dichlorostearic acid [m.p. 45-45.6°, from the low temperature additive chlorination of elaidic acid (20)] ethenoxylation was unsuccessful, perhaps because acidic by-products destroyed the alkaline catalyst. Accordingly 9,10-dichlorostearic acid was esterified with an equimolar ratio of a commercial polyethylene glycol, having an average of about 14 ethenoxy groups, in the presence of 0.1% naphthalene-$\beta$-sulfonic acid catalyst, in 24 hrs. at 125°. The product was a yellow liquid. Analysis for iodine number (zero), acid number (0.43), and percentage of chlorine (7.38) suggested almost complete conversion to $CH_3(CH_2)_7CHClCHCl(CH_2)_7CO_2(C_2H_4O)_{14}H$. Actually, however, a certain amount of polyethylene glycol and diester is to be expected. This chlorinated nonionic surface-active agent had solubility, wetting, foaming, and emulsifying properties similar to ethenoxylated oleic acid. The surface and interfacial tension values of a 0.1% solution at 28° were 33.8 and 6.0 dynes/cm., respectively.

## Summary

A laboratory survey of the properties of a series of ethenoxylated fatty acids and alcohols containing about 10, 15, 20, 30, and 40 ethenoxy groups per molecule has brought together information on solubility, cloud point, surface and interfacial tension, detergency, and wetting, foaming and emulsifying properties.

Ethenoxylated alcohols were generally more soluble and had better wetting and foaming properties than the acids. Ethenoxylated acids had generally lower surface and interfacial tension values. Both types of nonionics appeared to be excellent emulsifying agents. Most of the ethenoxylated acids and alcohols were equally effective as built detergents. Built ethenoxylated oleic acid (n = 10) and built hydroxy-, dihydroxy-, phenyl-, and xylylstearic acids (n = 20) were the best detergents.

Nonionic surface-active agents derivable from animal fats appeared to have an optimum range in the average number of ethenoxy groups per molecule, with respect to certain properties. The optimum was in the range of about 14 to 18 for wetting properties, the foaming properties of ethenoxylated alcohols, and the interfacial tension of ethenoxylated acids. This range is about equal to the value suggested for adequate solubility [3 less than the number of carbon atoms in the parent alcohol (3)] but somewhat higher than the general rule for maximum detergency [2/3 the number of carbon atoms in the parent acid or alcohol (1, 5)].

The rate of the reaction of octadecanol and stearic acid with ethylene oxide was compared. The alcohol reacted faster, in a non-specific manner. The acidity of the carboxyl group of stearic acid promoted conversion to ethylene glycol monostearate before further ethenoxylation occurred. After disappearance of the carboxylic acid the rate of the reaction of the ethenoxylated acid approached that for octadecanol. A reaction mechanism consistent with these results is proposed.

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# A Note on Improved Isolation of Concentrates of Linolenic Acid and Ethyl Linolenate from Linseed Oil[1]

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THE ISOLATION of concentrates of linolenic acid from linseed oil (1, 2, 3, 4, 6) or perilla oil (6) by urea complex separation methods has been described. Although 87% concentrates can be obtained in good yield from perilla oil, its limited availability makes it a poor choice of starting material for large-scale laboratory work. Linseed oil, on the other hand, is plentiful, but poor yields, low purity (70% or less), or a combination of the two, are obtained from it when published procedures are used.

The need developed in our laboratory for kilogram quantities of linolenic acid and ethyl linolenate of 80% or higher purity. This note describes the procedures used in their preparation in good yield from linseed oil fatty acids or ethyl esters. The success of the procedures depends upon the use of sufficient urea to blend with at least 50% of the linseed oil fatty acids or esters at room temperature. Lower temperatures (0-4°C.), as reported in the literature,

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[1] This note is IV in the series, "Application of Urea Complexes in the Purification of Fatty Acids, Esters, and Alcohols." Paper III is reference 6.

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give poor yields, and the use of less urea results in lower purities.

## Experimental

*Linolenic Acid Concentrate.* Linseed oil fatty acids (composition: 47% linolenic acid, 17% linoleic acid, 27% oleic acid, 9% saturated acids) were prepared from linseed oil by the rapid saponification technique (5). To a hot solution of 2,000 g. of urea in 5,000 ml. of methanol, 1,000 g. of linseed oil fatty acids were added with good mixing. Immediate precipitation occurred, and the solution was allowed to stand over-night at room temperature (16–24 hrs.). The complexes were filtered off and discarded. Most of the methanol was evaporated from the filtrate under a stream of nitrogen, and water was then added to dissolve the urea. The oil which separated was washed several times with water and dried by gentle heating under vacuum in a stream of nitrogen. The recovered acids weighed 425 g .; iodine number 241. Distillation from an alembic flask yielded 350 g. of linolenic acid concentrate, b.p. 160–162°/0.1, as a pale-yellow oil; iodine number 253; neutralization equivalent, 280; composition: linolenic acid 84%, linoleic acid 14%, oleic acid 0%, saturated acids 2%. The yield of linolenic acid recovered was 63%.

