

# A Note on Improved Isolation of Concentrates of Linolenic Acid and Ethyl Linolenate from Linseed Oil<sup>1</sup>

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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, 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.

<sup>1</sup> 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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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.

## REFERENCES

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