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Mid-chain carboxylic acids by catalytic refining of microalgae oil†

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Microalgae oil serves as a feedstock for a biorefinery approach to mid-chain (di-)carboxylic acid esters, currently only accessible *via* demanding synthetic routes. *Via* the butenolysis of mono- and poly-unsaturated fatty acids, short-chain unsaturated fatty acid methyl esters and mono- and di-enes were produced in a high selectivity. These olefins were further processed into value added linear mid-chain (di-)carboxylic acid esters *via* isomerizing alkoxycarbonylation. Model compounds such as eicosapentaenoic acid were used to study the reactions including the screening of metathesis catalysts and to identify all formed products. Notably, eicosapentaenoic acid, a five-fold unsaturated fatty acid relatively abundant in algae, is successfully converted to four equivalents of heptadiene, which was carbonylated to the linear diester (dimethyl azelate). The butenolysis and subsequent isomerizing alkoxycarbonylation were performed on the algae oil extracted from the diatom *Phaeodactylum tricornutum*. Despite the multicomponent mixture of numerous lipids and non-lipid compounds present in algae oil, high conversion and high selectivity for the desired products were achieved in both reactions. This approach provides access to several carboxylic mono- and di-acid esters of chain length ranging from **C6** to **C12** (amongst others azelaic acid ester, suberic acid ester and dodecanedioic acid ester), that are in demand but to which access is limited currently, fully based on algae oils as a renewable resource.

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Introduction

Due to their unique molecular structure, fatty acids in general are attractive substrates that offer themselves for further functionalization of the carboxylic acid ester group or transformation of the (unsaturated) alkyl chain.[1,2] This applies in particular to fatty acids present in algae oil, which have a unique composition. Poly-unsaturated fatty acids with unusual chain lengths such as eicosapentaenoic acid and docosahexaenoic acid are relatively abundant in algae oil, whereas these are barely found in traditional seed oils. Algae oils have received much attention as a new biomass source to produce renewable energy in the form of biodiesel. Approaches such as transesterification or deoxygenation/hydrocracking have been employed to obtain a suitable material for fuel. These aim at mimicking petroleum-based hydrocarbon fuels. They do not exploit the full potential of these algal fatty acids in making use of their functionality and the possibility for further functionalization.[3]

So far predominately fatty acids from seed oils such as sunflower, rapeseed and palm oil are being used for the production of chemicals or monomers for polymers.[2,4] However, growing plants for oil production raises issues such as occupation of arable land, consumption of irrigation water, a competition with food production, inefficient yields per time and area, and the associated logistics of harvesting and collection. In contrast, algae can be cultivated in brackish or salt water on non-arable land that is unapt for food production. Moreover, the oil production from microalgae is much higher compared to plants.[5,6] Short-chain dicarboxylic acids (up to **C6**) are produced on a large scale by petrochemical routes, and increasingly also by fermentation of carbohydrate feedstocks. By contrast, mid-chain (**C7–C12**) dicarboxylic acids are most commonly generated from seed oil fatty acids. Some of these dicarboxylic acids are only accessible *via* tedious synthetic routes. Azelaic acid (1,9-nonanedioic acid), for example, is produced industrially *via* ozonolysis of oleic acid on a scale of several 1000 tons per year.[7] However, ozonolysis is a technically challenging and potentially hazardous process.

An attractive concept of an algae-based refinery to produce mid-chain olefins and carboxylic acids or esters is the utilization of the double bond of unsaturated fatty acids in a cross-metathesis reaction. Moreover, by employing short-chain olefins, *e.g.* ethylene or butene, in cross-metathesis with unsaturated fatty acids, the chain length of the products can be modified, thus expanding the range of desirable products accessible by this algae-based refinery approach. An approach

