were also subjected to distillation, followed by urea fractionation to find out the extent of intradimerization and the cyclization in the monomeric fraction of the oils.

Experimental

I. Safflower oil (I.V. 144.1) was heat-bodied at 300°C. under an atmosphere of CO_2 for 3 hrs. Samples were taken at intervals of 1 hr. after the oil had attained temperature. These were analyzed for viscosity, refractive index, iodine value, and molecular weights, and the data are given in Table I.

Urea Fractionation. Samples were hydrolyzed and then esterified according to the method recommended by Bradley *et al.* (4). The esters were distilled from a liquid metal bath at 250°C. with 10-mm. of mercury pressure to estimate the amount of monomer in each sample. The total mixed esters as well as the distilled esters were fractionated with urea, using 1:4:4 proportion of esters : urea : methanol. The data of both the experiments are given in Tables II and III, respectively.

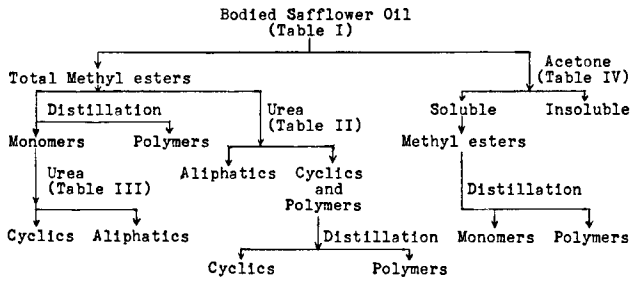

FIG. 1.

Acetone Fractionation. The samples were extracted with 5 vol. of cold acetone, and soluble and insoluble portions were separated. The acetone-soluble portions from samples of bodied oil were converted to methyl esters and subsequently subjected to distillation.

II. Safflower oil was heat-bodied under the atmosphere of CO_2 at 300°C. for 6 hrs. Methyl esters of the bodied oil were prepared as above, and the cyclic esters were concentrated by fractionation with urea.

The total mixed methyl esters were first treated with urea in this case to remove all the straight chain monomeric esters as urea adducts. From the non-adduct esters the cyclic material was concentrated by distillation at 10 mm. of mercury pressure to separate it from polymers, followed by urea fractionation of the distillate (1:4:4) to ensure complete removal of non-cyclic material. The monomeric urea non-adduct concentrate was analyzed for iodine value (Wijs and Benham and Klee methods), saponification value, and refractive index. The results are given in the discussion section.

The experimental procedure has been shown in Figure 1.

TABLE I

Safflower Oil Heat-Bodied Under the Atmosphere of CO_2 for 3 hrs. and 6 hrs. at 300°C.

Sample No.	1	2	3	4	5
Heating time in hours after attaining temperature	0	1	2	3	6
Viscosity in poises at 29°C	0.59	1.15	2.74	5.7	80.0
Refractive index at 20°C	1.4802	1.4828	1.4848	1.4868	1.4906
Iodine value (Wijs) 1 hr.	136.1	126.7	116.7	110.2	85.2
Iodine value drop					
Theoretical[a]	1.8	3.1	4.75	6.9	....
Observed	8.1	17.4	27.4	33.9	....
Molecular weight (uncorrected) M_n	908.1	928.0	959.0	1000.0	....

[a] I.V. drop calculated from the equation: $Y = 57.8 \times 875(1/880 - 1/M_n)$.
M_n: Molecular weight of the bodied glyceride.

TABLE II

Urea Fractionation of Total Mixed Methyl Esters of the Bodied-Oil Samples

Sample No.	1	2	3	4	5
Yield, %					
Adduct esters	....	81.5	80.7	76.8	55.6
Non-adduct esters	....	13.8	16.5	21.8	44.4
Losses	....	4.7	2.8	1.4	....
Iodine value, Wijs 1 hr.					
Total mixed esters	....	122.7	113.1	106.9	82.2
Adduct esters	....	128.5	115.4	108.4	79.8
Non-adduct esters	....	97.2	92.0	....	....
Refractive index at 20°C.					
Total Esters	....	1.4658	....	1.4700	1.4772
Adduct esters	....	....	....	....	1.4701
Non-adduct esters	....	....	....	....	1.4862
Molecular weight					
Total esters	300.0	310.0	317.0	320.0	....

