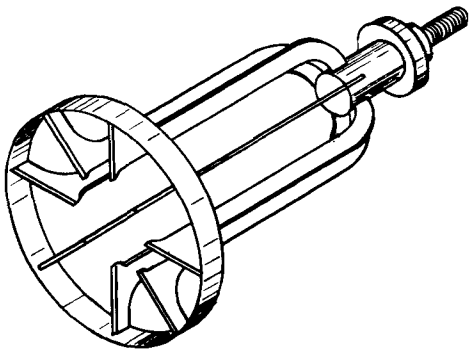

FIG. 4. Knife.

it is forced downwards to the milling faces. These milling faces are perpendicular to the axis with material forced inward against centrifugal force in order to pass through the zone of high-shear-force energy. The mill, operating on mayonnaise, requires external pressure to obtain proper feed rates although in many industrial applications the integral impellers supply this pump pressure. During the experimental work it was necessary on many occasions to cut the mill speed to one-half its normal operating speed since sufficient capacity was not available to feed material at adequate rates.

For standardization purposes we have adapted the Gaulin Curd Tension Meter to mayonnaise in order to measure stiffness of final product. This instrument drives a knife-edged grill (Fig. 4) down through a sample at a constant speed of 8 in./min. and measures the resistance in grams offered by the sample to this standard grill, moving at this constant speed.

Figure 5 shows the effect of changing the colloid mill settings while holding formulation and plant capacity constant. Note that the stiffness levels off below .010 in. separation of the mill faces but that mayonnaise can be made, at least on this formulation, with settings up to .020 in. Tests were made by changing settings while the mill was running on a single complete base, a procedure made possible by the Gaulin design.

After measuring these samples, identical samples were shipped 400 miles and held under shelf-storage conditions for one week. The effect of time on this mayonnaise is shown.

By way of comparison three brands of mayonnaise were obtained locally and measured with the same equipment. These results are shown in Figure 6. Note how much more stiff mayonnaise can be made if the market were available.

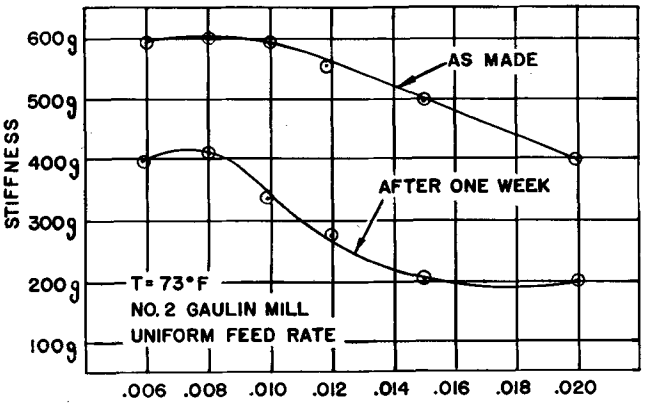

FIG. 5. Mill separation.

By use of this continuous system and the Gaulin mill we have been able to expand our formulation quite radically. We have dropped from 78% oil to 65% oil without changing egg percentage and have been able to drop the egg content 3% without addition of more oil. In each case color has been affected, but an acceptable product can be made.

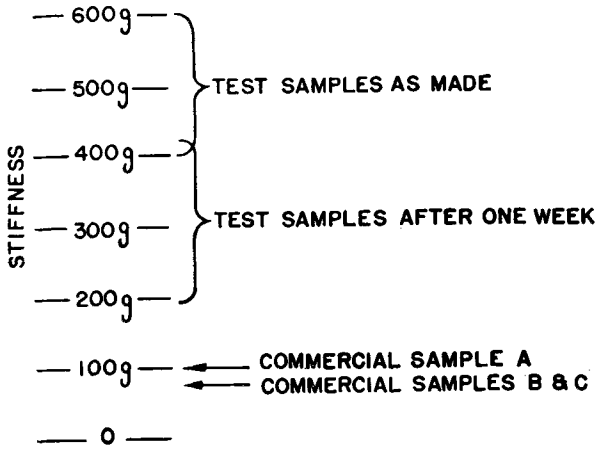

FIG. 6. Comparison of mayonnaise samples.