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to use microbial and yeast strains for the production of biofuels by metathesis was reported by Chuck *et al.*[8] Ethenolysis of microalgae oil from *Pseudochorisystis ellipsoidea* occurred with a selectivity of 35–40% towards terminal double bonds while for the oil from *Scenedesmus obliquus* only cross- and self-metathesis products of the fatty acids were found, and no terminal double bonds were obtained. During ethenolysis, an unstable methylidene intermediate catalyst species is formed, which can lead to rapid decomposition of the catalyst. This results in limited productivity. In cross-metathesis with internal olefins, no such methylidene intermediate is formed.[9–11] As products, internal olefins are obtained. The butenolysis of seed oils such as sunflower, canola, soy and linseed was demonstrated by Robinson[12,13] along with the subsequent alkoxycarbonylation of these mixtures.[14] The butenolysis of neat commercially available methyl oleate occurred with a total of 1800 turnovers. Concerning the industrial applicability of olefin metathesis, it is notable that butenolysis of palm oil is applied on an industrial scale in the Elevance biorefinery process.[4,15]

Here, we present a two-step fully catalytic route towards value-added products from microalgae oil.

Results and discussion

The microalgae strain *Phaeodactylum tricornutum*, a unicellular diatom, was used as a lipid source, as it produces relatively large amounts of unsaturated fatty acids.[16] The algae oil was extracted by a modified Folch method[17] (*cf.* ESI†). In this way, from 30 L algae culture, being in the stationary phase for 5 weeks, typically 6.3 g of crude algae oil was obtained. These results compare favourably with the optimized yields reported from the established methods for lipid extraction.[18,19] The composition of the oil as determined *via* gas chromatography after transesterification with methanol agrees with expected values[16] (Fig. 1 and Table 1). Gas chromatography with an internal standard showed that on average 3.3 mmol double bonds per g of algae oil are present.

The fatty acids in algae oil are not only present as triacylglycerides but also as diacylglycerides, substituted with polar substituents such as galactosyl or phosphate groups on the third hydroxy moiety of glycerol.[20] Furthermore, as indicated by its green colour, the extracted algae oil also contains other components such as carotenoids and chlorophylls.

Table 1 Composition of the algae oil extracted from *Phaeodactylum tricornutum* (transesterified to the methyl ester for GC analysis)[a]

Compound	Content[b] [%]
Myristic acid methyl ester (**FA14:0**)	8
Palmitoleic acid methyl ester (**FA16:1**)	40
Palmitic acid methyl ester (**FA16:0**)	32
Oleic acid methyl ester (**FA18:1**)	10
Eicosapentaenoic acid methyl ester (**FA20:5**)	9

[a] The oil was extracted *via* a modified Folch method. [b] Determined by gas chromatography after transesterification.

For the identification of the possible products arising from the variety of different unsaturated fatty acids present in the crude algae oil, metathesis was conducted on selected individual fatty acids as model compounds.

One unique component present in the algae oil is the five-fold unsaturated fatty acid eicosapentaenoic acid (EPA or **FA20:5**, Scheme 1). The butenolysis of such poly-unsaturated fatty acids has not been reported to date, although it can give access to a range of versatile building blocks. Complete butenolysis of EPA can generate up to four equivalents of 2,5-heptadiene (**HC7:2**, Scheme 1). The major challenge in cross-metathesis with EPA is the suppression of the favoured intramolecular metathesis to 1,4-cyclohexadiene (**CHD**, Scheme 1).

A range of ruthenium based metathesis catalysts were screened to achieve high selectivity for the expected butenolysis products (Fig. 2 **C1–C9**, Table 2 and Fig. S4†). In these reactions, 0.1 mol% catalyst and a 10-fold excess of 2-butene with respect to the double bonds were employed. From this study, the Hoveyda–Grubbs 2nd generation catalyst (**C3**, Fig. 2) appeared to be the most efficient in terms of conversion and selectivity for the butenolysis products. Moreover, even at high conversion only little self-metathesis occurred. Nevertheless, butenolysis was incomplete and mainly two- and three-fold unsaturated fatty acids and alkenes were obtained (*cf.* Scheme 1, Fig. 3 bottom). At an increased catalyst loading of