*Ethyl Linolenate Concentrate.* Some 2,000 g. of linseed oil fatty acids, 2,000 ml. of absolute ethanol, and 40 g. of naphthalenesulfonic acid were refluxed for 6 hrs. A large quantity of water was added, and the upper layer was washed several times with water and dried. The crude ethyl esters weighed 2,122 g. (97% yield); acid number 10. These were dissolved in a hot solution of 4,240 g. of urea in 10,600 ml. of methanol, and the complexes were separated as described above. From the filtrate 775 g. of esters were obtained; iodine number 210; saponification number 182. (Considerable difficulty was experienced with emulsions in the separation of the oily layer from the water. Petroleum naphtha, hexane fraction, was used to assist the separation.) Distillation yielded 620 g. of ethyl linolenate concentrate, b.p. 134–138°/0.1, iodine number 230; saponification number 183; acid number 14; composition: linolenate 82%, linoleate 12%, oleate 3%, saturated 3%. The yield of recovered linolenate was 54%.

## Summary

Linolenic acid and ethyl linolenate concentrates (80–85%) have been obtained from linseed oil fatty acids or ethyl esters in 50–60% yield, based on linolenic recovery, by a single urea complex separation at room temperature.

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# ABSTRACTS . . . . . . . . . . . . . . . R. A. Reiners, Editor

## • Oils and Fats

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**Oil from the seed of Hippophaë rhamnoides III. Refining, hydrogenation, and drying tests and the possible use of interfacial tension as a measure of degree of refining.** H. P. Kaufmann and A. Vázquez Roncero. *Grasas y aceites(Servilla, Spain)* **7**, 21–6(1956). The seed oil of *H. rhamnoides* was found to be a drying oil as expected from its fatty acid content which includes linoleic 35 and linolenic acids 27%. Refined oils have a lower interfacial tension toward distilled water than do the crude oils. The interfacial tension of an oil toward distilled water might be used as a measure of the degree of refining of the oil. (*C. A.* **50**, 10428)

**Seed fats of the Euphorbiaceae family. I. Chemical examination of the seed from Trewia nudiflora.** S. Sarkar and M. M. Chakrabarty(Bose Inst., Calcutta). *Science and Culture(India)* **21**, 473–4(1956). The mixed fatty acids obtained from the oil extracted from the seeds of *T. nudiflora* contained α-eleostearic acid 39.50, linoleic acid 25.13, and oleic plus saturated acids 35.37%. The oil is similar to tung oil. (*C. A.* **50**, 10427)

**Changes in olive oil foots(orujo).** J. Gracián Yous, G. Arévalo, F. Albi, and A. Plasencia(Inst. grasas, Serville). *Grasas y aceites(Servilla, Spain)* **6**, 276–83(1955). Moisture and oil content on a dry basis and the iodine value of the oil decreased during 150 days' storage whereas the free fatty acids increased. These changes were due principally to hydrolysis, oxidation, and polymerization. (*C. A.* **50**, 10428)

**Analysis and constitution of "oxidized acids."** C. Paquot and M. Querolle(Lab. general corps gras C.N.R.S., Paris). *Compt. rend. 27ᵉ congr. intern. chim. ind., Brussels* **1954**, 3; *Industrie chim. belge* **20**, Spec. No., 724–6(1955). The acidic products arising from the slow spontaneous autoxidation of oil from olive husks are separated into 4 fractions by fractional precipitation from hot aqueous alcohol or acetone, or by precipitation from ethyl acetate with hexane. These contained: a Diels-Alder dimer of hydroxylinoleic acid; *cis*-9, 10-dihydroxystearic acid; a normal fatty acid fraction entrained during precipitation of the oxidized acids; and a dark viscous residue containing the first two and unidentified carbonyl compounds. (*C. A.* **50**, 10428)

**Continuous distillations of synthetic fatty acids.** A. Ya. Koldovkin and A. N. Bodan. *Khim. i Tekhnol. Topliva* **6**, 1-8(1956). European and American methods for the purification of natural fatty acids are analyzed with regard to use for separation of the fatty acids obtained by the oxidation of paraffins. (*C. A.* **50**, 16137)

**Liquid n-paraffins as raw material for the synthesis of higher fatty acids.** V. K. Tsyskovskii, Ts. N. Shcheglova, and E. M. Nebylova(Leningrad Petroleum Inst.). *Khim. i Tekhnol. Topliva* **6**, 9–14(1956). Oxidation of *n*-alkanes ($C_{12}$–$C_{22}$) was carried out in all-glass equipment at 130 ± 1° with manganese naphthenate as the catalyst. The concentration of *n*-alkanes in the starting material was found to be the main factor determining the composition and kinds of fatty acids in the product. (*C. A.* **50**, 16138)

**The preparation of fatty acids by the direct oxidation of (petroleum) solar oils.** St. Anastasiu and T. Wexler. *Rev. chim. (Bucharest)* **6**, 241(1955). In preliminary experiments, the aeration of solar oils (36 hours at 85–100°) in the presence of 1% Mn stearate gave, on decantation and removal of the nonsaponifiable fraction, technical grade fatty acids in 25% yield. (*C. A.* **50**, 16139)

**Guiding principles in the production of a catalyzer for hardening fats.** J. Górniak. *Przemysl Spożywczy* **10**, 169–71(1956). Detailed description is given of methods for production and regeneration of a catalyst produced from nickel formate. (*C. A.* **50**, 16139)