# SHORT COMMUNICATIONS

# Lauric Acid-Containing Triglycerides in Seeds of Umbellularia californica Nutt. (Lauraceae)

# T. Reynolds\*, J.V. Dring and C. Hughes

Jodrell Laboratory, Royal Botanic Gardens, Kew, Richmond, Surrey, United Kingdom

A white crystalline material isolated from the seeds of Umbellularia californica consisted mainly of the mixed triglyceride, dilaurocaprin, with smaller amounts of trilaurin and dicaprolaurin and a trace of tricaprin. The yield of crude oil from a tree growing at Royal Botanic Gardens, Kew, was considerably less than that reported previously for trees growing in California.

KEY WORDS: Tricaprin, triglycerides, trilaurin, Umbellularia.

There is an increasing demand for oils containing lauric acid (dodecanoic acid), which has a variety of sophisticated uses according to a review by Arkcoll (1). At present, demand for such oils is met from members of Palmae, especially coconut and oil palm, although recently other plants have been investigated as potential sources, i.e., Cuphea (Lythraceae) (2,3), and Lindera (Lauraceae) (4). Interest in other lauric acid sources arises from concern that supply from tropical plants may become uncertain during political disturbances. The seeds of a temperate tree, the California Laurel (Umbellularia californica Nutt., Lauraceae) are reported to yield an oil with a high proportion of lauric acid residues by a number of authors (Table 1), the yield of extracted oil reaching 70% as quoted in a review by Hegnauer (8). The effects of the 1987 hurricane provided an opportunity for us to examine a quantity of fruit dropped by a mature U. californica tree growing at Royal Botanic Gardens, Kew.

# **MATERIALS AND METHODS**

Lipid extraction. One hundred and fifty-six mature fruits (209 g dry weight) of *U. californica* were separated into flesh and kernels, and the latter (190 g dry wt) were crushed and extracted with chloroform (400 mL). The chloroform extract after removal of the solvent (58.4 g, 31% dry wt) was extracted with hot ethanol, which on cooling gave white needle-shaped crystals. They were repeatedly recrystallized from ethanol to yield a purified product (20 g, 10.5% dry wt) of m.p. 35°C. Found C, 72.8%; H, 11.4%; O, 15.8% (diff.); N, 0%.

Chromatography and mass spectrometry. The crystalline material was analyzed by using a Perkin-Elmer (Norwalk, CT) Model 8500 gas chromatograph (GC) with an OV1 capillary column (0.2 mm  $\times$  15 m), helium carrier gas (10 mL/min), and a temperature gradient of 10°/min from 200° to 300° followed by 30 min at 300°C. Methyl esters were analyzed with the same system with a temperature program of 4 min at 40°C followed by a 10°/min gradient to 180°C, then 12 min at 180°C. Effluent from the GC column was carried *via* a transfer line at 250°C to an ion trap detector (Perkin-Elmer ITD 800). Chemical ionization with ammonia was used for the unhydrolyzed lipids, and for the hydrolysis products the electron impact mode was used.

Hydrolysis of lipids. A portion of crystalline material (50 mg) was dissolved in 0.5 M sodium hydroxide in methanol (4 mL). To this was added boron trifluoride in methanol (14%, BDH Ltd., Poole, U.K.) (10 mL). The mixture was heated under reflux at 100°C for 2 min. After cooling, saturated aqueous sodium chloride (15 mL) was added, followed by petroleum ether ( $40^\circ$ - $60^\circ$ C boiling range) (15 mL) and the mixture was shaken. The upper layer was used for chromatographic analysis.

C, H and N analysis. This was performed on the crystalline material by combustion at the Chemistry Department, University College, London.

#### **RESULTS AND DISCUSSION**

Chloroform extraction of the seeds yielded a material that crystallized from ethanol. The crystals had a sharp melting point  $(35^{\circ}C)$ , but subsequent analysis showed them to contain at least four related compounds with similar melting points (Table 2).

Carbon and hydrogen analysis of the crystals agreed well with the calculated values of the four postulated components (Trilaurin C = 73.4%, H = 11.6%; Tricaprin C = 71.5%, H = 11.2%; Dicaprolaurin C = 72.8%, H = 11.5%; Dilaurocaprin C = 72.2%, H = 11.3%).

The yield of fatty material from the seeds of the British tree was considerably less than that recorded from trees growing in America (Table 1), which may be an effect of climate or just the physiological state of the particular plant. The weight of the crystalline material (not previously described) was a third of the total chloroform-soluble extract. The yield of lauric acid from saponification of the purified crystals was high (66%), comparable with yields from American crude seed oils. The yield from the whole Kew crude chloroform-soluble material calculated from these figures was, however, lower (23%). The only other principal component from the crystals was capric acid.