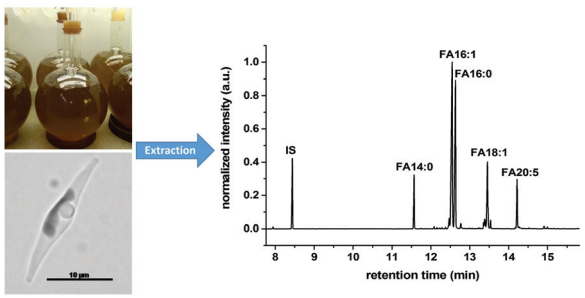
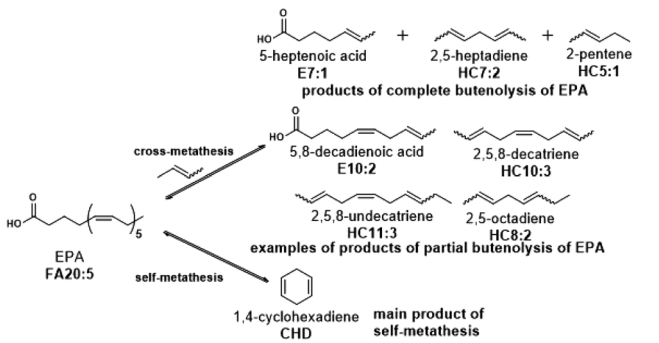


Fig. 1 GC trace of the crude algae oil extracted from *Phaeodactylum tricornutum* with nonanoic acid as an internal standard (IS) (after transesterification with MeOH). Integrals of the signals are listed in Table 1.



Scheme 1 Self-metathesis and cross-metathesis with 2-butene of EPA.

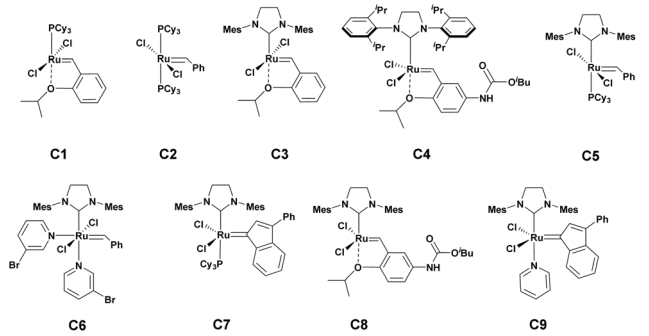


Fig. 2 Ruthenium-based homogeneous catalyst precursors. **C1**: Hoveyda–Grubbs 1st generation; **C2**: Grubbs 1st generation; **C3**: Hoveyda–Grubbs 2nd generation, **C4**: Umicore M73 SIPr; **C5**: Grubbs 2nd generation; **C6**: Grubbs 3rd generation; **C7**: Umicore M2; **C8**: Umicore M73 SIMes; **C9**: Umicore M31.

Table 2 Catalyst screening for the butenolysis of EPA (**C1**: Hoveyda–Grubbs 1st generation; **C2**: Grubbs 1st generation; **C3**: Hoveyda–Grubbs 2nd generation, **C4**: Umicore M73 SIPr; **C5**: Grubbs 2nd generation; **C6**: Grubbs 3rd generation; **C7**: Umicore M2; **C8**: Umicore M73 SIMes; **C9**: Umicore M31)

Catalyst	Conversion[a] [%]	Methyl 5-heptenoate[b] [%]	1,4-Cyclohexadiene[c] [%]
C1	<1	—	
C2	10	15	30
C3	88	40	3
C4	52	28	1
C5	97	48	24
C6	<1	—	—
C7	<1	—	—
C8	64	28	3
C9	22	17	1

0.1 mol% catalyst-loading per double bond, 10 equivalents of 2-butene per double bond, −5 °C. [a] Reactions were stopped when no further progress was observed. [b] Product selectivity, which is defined as the ratio of methyl 5-heptenoate to all formed esters. [c] Product selectivity, which is defined as the ratio of 1,4-cyclohexadiene to all olefins and poly-unsaturated esters.