Discussion

The data summarized in Table I indicated that there was little polymerization of safflower oil in 3 hrs. of bodying. The viscosity of sample 4 was 5.7 poises, and its molecular weight was only 1,000. The gradual drop in the iodine value was inadequately explained by the increase in molecular weight unless it was assumed that some intramolecular reactions took place. However it was shown by Mehta and Sharma (1), Paschke and Wheeler (3), and Joubert and Sutton (6) that intradimerization takes place to a limited extent in the monomeric portion of bodied oil. Mehta *et al.* also observed that the cyclization predominated in the earlier stages of polymerization of linseed oil. It was expected that cyclization of linoleic acid would result hence the methyl esters of bodied oil samples were prepared. The total esters as well as the distilled monomeric esters were fractionated with urea to separate the cyclic compounds from the non-cyclic and the polymeric material.

The urea fractionation of the total mixed esters (Table II) showed that 81.5, 80.7, and 76.8% were straight chain esters and the non-adduct-forming material contained cyclic monomers, dimers, and polymers. Although the monomeric distillates from the total mixed esters amounted to 92.6, 90.0, and 86.4%, they contained only 81.7, 80.0 and 76.9% straight chain esters, respectively (Table III). The remaining were cyclic because they did not form adducts with urea and because branched chain compounds were not formed in this case. These cyclic compounds amounted to 5.2, 5.0, and 9.5% of the total esters, and these values were in fair agreement with the calculated values 6.4, 6.5, and 8.2% obtained from non-adduct-forming total mixed esters—nondistillable esters = % cyclic. These products had about the same iodine value and refractive index (92.6, 94.5, and 94.8; and 1.4794, 1.4798, and 1.4801, respectively). Molecular weight determinations on the cyclic compounds indicated their monomeric nature. The I.V. of the non-adduct-forming distillate was approximately 92 to 94, indicating the presence of traces of dienoic esters in this fraction. The mean unsaturation calculated from Wijs iodine value and molecular weight was —2.20H to —2.26H. The saponification value was 193, and the acid value of the cyclic acid obtained by saponification of these esters was found to be 198.

The intradimerization in the monomeric portion of the oil was also calculated from its acetone-soluble fractions (Table IV). As described in a preceding publication (1), the percentage of intradimerization was calculated and amounted to 1.9 to 7.8.

Molecular weights, saponification value, and the acid value of the saponified cyclic product indicated no disproportionation in the fatty acid chains hence the slightly higher iodine value was caused by the presence of a very slight amount of unpolymerized linoleate. Therefore the oil was bodied for 6 hrs. (sample No. 5, Table I) to a higher viscosity of 80-poises so as to obtain the cyclic products in higher yield and to minimize the presence of unreacted linoleic acid in the bodied oil.

From the methyl esters of this bodied oil (6 hrs.) the cyclic and polymeric esters were first concentrated with urea, then distilled to remove polymers. Finally the cyclic compound was isolated by treatment with urea so that no linoleate would remain in it. The yield was 16.1% of the total esters. The results of the fractionation of the total mixed esters and the distillable esters by the single addition of urea are also given in Tables II and III, sample No. 5. This product had I.V. 85.2 (Wijs), and the total unsaturation as determined by the Benham and Klee method (1 hr. of reaction time) was 84.2. The mean molecular weight calculated from the saponification value (191.2) was 293.7 (theo. 295). The mean unsaturation calculated from the mean molecular weight and Wijs iodine value was —1.96H or —2.00H approximately. This was therefore the cyclized product of methyl linoleate.

During the polymerization of methyl linoleate at 300° and 290°C. Paschke, Jackson, and Wheeler (7) isolated monomeric fractions of 19.4 and 17.6% with I.V.'s of 100.5 and 101.6, respectively. By spectral analysis these were shown to contain a small amount of normal and conjugated linoleates. From the data given by Paschke, Jackson, and Wheeler (7) the iodine values of the supposed cyclic esters [*viz.*, $19.4 - (1.6 + 1.6) = 16.2\%$ and $17.6 - (1.5 + 1.5) = 14.6\%$] alone can be calculated to be 86.4 and 87.0%, respectively. Thus the iodine values calculated closely correspond to those obtained by us for the cyclic product.

Although it is difficult to establish the structure of the cyclic compound from the data available, it may be reasonably noted that this urea non-adduct-forming fraction is cyclized methyl linoleate with monoethenoid unsaturation. Further investigation regarding its structural formula is in progress.

Summary

Safflower oil was heat-bodied at 300°C., and its methyl esters were fractionated by vacuum-distillation and with urea. A monomeric cyclic compound was isolated as the non-adduct-forming distillate. It

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.