The crystalline material was separated by gas chromatography into four components present in the ratios indicated in Table 2. Mass spectrometry with chemical ionization revealed molecular ions at m/e = 572, 600, 628 and 656 corresponding to molecular weights of 554, 582, 610 and 638, respectively. Fragment ions appear at m/e 383, 411 and 439 representing M-OCO(CH<sub>2</sub>)<sub>10</sub> CH<sub>3</sub>. The species with molecular weights 554 and 638 have the same retention times and fragmentation patterns as standard tricaprin and trilaurin, respectively. The other two species represent the mixed triglycerides dicaprolaurin (MW 582) and dilaurocaprin (MW 610), the latter being by far the larger component. This was implied, but not stated, by the data of Litchfield et al. (6). The ratios of the four components shown in Table 2 indicate a lauric acid content of 65.1% in agreement with the observed yield (66%) of lauric acid by saponification. The position of the acyl residues was not determined. Confirmation that capric and lauric acids were the only fatty acid structures in the crystalline material was obtained by saponifi-

<sup>\*</sup>To whom correspondence should be addressed.

# TABLE 1

% Yield of crude oil from seed	Ratio capric:lauric acids in hydrolysate of oil	% Lauric acid in hydrolysate of crude oil	Reference
58.5	1:1.6	62	(5)
56.8	1:3	70	(4)
43.3	1:2.4	67	(6)
64.0	_	58,	(7)
31.0	$1:2^a$	23 <sup>b</sup>	Present study

Extracts of Fatty Material from Umbellularia Seeds

<sup>a</sup>Ratio found in crystalline material.

<sup>b</sup>Calculated from the level (66%) in crystalline material, assuming no other source of lauric acid in crude extract.

#### TABLE 2

Properties of Umbellularia Triglycerides; Comparison of Separated Components of Crystals from Seed with Known Compounds

Literature values		Separation of crystalline product	
Molecular weight	Melting point	Retention time in GLC (min)	Ratio of integrated peaks
638	46.5°	26.7	17
554	32°	14.2	1
582	30°		
		17.0	16
582	37.5°		
610	35.5°		
		21.4	133
610	38.5°		
a	35°		_
	Molecular weight 638 554 582 582 610 610	Molecular weight Melting point   638 46.5°   554 32°   582 30°   582 37.5°   610 35.5°   610 38.5°	Molecular weight Melting point Retention time in GLC (min)   638 46.5° 26.7   554 32° 14.2   582 30° 17.0   582 37.5° 17.0   610 35.5° 21.4

 $a_{\text{See text.}}$ 

cation and methylation, followed by gas chromatography. Integration of the peaks gave a capric acid:lauric acid ratio of 1:2.

The data indicates that the crystals, despite their sharp melting point, are a mixture of trilaurin, tricaprin and some or all of the four mixed triglycerides, the main component being dilaurocaprin.

The yield of fatty material from the seeds of the Kew tree is considerably less than that from specimens growing in California, although the yield data cannot be considered strictly comparable because of the different extraction methods used by different authors. Reported ratios of capric to lauric acids vary from 1:1.6 to 1:3, and this may also reflect differences in the quantitative extraction of the plant material. In a recent study, analysis of seeds of different sizes from different trees growing in California and Oregon showed an approximately constant ratio of the two acids (9), in the region of 1:2 to 1:3. In Cuphea spp, a genetically correlated variation of the same order was reported within species (10) with wider variations between species (2). In the present study, the preparation of a crystalline product affords the opportunity of obtaining lauric acid contaminated only with capric acid.

# ACKNOWLEDGMENTS

GC/MS measurements were carried out by Dr. G. Kite of this laboratory. C. Hughes is grateful to the University of Reading for study leave during an intercalated year.

#### REFERENCES

- 1. Arkcoll, D., Econ. Bot. 42:195 (1988).
- Graham, S.A., F. Hirsinger and G. Röbbelen, Am. J. Bot. 68:908 (1981).
- Bafor, M., L. Jonsson, A.K. Stobart and S. Stymne, *Biochem. J.* 272:31 (1990).
- 4. Hopkins, C.Y., M.J. Chisholm and L. Prince, Lipids 1:118 (1966).
- 5. Noller, C.R., I.J. Millner and J.J. Gordon, J. Am. Chem. Soc. 55:1227 (1933).
- Litchfield, C., E. Miller, R.D. Harlow and R. Reiser, *Lipids* 2:345 (1967).
- Princen, L.H., and J.A. Rothfus, J. Am. Oil Chem. Soc. 61:281 (1984).
- 8. Hegnauer, R., Chemotaxonomie der pflanzen Band 8:654 (1989).
- 9. Pollard, M.R., L. Anderson, C. Fan, D.J. Hawkins and H.M. Davies, Arch. Biochem. Biophys. 284:306 (1991).
- Thompson, A.E., D.A. Dierig, S.J. Knapp and R. Kleiman, J. Am. Oil Chem. Soc. 67:611 (1990).

[Received May 29, 1991; accepted September 23, 1991]