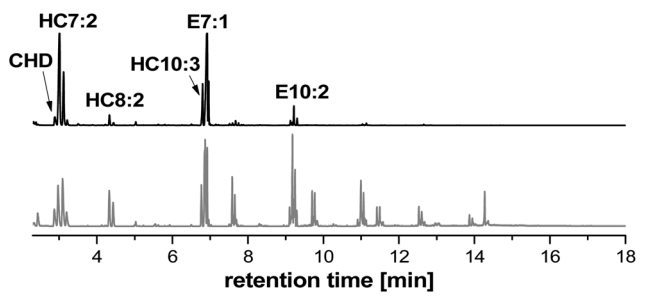


Fig. 3 GC trace of the reaction mixture of the butenolysis of EPA with Hoveyda–Grubbs 2nd generation catalyst (top, black: 0.2 mol% catalyst-loading; bottom, gray: 0.1 mol% catalyst-loading) with labelling of the formed major products (**CHD** 1,4-cyclohexadiene, **HC7:2** 2,5-heptadiene, **HC8:2** 2,5-octadiene, **HC10:3** 2,5,8-decatriene, **E7:1** methyl 5-heptenoate, **E10:2** methyl 5,8-decadienoate).

0.2 mol% per double bond, under otherwise identical conditions, EPA was completely consumed after 30 minutes and the composition of the reaction mixture did not change anymore after 120 minutes (Fig. 3 top). The selectivity for methyl 5-heptenoate (**E7:1**), which is defined as the ratio of methyl 5-heptenoate to all formed esters, increased to 95%. For methyl 5-heptenoate a *cis* : *trans* ratio of 17 : 83 was found, matching well with the reported isomer ratios for similar reactions.[13] Accordingly, in the final reaction mixture 2,5-heptadiene (**HC7:2**) was found to account for 80% of all olefins. All three possible isomers of 2,5-heptadiene were observed with the *trans–trans* isomer predominating. The intramolecular formation of 1,4-cyclohexadiene (**CHD**) remained suppressed to a large extent, **CHD** was only a total of 12% of all olefins. The remainder consisted of poly-unsaturated olefins and esters from incomplete butenolysis, accounting in total for 8%. The smallest component, 2-pentene (**HC5:1**) resulting from the butenolysis of the chain end of EPA, was not detected in GC analysis due to its low boiling point and overlap with the solvent signal.

In summary, butenolysis of the individual fatty acids present in algae oil proceeds with high conversion and high selectivity under the reaction conditions studied (see the ESI† for butenolysis data on methyl oleate and methyl palmitoleate). All expected butenolysis products could be identified analytically. In addition, the favoured self-metathesis of EPA is successfully suppressed and the poly-unsaturated nature of the fatty acid is not problematic for metathesis itself.

However, as mentioned previously, algae contain diacylglycerides with an additional polar moiety, which might interfere with catalysis. The influence of the components present in algae oil, *e.g.* phosphocholines, was therefore investigated. Methyl oleate was used as a model substrate with additional 1,2-dipalmitoyl-*sn-glycero*-3-phosphocholine (1 mol%) in a butenolysis reaction (ESI†). Even in the presence of such an excess of phosphocholine (compared to the catalyst loading of 0.1 mol%) a conversion of 71% after 30 min and 90% after 60 min was achieved. The reaction is somewhat slower compared to the pure mono-unsaturated fatty acid methyl ester (ESI†), but comparably selective with a selectivity of 94% for butenolysis products.

With the butenolysis products of the components of algae oil identified, butenolysis was performed on the extracted crude algae oil (after degassing). A catalyst loading of 0.1 mol% and a tenfold excess of 2-butene, referring to the number of double bonds, were used. This lower amount of catalyst compared to the butenolysis of EPA was considered reasonable as the algae oil not only consists of EPA but also mostly mono-unsaturated fatty acids, which require a lower catalyst loading per double bond. GC analysis revealed a virtually complete conversion of the unsaturated fatty acids (98% for the mono-unsaturated fatty acid and 100% for EPA) after 3 h and showed no further change in the composition of the reaction mixture. The reaction of such a complex mixture is, unsurprisingly, somewhat slower compared to the isolated fatty acids and esters. As expected, a mixture of the butenolysis

