Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

An integrated biorefinery to produce 5-(hydroxymethyl)furfural and alternative fuel precursors from macroalgae and spent coffee grounds

Supporting information

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1. Lipid analysis

Lipid composition was determined using ^{1}H nuclear magnetic resonance (NMR). The use of NMR techniques to study olive oil is well established and reasonable methods exist based on integration of the signals for distinct components of the triglyceride (Figure S1) [1], [2]. The composition can be calculated by combining the various signal intensities, such as the glyceryl proton at 5.25 ppm, the unsaturated protons between 5.3 and 5.45 ppm, and the bis-allylic protons (linoleic and linolenic) at 2.76 and 2.80 ppm. The method used herein was derived from that of Seijas *et al*, however rather than use a 750 MHz spectrometer to reduce the overlap of the bis-allylic protons, a simple homo-decoupling step was used to reduce the overlapped triplets to singlets, allowing for a direct determination of the ratio of linoleic and linolenic components (Figure S2) [3]–[5].

A further complication is the high presence of free fatty acids in the samples under study. This was corrected for by comparison of the glyceryl peak and that for the β-CH2 signal. For a triglyceride this is 1:6. Where free fatty acids are present the ratio will increase and the amounts can be determined. The overall composition of the alkyl chains can be determined, as the chemical shifts of the relevant protons virtually identical for free fatty acid and triglyceride.

Some of the samples contained an unexpected peak in the bis-allylic region, notably CF samples. After homo-decoupling, there are three peaks present between 2.75 and 2.85 ppm, rather than the expected two (for linoleic and linolenic, Figure S3). Although not fully confirmed, it is likely that this peak arises from stearidonic acid (Figure S4), based on the chemical shift.

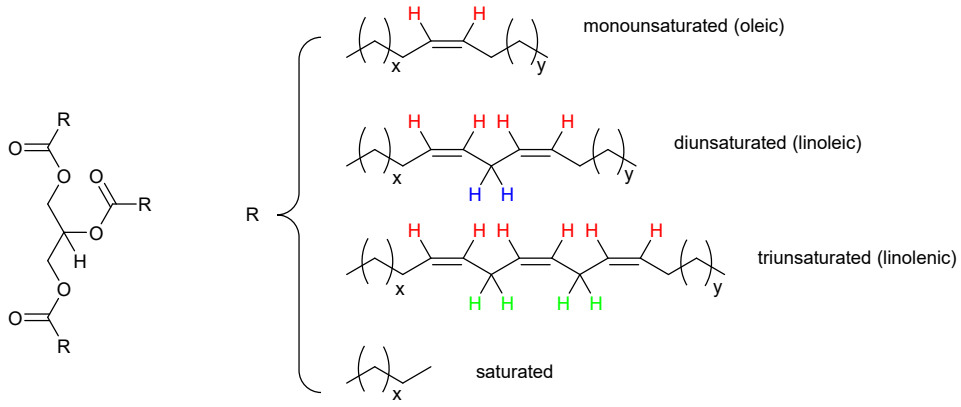
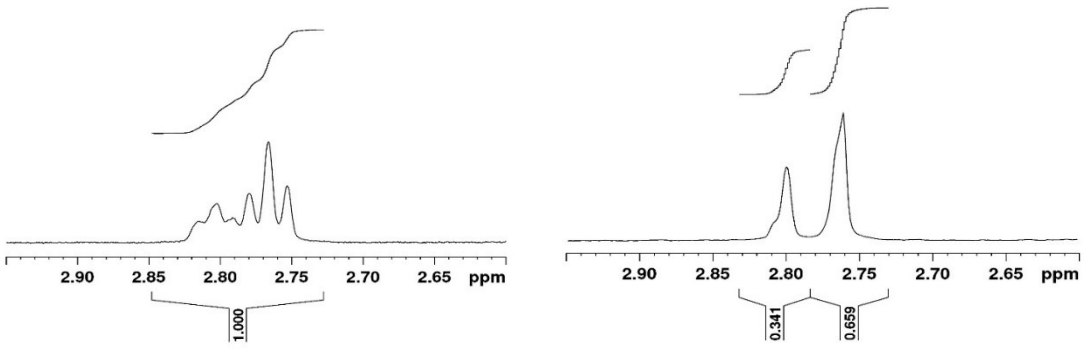


Figure S1 – Structure of triglycerides, where the alkyl chain may be mono-, di-, tri-unsaturated or saturated. ^{1}H NMR signals for the tertiary hydrogen of the glycerine head unit, the alkene protons and the vinyl protons can be used to calculate the relative composition of the fatty acids.



(a) (b)

Figure S2 – (a) Bis-allylic protons of linoleic (right) and linolenic (left) as overlapping broad triplets. (b) Fully resolved singlets following homo-decoupling of the unsaturated protons, allowing for direct integration.

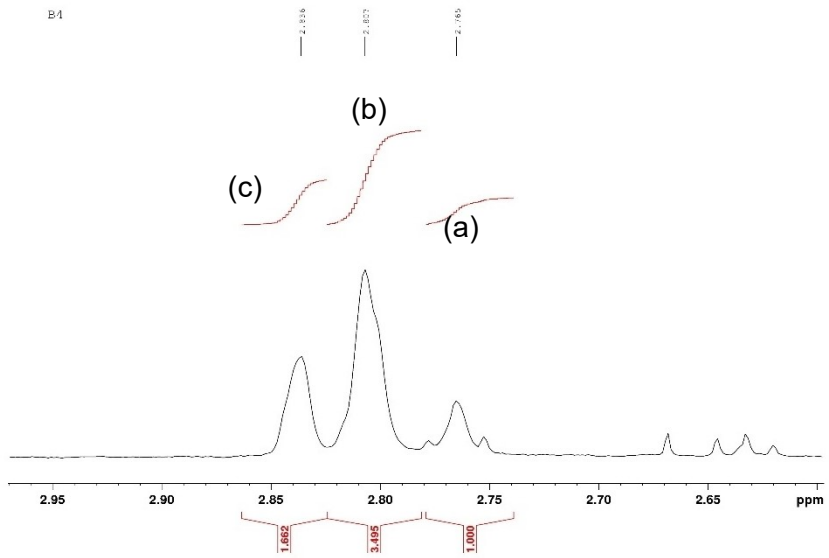


Figure S3 – Bis-allylic protons for C. filum. Peak labelled (a) for linoleic acid, (b) is for linolenic, (c) an undefined peak, which may be stearidonic acid.

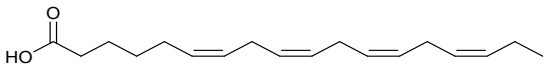


Figure S4 – Stearidonic acid

References

[1] R. Sacchi, F. Addeo, and L. Paolillo, “1H and 13C NMR of virgin olive oil. An overview,” *Magn. Reson. Chem.*, vol. 35, 1997.

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[3] X. Feás *et al.*, “Triacylglyceride, antioxidant and antimicrobial features of virgin Camellia oleifera, C. reticulata and C. sasanqua Oils,” *Molecules*, vol. 18, no. 4, pp. 4573–4587, Apr. 2013.

[4] C. Salinero *et al.*, “H-1-Nuclear Magnetic Resonance Analysis of the Triacylglyceride Composition of Cold-Pressed Oil from Camellia japonica,” *Molecules*, vol. 17, pp. 6716–6727, 2012.

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