introduced, is approximately half for sulfur trioxide compared with chlorosulfonic acid at current bulk prices.

With sulfur trioxide there is no formation of hydrogen chloride, the reaction time is shorter, and heat evolution and foaming are balanced while these of chlorosulfonic acid are unbalanced. Total evolution of heat is greater with sulfur trioxide, and vaporization of this reagent is required.

Sulfur trioxide gives no sodium chloride and considerably less sodium sulfate. This reagent gives products of darker but acceptable color in yields which are the same or slightly lower. Product performance with the two reagents is the same.

A practical alternative process to the use of either pure reagent comprises employing chlorosulfonic acid as the sulfating reagent, with collection of the evolved hydrogen chloride in a tail tower charged with Sulfan, thereby regenerating chlorosulfonic acid for re-use. The engineering factors involved in this modification have been discussed by the authors in an earlier publication (6). This approach is often well suited to existing installations using chlorosulfonic acid since reagent cost is reduced, plant and process changes are minor, hydrogen chloride disposal is eliminated, and product quality is unchanged. Obviously the extent to which this substitution can be effected depends upon the efficiency of hydrogen chloride evolution, which in the present process is at most about two-thirds of theoretical.

Acknowledgment

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Composition of Zelkova Seed Oil[1, 2]

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THE Japanese Zelkova tree, which grows to a height of 100 feet, is native in Eastern Asia. It is hardy in the northern hemisphere and is grown as a shade tree in North America. The greyish-brown seeds are about 3–4 mm. long, roughly tetrahedral in shape, and wingless. The kernel is white, soft, and oily. There appears to be no published information on the oil.

The tree is known botanically as *Zelkova serrata* and belongs to the genus *Zelkova* of the family *Ulmaceae.* It was chosen for this investigation because one genus of *Ulmaceae,* namely *Ulmus,* which includes the common elm tree, has been regarded as unique in having capric acid as the chief fatty acid in the seed oil. Three species of *Ulmus* have been shown to exhibit this characteristic, *U. campestris* (1), Manchurian elm (2), and *U. americana* (3). A complete analysis of the seed oil of the last-named species was reported (4). Capric acid amounted to 61% of the total fatty acids.

Examples of two other genera of *Ulmaceae, Celtis* and *Trema,* did not yield capric acid or any acids of chain length shorter than C_{16} (5).

In the present work the seed oil of *Zelkova serrata* was found to contain capric acid to the extent of 73% of the total fatty acids, the highest proportion found up to the present time in any natural oil or fat. All of the even-numbered carbon saturated acids from C_8 to C_{18} were present. The general composition was similar to that of the oil of *Ulmus americana.* Thus these two genera, *Ulmus* and *Zelkova,* share the distinction of high capric acid content.

Experimental

Seed of *Zelkova serrata,* Makino (grown in Japan), was obtained from a commercial seed house. The seed was ground in a Wiley mill, the moisture content was determined, and the oil was extracted with petroleum ether. The oil content was 21.7% on a 10% moisture basis. The constants were as follows:

Iodine value	12.9	Acid value	11.2
Saponification value	292.1	Free acid as capric, %	3.4
Unsaponifiable matter, %	0.57	Glycerol yield, %	13.6

The petroleum ether distilled from the extracted oil was examined and found to contain no acid. The oil was washed with water, and the washings were also neutral. Thus there was no free water-soluble acid in the oil. On saponification a small amount of volatile water-soluble acid was found. The Reichert-Meissl value was 4.8. If calculated as caproic acid, this is equivalent to 1.2% of the total fatty acids. The Polenske value was 43 8, indicating a considerable content of acid in the C_8–C_{12} range.

A portion of the oil was converted to methyl esters and examined by gas chromatography. The column was one meter in length and was packed with Apiezon M vacuum grease on Celite. The detector was a thermistor type of thermal conductivity cell. The lower-boiling esters were chromatographed at 150° and a helium flow rate of 75 ml./min. The higher

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[2] Issued as N.R.C. No. 5176.