The advantages of such a system are as follows: a) truly continuous operation reduces equipment size, thereby effecting savings in investment; b) product uniformity is assured with use of minimum formulations, thereby effecting raw-material savings; and c) operator training-time is markedly reduced, and relatively little attention is required from operator.

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Isolation of Vernolic Acid from *Vernonia anthelmintica* Oil

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VERNOLIC ACID, the chief fatty acid of *Vernonia anthelmintica* seed oil, has been characterized by Gunstone (1) as *cis*-12,13-epoxy-*cis*-9-octadecenoic acid. This acid has also been shown by Bharucha and Gunstone (2) to occur in the oil of *Cephalocroton cordofanus,* and by Chisholm and Hopkins to occur in oils of *Hibiscus esculentus* (3) (okra) and *Hibiscus cannabinus* (4) (kenaf). Despite Gunstone's thorough degradative work on vernolic acid and subsequent stereochemical work (5) on glycols derived from it, the isolation of this compound in the free state, with its epoxy group intact, appears never to have been reported in the literature.[1]

[1] Just as this work was being completed, the authors were informed that C. Y. Hopkins and M. J. Chisholm had submitted to this journal a manuscript describing isolation of vernolic acid from *Hibiscus cannabinus* by a somewhat similar method.

This note describes conditions under which approximately 74% of the vernolic acid in *Vernonia anthelmintica* seed oil can be recovered in the mixed acids obtained upon saponification. A procedure for isolation of pure vernolic acid is also described. Variations of the fractionation procedure were not attempted but could probably be improved to increase recovery of pure vernolic acid.

It was found that the reactive epoxy group could be preserved after saponification of the oil with *ca.* 1 *N* ethanolic potassium hydroxide, provided the alcoholic alkali after completion of refluxing was rendered only very slightly acidic (pH 4–5) and extraction was carried out immediately. Concentration and purification of vernolic acid were then effected by a sequence of low-temperature crystallization, urea complex fractionation, solvent partitioning, and a final recrystallization. The course of the purification was followed by Durbetaki's method for determining oxirane oxygen (6). The purified acid was a poorly crystalline solid, m.p. 25–28°.

Experimental

Oil Extraction. Coarsely ground, air-equilibrated seeds of *Vernonia anthelmintica* (Willd.) (76.6 g.) were extracted over-night in a Soxhlet apparatus with 30–60° petroleum ether. The bulk of the solvent was evaporated under an atmosphere of nitrogen, and the balance was removed *in vacuo* by means of a rotating evaporator. A yield of 17.9 g. of greenish oil (I) was obtained containing 3.5% oxirane O; infrared showed maxima at 11.85, 12.17 μ (med. intensity).

Saponification. A mixture of 6.3 g. of I, 1.5 g. of potassium hydroxide in 2 ml. of water, and 18 ml. of 95% ethanol was refluxed for 30 min. The solution was then cooled, diluted with water, and extracted with ether to remove unsaponified matter; the yield of such material was 0.4 g. The alkaline liquor was then carefully acidified to pH 4–5 by dropwise addition of dilute hydrochloric acid and was immediately extracted three times with ether. The combined ether extracts were dried with sodium sulfate and evaporated under nitrogen, yielding 4.1 g. of mixed fatty acids (II) containing 4.0% oxirane O.

Low Temperature Crystallization. A solution of 4.1 g. of II in 40 ml. of 30–60° petroleum ether was cooled for 3 hr. at −10° with occasional stirring. The supernatant liquid was then withdrawn with a fritted glass filter stick. The solid material was dissolved in petroleum ether, and the process was repeated three times, yielding concentrate III containing 4.6% oxirane O. The over-all yield in these successive recrystallizations was 57%.

