with evolution of bromine vapor. Additional peaks occur at 6.33, 7.66, 11.08 μ.

Infrared spectra were determined in Nujol mulls in a cell of 0.025-mm. thickness with a Perkin–Elmer spectrophotometer, model 12AB; the slit width in the region of 6 μ was 0.043 mm. Ultraviolet spectra were taken in chloroform on a Cary ultraviolet spectrophotometer, model 11.[8]

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[8] These spectra have been deposited as Document number 4614 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm payable to Chief, Photoduplication Service, Library of Congress.

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Fractionation and Stabilization of Fatty Acid Cyclohexyl Esters by Means of Thiourea[1]

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Previous work showed that fatty acids can be separated from mixtures by fractional inclusion in urea. Furthermore, it was found that inclusion protects autoxidizable fatty acids or esters against attack by oxygen.[2] Experiments showing segregation and protection by thiourea inclusion are reported here. The results show the strong resemblance of thiourea to urea. Mixtures of molecules of equal chain length can be fractionated by means of thiourea according to their degree of unsaturation. As with urea, the more saturated components react preferentially.

TABLE I

FRACTIONATION OF FATTY ACID CYCLOHEXYL ESTERS

Type of esters	Precipitant	Methanol, ml.	Percentage of total esters bound in Fraction 1	Fraction 2	M.L.
30 g. corn oil, I.V. 104	90 + 60 g. thiourea	900	50.4, I.V. 85	38.0, I.V. 121	7.7, I.V. 119
30 g. cottonseed, I.V. 86	90 + 60 g. thiourea	900	48.8, I.V. 58	31.8, I.V. 96	11.3, I.V. 100
30 g. cottonseed, I.V. 86	90 g. thiourea	450	78.2, I.V. 72		18.8, I.V. 115
30 g. cottonseed, I.V. 86	90 g. urea	300	63.2, I.V. 63		30.7, I.V. 123
30 g. cottonseed, I.V. 86	90 g. urea	900	17.1, I.V. 16	8.0,[a] I.V. 45	..., I.V. 108

[a] This fraction was obtained by cooling to −10°. The precipitate contained only 3.8% ester.

These effects were indicated strongly when commercial terpinolene or other terpene mixtures were used to form inclusion compounds with thiourea. Due to the low stability of such adducts it is difficult to obtain results as clear-cut as those obtained with urea and fatty acids. Although McLaughlin and McClenahan reported that thiourea can react with straight chain hydrocarbons,[3] the instability of such compounds doubtless would not permit practical studies of the fractionation and preservation of natural fatty acids or their common esters. Introducing the cyclohexane ring as an ester group, however, enhances greatly the stability of the thiourea–fatty ester compound. It is even possible to bind the cyclohexyl esters of the more unsaturated, autoxidizable fatty acids. These adducts are resistant to attack by oxygen. On the other hand, the same esters, because of their long alkyl chains, still react with urea, and the two including molecules, urea and thiourea, can be compared in their reactions with the same substrate. The components of the mixtures of esters exhibit the same order in their reactivity for both cases. Unsaturation shifts the equilibria toward dissociation for both urea and thiourea inclusion complexes. This is in agreement with previous observations.[4]

Experimental

Cyclohexyl esters of fatty acids were prepared from commercial corn oil and from cottonseed oil by means of alkaline interesterification. The esters boiled at 1 mm. pressure between 168 and 183°, the yields being 70–80%. In a representative experiment, 30 g. of corn oil fatty esters was added to a warm solution of 90 g. of thiourea in 900 ml. of methanol. After cooling slowly and crystallizing at 4°, the precipitate was filtered and dried. The crystals had the typical appearance of thiourea adducts, they weighed 56.2 g. and contained 27% esters (15.1 g.). An additional 60 g. of thiourea was added to the mother liquor and a second fraction was obtained at 4°, which weighed 57.7 g. This fraction contained only 20% esters (11.4 g.) and obviously consisted of adduct and free thiourea. The recovery of the esters from the adducts or from the mother liquor was carried out as with urea compounds.[5] Data for this and other experiments are given in Table I.

The tests for autoxidation were carried out in a Warburg apparatus, as previously described for adducts of urea,[5] or other host molecules.[6] An aliquot of the second adduct fraction described above, equivalent to 60 mg. of cyclohexyl esters, released 372 μl. of gas in 50 hours[7] and showed no further gas release or absorption for an additional 90 hours. In contrast, 100 mg. of the esters recovered from this adduct absorbed 2880 μl. in 77 hours. The rate of autoxidation then was still increasing.

From Table I it is seen that virtually all components of the mixture can be bound by thiourea, whereas urea will not bind the more unsaturated esters. The first fractions of the thiourea adducts contained between 26 and 28% esters. The subsequent fractions always contained considerable amounts of free thiourea.

Terpinolene and thiourea reacted on mixing the components in a mortar in presence of enough methanol to form a thick paste. We failed to establish a reproducible ratio of host to guest molecules. The oxygen uptake of typical samples after two hours in the Warburg apparatus were: commercial terpinolene, 1200 μl.; fraction recovered from adduct, 260 μl.; fraction recovered from mother liquor, 2500 μl; thiourea adduct (17% hydrocarbon), −85 μl. after 30 hours, no change after 10 additional hours.

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[2] H. Schlenk, *Urea Inclusion Compounds of Fatty Acids*, in "Progress in the Chemistry of Fats and Other Lipids," Vol. II, Pergamon Press Ltd., London, 1954, pp. 243–267.

[3] R. L. McLaughlin and W. S. McClenahan, THIS JOURNAL, **74**, 5804 (1952).

[4] W. Schlenk, *Ann.*, **573**, 142 (1951).

[5] H. Schlenk and R. T. Holman, THIS JOURNAL, **72**, 5001 (1950).

[6] H. Schlenk, D. M. Sand and J. A. Tillotson, *ibid.*, **77**, 3587 (1955).

[7] The negative values often encountered in such experiments are discussed in ref. 6.