products of the fatty acids present in the algae oil is observed: 2-nonene, 2-undecene and methyl 9-undecenoate (Fig. S1†) as butenolysis products of the mono-unsaturated fatty acids, methyl oleate and palmitoleate, and methyl 5-heptenoate and 2,5-heptadiene (Scheme 1) formed from the five-fold unsaturated fatty acid EPA. All butenolysis products are present in a *cis* : *trans* ratio of about 20 : 80. The butenolysis products of the mono-unsaturated fatty acids were produced in 85% selectivity. For EPA, the selectivity towards 2,5-heptadiene was found to be 71% compared to all olefins. Also here, self-metathesis was suppressed to a larger extent, only 12% of 1,4-cyclohexadiene was formed. These results are comparable to the butenolysis of pure EPA. Minor unassigned signals in the GC trace of the butenolysis product of algae oil (Fig. 4) possibly arise from the components present in the starting algae oil, or cross-metathesis products. As expected, the content of saturated fatty acids, myristic and palmitic acid, remained unchanged during the metathesis reaction. Overall, the butenolysis of algae oil proceeds with virtually complete conversion of the unsaturated fatty acids and high selectivity to the desired ω2-unsaturated products. The Hoveyda–Grubbs second generation catalyst (**C3**) is compatible with the various components of algae oil and converts the unsaturated long chain fatty acids to a range of olefins and unsaturated acids suitable for the production of higher value mid-chain chemicals.

Isomerizing alkoxycarbonylation

For further upgrading of the butenolysis products, the reaction mixtures from butenolysis were subjected to isomerizing alkoxycarbonylation. With this reaction, an internal double bond is converted to a terminal ester with CO and methanol. Pd-Complexes with sterically demanding diphosphine ligands, for example [Pd(dtbpx)(OTf)$_2$] (dtbpx = 1,2-bis((di-tertbutylphosphino)methyl)benzene), catalyse this reaction with high linear selectivities. Initially, the mixture resulting from the butenolysis of the model compound EPA was subjected to isomerizing alkoxycarbonylation under conditions previously reported for seed oils (90 °C, 20 bar CO, 0.8 mol% [Pd(dtbpx)(OTf)$_2$]).[21,22] Mainly 2,5-heptadiene (**HC7:2**) and methyl 5-heptenoate (**E7:1**) were present in the starting mixtures, which will produce dimethyl nonanedioate (**DE9:0**, Fig. 5) and dimethyl octanedioate (**DE8:0**, Fig. 5). Additionally, methyl hexanoate (**E6:0**, Fig. 5) as an alkoxycarbonylation product from 2-pentene can be expected. For all alkoxycarbonylation reactions, the selectivity to a product is defined as the ratio of the product to the theoretical maximum amount of this product based on the butenolysis reation mixture as determined *via* an internal standard. Methyl 5-heptenoate (**E7:1**) was completely converted after 3 days to the linear **DE8:0** in 90% selectivity. Methyl hexanoate (**E6:0**), as the alkoxycarbonylation product of 2-pentene, was formed with a selectivity of 58% with respect to the amount of EPA in the starting material employed for butenolysis. This is a reasonable amount, considering the volatility and low boiling point of 2-pentene. The conversion of heptadiene was somewhat slower, it was fully converted after 7 days to **DE9:0** in 58% overall selectivity. In addition, methyl pentanoate was found, which results from the isomerizing alkoxycarbonylation of the remaining 2-butene. The limited selectivity for **DE9:0** can be traced to the two double bonds in heptadiene, which can form a Pd-allyl complex. Such complexes are known to decrease the rate of the alkoxycarbonylation significantly.[23] Because of the lower reaction rate, side reactions can become relevant to some extent affecting the selectivity towards the linear 1,9-diester.

To this end, 2,5-heptadiene was isolated from an EPA butenolysis reaction and the isomerizing alkoxycarbonylation of this compound was investigated in detail. The isolation of 2,5-heptadiene from the reaction mixture was possible by both distillation and column chromatography (ESI†). Isomerization to 2,4-heptadiene occurred during isolation to some extent, but it did not change the outcome of the alkoxycarbonylation, as under alkoxycarbonylation conditions a rapid isomerization usually occurs in any case (*cf.* ESI Fig. S14†). The isolated mixture of heptadienes (2,5- and 2,4-heptadiene) was subjected to isomerizing alkoxycarbonylation under the standard conditions and monitored over time (Fig. 6 and Fig. S14†). The samples were analysed by GC, GC-MS and NMR spectroscopy.