Urea Complex Fractionation. A 1.56-g. portion of III was dissolved in 30 ml. of absolute methanol containing 4 g. of urea and let stand over-night at room temperature. After the solution had been chilled at 0° for 2½ hr., a crop of crystals appeared that was removed by filtration. The yield of urea adduct (IV) was 1.98 g., m.p. *ca.* 102° dec. IV was decomposed with water, and the resulting aqueous mixture was extracted with ether twice. The combined ether extracts were washed with water, dried with sodium sulfate, and evaporated. A yield of 0.47 g. of fatty acid concentrate V, containing 4.8% oxirane O, was obtained.

Hexane-Acetonitrile Solvent Partitioning. A 0.35-g. portion of V was dissolved in 10 ml. of *n*-hexane and extracted with 20 ml. of acetonitrile. The acetonitrile layer was then re-extracted twice with hexane. Upon evaporation, the acetonitrile solution yielded 0.22 g. of vernolic acid. After recrystallization from hexane at −20° the acid was a poorly crystalline solid, m.p. 25–28° (Fisher-Johns melting point apparatus).

Anal.: Calcd. for $C_{18}H_{32}O_3$: C, 72.9; H, 10.9; oxirane O, 5.4. Found: C, 73.0; H, 10.7; oxirane O, 5.4.

Acknowledgments

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REFERENCES

1. Gunstone, F. D., J. Chem. Soc., *1954*, 1611.
2. Bharucha, K. E., and Gunstone, F. D., J. Sci. Food Agric., *7*, 606 (1956).
3. Chisholm, M. J., and Hopkins, C. Y., Canadian J. Chem., *35*, 358 (1957).
4. Hopkins, C. Y., and Chisholm, M. J., Abstracts, 31st Fall Meeting, American Oil Chemists' Society, Cincinnati, O., Sept. 30–Oct. 2, 1957, No. 39.
5. Bharucha, K. E., and Gunstone, F. D., J. Chem. Soc., *1956*, 1611.
6. Durbetaki, A. J., Anal. Chem., *28*, 2000 (1956).

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ABSTRACTS . . . . R. A. REINERS, Editor

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• Fats and Oils

DEVICE FOR ISOLATION OF COMPONENTS SEPARATED BY GAS CHROMATOGRAPHY. J. M. Lesser (Barrett Division, Allied Chemical Corp., Philadelphia, Pa.). *Anal. Chem.* 31, 484 (1959). When the desired peak appears on the chromatogram, the collector is attached via the metal connector to the effluent gas exit, care being taken that both holes are open. After the elution of this component, the collector is removed and sealed at both ends with suitable plugs. Additional collectors can be used to collect other components from the same run.

INFRARED DETERMINATION OF HYDROXYL EQUIVALENTS IN STEROIDS. P. Kabasakalian, E. R. Townley, and M. D. Yudis (Res. Division, Schering Corp., Bloomfield, N. J.). *Anal. Chem.* 31, 375–6 (1959). The number of hydroxyl groups contained in a steroid molecule can be determined by using the fundamental hydroxyl stretching absorption in the infrared region. Hydrogen bonding and solubility problems which have heretofore complicated the measurement have been overcome by selecting pyridine as the solvent. The absorbance is linear with concentration for the associated band which appears near 3.05 microns and is essentially independent of the type of hydroxyl group.

GAS–LIQUID CHROMATOGRAPHY. DETERMINATION OF COLUMN EFFICIENCY. H. W. Johnson, Jr., and F. H. Stross (Shell Development Co., Emeryville, Calif.). *Anal. Chem.* 31, 357–65 (1959). Gas-liquid chromatography (GLC) can be used to determine physical constants as well as for quantitative analyses. For the latter, only peak areas need be accurately known, but accurate determination of physical constants, such as par-