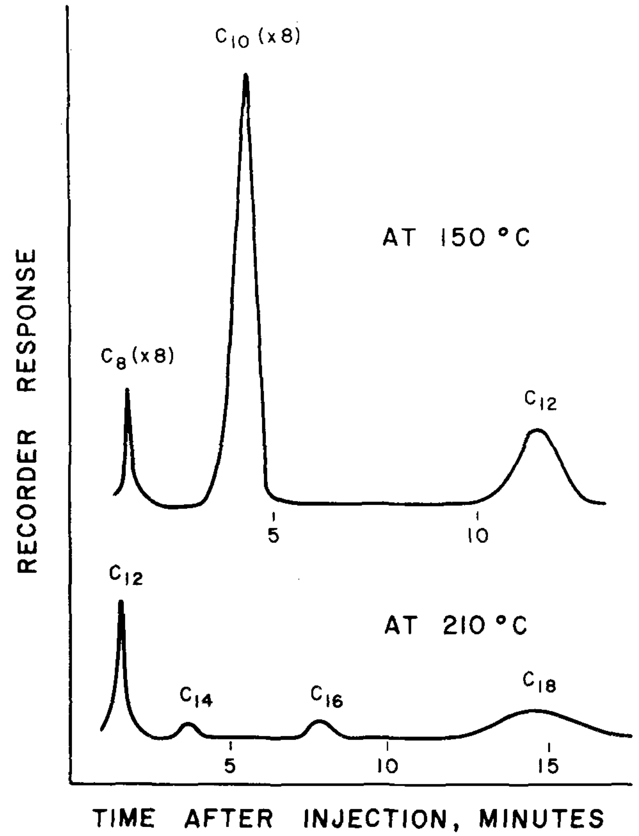

Fig. 1. Gas chromatogram of the methyl esters, compiled from two runs at different temperatures. Peak areas for esters of C_8 and C_{10} acids are to be multiplied by 8.

esters were chromatographed at 210° and a flow rate of 95 ml./min. The results are shown in Figure 1.

A sample of the mixed methyl esters was subjected to alkali isomerization and examined for polyenoic acid by ultraviolet absorption. The results showed a content of 3.1% of dienoic acid and 0.6% of trienoic acid.

To complete the identification of the major acids, 48 g. of the mixed methyl esters were distilled through a spinning band column (Table I). Fractions 1–7 were distilled at 9-mm. pressure. At this point 5 g. of pure methyl eicosenoate were added to the charge to act as a chaser. The remainder of the distillation was done at 0.5 mm. pressure.

Fractions 2 and 5 were saponified, and the acids were identified as caprylic and capric acids, respectively, by conversion to the p-phenylphenacyl esters (Table II).

TABLE I
Distillation of Methyl Esters

Fraction	Temperature	Weight	Predominant chain length	Iodine value	Refractive index
	°C.	g.			25°
1	67– 69[a]	0.40	......	0	1.4150
2	69– 70	3.32	C_8	0	1.4150
3	70– 89	1.60	......	0	1.4225
4	89– 90	4.46	C_{10}	0	1.4239
5	90	12.85	C_{10}	0	1.4240
6	90– 91	7.44	C_{10}	0	1.4240
7	91– 93	8.14	C_{10}	0	1.4240
8	65– 80[b]	1.13	C_{12}	0	1.4292
9	80–100	0.77	C_{14}	2.6	1.4326
10	100–135	1.61	C_{16}	50.9	1.4440
11	135–140	2.54	C_{18}	118.4	1.4543
12	140–150	1.19	......	89.7	1.4535
13	150–153	1.98	......	80.5	1.4530
R	......	3.94	......	......	......

[a] Pressure 9 mm.
[b] Pressure reduced to 0.5 mm.

Fraction 10 yielded palmitic acid by saponification and crystallization of the acids. Fraction 11 was sampled and analyzed quantitatively by alkali isomerization. The main portion of this fraction was then crystallized from acetone at low temperature. Stearic, oleic, and linoleic esters were separated and identified in the crystals at −40° and −55° and the filtrate, respectively. The identity of each acid or its derivative (Table II) was confirmed by mixed melting point with an authentic sample.

TABLE II
Identification of Acids

Fraction	Acid	Identified as:	Melting point
			°C.
2	Caprylic	p-Phenylphenacyl caprylate	67.5– 68.0
5	Capric	p-Phenylphenacyl caprate	77
10	Palmitic	Palmitic acid	62.0– 62.5
11	Stearic	Stearic acid	68 – 69
11	Oleic	*erythro*-9,10-Dihydroxystearic acid	129 –130
11	Linoleic	Tetrahydroxystearic acid	172 –173

Lauric, myristic, and palmitic acids were identified by their emergence times in the chromatographic analysis. Several of the intermediate fractions of the distillate were also submitted to gas chromatography to aid in the quantitative estimation of the various acids. This procedure showed that the unsaturation of fraction 10 was accounted for by its content of C_{18} acids and that fraction 13 consisted mainly of the methyl eicosenoate added as a chaser. The chromatogram of the original mixed esters showed that there was no C_{20} acid in the glycerides.

Composition of the Total Fatty Acids. The proportions of the various acids were estimated from all of the data and are shown in Table III. The undetermined portion includes about 1% of acid of shorter chain length than C_8 and about 0.6% of octadecatrienoic acid.

TABLE III
Estimated Fatty Acid Composition
(percentage of total fatty acids)

Acid	%	Acid	%
Caprylic	8	Stearic	1
Capric	73	Oleic	3
Lauric	3	Linoleic	3
Myristic	1	Undetermined	6
Palmitic	2		

Discussion

The oil under study is shown to have a high content of capric acid, 73% of the total fatty acids as compared to 50–61% in elm seed oils (*Ulmus* sp.) (1–4). In relation to the American elm (4), *Zelkova* has a greater proportion of caprylic and capric but less of oleic and linoleic acids. Stearic acid, present in *Zelkova* oil to the extent of 1%, was not observed in the American elm. Otherwise the same components are present in both. Indications of linolenic acid were noted in both oils although positive identification was not made.