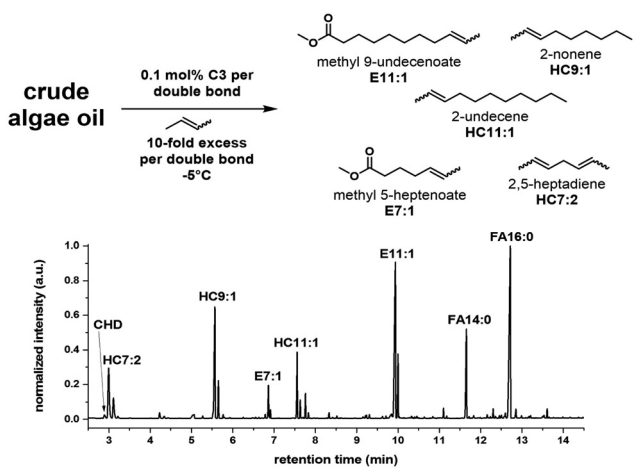


Fig. 4 GC trace of the butenolysis of crude algae oil (after trans-esterification for GC analysis) with Hoveyda–Grubbs 2nd generation catalyst (**C3**) and assignments of the butenolysis products, self-metathesis products (**CHD** 1,4-cyclohexadiene) and the saturated fatty acid ester (**FA14:0** methyl myristate, **FA16:0** methyl palmitate).

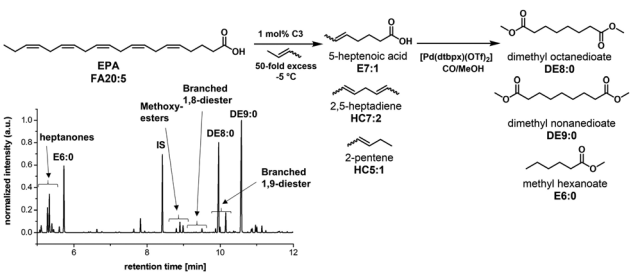


Fig. 5 GC trace of the methoxycarbonylated butenolysis products of EPA with nonanoic acid as an internal standard (IS) and Hoveyda–Grubbs 2nd generation catalyst (**C3**). The structures of the butenolysis products of EPA and the corresponding alkoxycarbonylation products are shown.

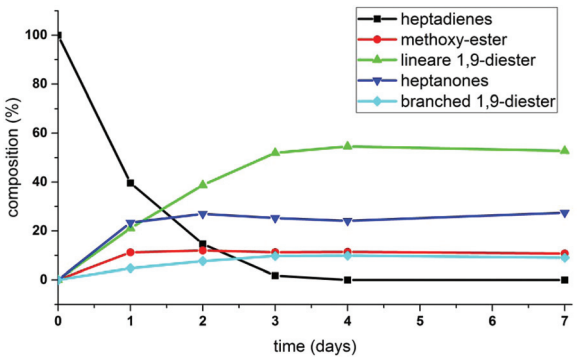


Fig. 6 Reaction profile of the alkoxycarbonylation of heptadiene. Conditions: 0.8 mol% [Pd(dtbpx)(OTf)$_2$], substrate, MeOH, 20 bar CO, 90 °C. ■ = heptadiene, ▲ = 1,9-diester, ▼ = ketones, ● = methoxy esters, ◆ = branched diesters.

Besides the expected linear 1,9-diester (**DE9:0**, Fig. 5), which is formed with a selectivity of 55%, branched diesters (*cf.* Fig. S14†) were observed in 10% selectivity which is typical of this catalyst for mono-unsaturated substrates.[24] For the largest part (7%) these are composed of dimethyl 2-methyl-octanedioate. Furthermore, three different ketones (2-heptanone, 3-heptanone and 4-heptanone, Fig. S14†) were identified by enrichment experiments with genuine samples of these ketones. The ketones made up 24% of the formed products. These ketones are formed *via* methanol or water addition to a double bond, followed by the isomerization to the enol. *Via* deprotonation this subsequently forms a saturated ketone.[25] Finally, based on the GC-MS data (ESI†) it can be assumed that the remainder is methyl methoxyoctanoates (methoxy-esters, 11%, Fig. 5 and Fig. S14†), from the nucleophilic addition of methanol and only one isomerizing alkoxycarbonylation step of heptadiene.

With all products identified from these experiments, the reaction mixture of the butenolysis of algae oil was subjected to the isomerizing alkoxycarbonylation without any intermediate purification step (Fig. 7). All butenolysis products were converted after three days. The butenolysis products from the mono-unsaturated fatty acids methyl oleate and methyl palmitoleate are 2-undecene and 2-nonene, respectively, and for both methyl undecenoate. These butenolysis products are expected to be converted into methyl dodecanoate (**E12:0**), methyl decanoate (**E10:0**) and dimethyl dodecanedioate (**DE12:0**). The selectivity was determined based on the theoretical maximum value in the case of complete conversion of the corresponding butenolysis products. The selectivity for methyl dodecanoate (**DE12:0**), the alkoxycarbonylation product of 2-undecene formed from methyl oleate, is 92%. Methyl decanoate, which is formed from 2-nonene (butenolysis product of methyl palmitoleate), was found in a selectivity of 86%. These selectivities are in accordance with the literature values for the isomerizing alkoxycarbonylation of a neat linear mono-unsaturated substrate.[24] The selectivity of the alkoxycarbonylation of 2,5-heptadiene (61%) is also comparable to the observed selectivity on the isolated EPA as a starting material. The isomerizing alkoxycarbonylation catalyst was compatible with the remaining components in algae oil, and was also not disturbed by the quenched metathesis catalyst.

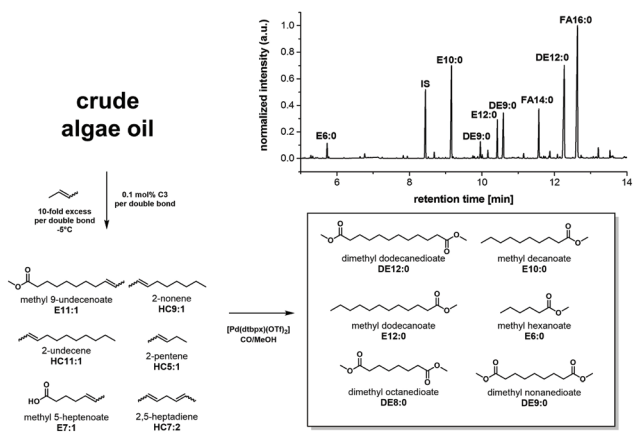


Fig. 7 GC trace of the methoxycarbonylated butenolysis products of crude algae oil and the assigned products.

Conclusion

We have shown the production of mid-chain carboxylic acids *via* an all catalytic route from microalgae oil extracted from the diatom *Phaeodactylum tricornutum* as a renewable feedstock. The Hoveyda–Grubbs 2nd generation metathesis catalyst appeared to be compatible with a multi-component mixture consisting of numerous lipids and non-lipid compounds and leads to quantitative conversions and high selectivities. Notably, also the highly unsaturated EPA (**FA20:5**) is converted selectively, with 2,5-heptadiene as the major product. In the subsequent isomerizing alkoxycarbonylation of the crude butenolysis mixture, the catalyst was also compatible with the remaining components in algae oil. The consecutive butenolysis and alkoxycarbonylation can be performed as a one-pot reaction, without intermediate purification steps of the crude starting material. This approach provides new possibilities to carboxylic mono- and di-acids with the chain length ranging from **C6** to **C12**, fully based on algae oils. The resulting mono-carboxylic acid esters (**E12:0** and **E10:0**) can serve as surfactants or food additives (**E6:0**), while dicarboxylic acid esters are useful as lubricants or monomers in polycondensation reactions. The **C9** diester azelaic acid ester (**DE9:0**) is interesting especially, as the current production requires the technically challenging and potentially hazardous ozonolysis. Moreover, our route provides an additional approach to other diesters (**DE10:0** and **DE12:0**) and also a new, potentially interesting diester, **DE8:0**. The entire two-step catalytic route yields a number of desirable products by exploiting the entire fatty acid spectrum present in the algae oil from *Phaeodactylum tricornutum*.

As a further prospect, a reduction of catalyst loading and in this context an understanding of the role of impurities present in the substrate are desirable.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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