Capric acid is therefore the major acid of elm and *Zelkova* oils and may occur more generally in *Ulmaceae* oils than previously supposed.

Monoenoic C_{10}–C_{14} acids have been reported to occur in *Lindera* oils (family *Lauraceae*), along with saturated acids of the same chain length (6). Such monoenoic acids are absent from *Zelkova* oil, as shown by the iodine values of zero or nearly zero for fractions 1–9 (Table I). The saturated acids of *Zelkova* are nearly all C_8–C_{12} while the unsaturated acids apparently occur entirely in the C_{18} chain length. This finding lends support to the view of Hilditch (7) that saturated and unsaturated acids are formed in the plant by separate mechanisms.

Summary

Seeds of the tree *Zelkova serrata,* family *Ulmaceae,* were found to contain 21.7% of glyceride oil having iodine value 12.9, saponification value 292, and glycerol yield 13.6%. The oil was converted to methyl esters and examined by gas chromatography, followed by fractional distillation of the esters and identification of the individual acids. The percentage composition of the acids is estimated as follows: caprylic 8, capric 73, lauric 3, myristic 1, palmitic 2, stearic 1, oleic 3, linoleic 3, undetermined 6. The content of capric acid is higher than has been found in any natural oil or fat. Comparing it with other genera of *Ulmaceae,* the oil of *Zelkova* is seen to resemble closely that of *Ulmus* sp. but to be quite different from the oils of *Celtis* and *Trema.*

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Labelling Fatty Acids by Exposure to Tritium Gas.

I. Saturated Methyl Esters[1]

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A SIMPLE PROCESS for the labelling of organic compounds by exposure to tritium gas has been described by Wilzbach (4); it has been applied to a variety of compounds including n-heptane and other hydrocarbons (5). While the tritium incorporated in these aliphatic compounds was not labile, the production of radiation decomposition products necessitated the application of rigorous purification procedures to obtain the desired substituted hydrocarbons. No attempts have been reported to date in which fatty acids have been labelled by the gas-exposure technique.[2]

The present paper describes the application of this procedure to the labelling of methyl esters of saturated fatty acids in which the anticipated substitution of hydrogen by tritium is found to take place. More complicated reactions, principally addition, occur in the labelling of unsaturated fatty methyl esters and will be the subject of a subsequent paper.

Experimental

a) Methyl esters of stearic and palmitic acids were obtained from the Hormel Institute. Methyl laurate and methyl myristate were prepared from coconut oil and separated by distillation through a Podbielniak 13-mm. diameter column with 4 ft. of "Heligrid" packing.[3]

b) Irradiations on gram amounts of methyl esters of palmitic and stearic acids were carried out at room temperature in the solid state, deposited as thin layers by solvent evaporation on the inside walls of a 1 × 10-cm. reaction tube, using a source of approximately 1 curie.

Methyl laurate and methyl myristate are liquid at room temperature and require the use of sealed ampoules equipped with break seals. The ampoules were rotated to provide continuously renewed thin films and were irradiated by a 5-curie source.

c) Purification of the tritiated methyl ester includes saponification and extraction of unsaponifiables (1), exchange of labile tritium by distillation of 1.5 liters of anhydrous ethanol from the soaps in 50-ml. batches, and acidification and extraction of the free acids with diethyl ether.

d) Chromatographic methods, both partition and gas-liquid, were used to establish freedom of the chemically purified fatty acids from radiation decomposition products and from exchangeable tritium. The Nijkamp (2) procedure was used for the separation of monobasic acids. Alternate 1-ml. fractions of eluate were: a) titrated in a nitrogen atmosphere with 0.04 N NaOH to a thymol blue end-point, using a Gilmont micro-buret and b) diluted with 15 ml. of scintillation solution for radioactive assay with an automatic "Tri-Carb" scintillation spectrometer. Quenching of fluorescence by the fatty acids and by the chromatographic solvent was negligible.

Gas chromatography of methyl esters before purification and of purified fatty acids, after methylation with diazomethane, was carried out in "Aerograph" equipment at 205°C. on a 5-ft. Resoflex 296 column. Simultaneously with the recording of thermal conductivity, an ion chamber electrometer system recorded radioactivity (ion currents) on the gas stream issuing from the thermal conductivity cell. Alterna-

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[2] Rosenthal and Kritchevsky in a publication of the Radiation Laboratory (UCRL-1331) report the production of tritiated stearic acid through a catalyzed exchange reaction with tritiated water.

[3] Mention of commercial equipment or products does not constitute endorsement by the U. S. Department of Agriculture over those of other manufacturers.