

Synthesis of industrially important platform chemicals via olefin metathesis of palash fatty acid methyl esters

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ABSTRACT

The study signifies the importance of olefin metathesis in developing industrially important platform chemicals from a non-edible renewable resource, palash oil using Grubb's second generation catalyst. The reaction conditions were optimized by varying the concentration of the catalyst, 0.03-0.05 mM and the temperature, 45-100 °C of the reaction. Maximum yield of the metathesized products, as analysed using GC/GC-MS were obtained employing lower concentration of the catalyst, 0.03 Mm and temperature, 45 °C for 36 h. The metathesized products showed the formation of hydrocarbons namely 9-octadecene (10.9%) and cyclodecacyclotetradecene (27%) as major. The formation of cyclodecacyclotetradecene was observed for the first time. The study also describes the possible routes and the molecules involved in the formation of the metathesized products.

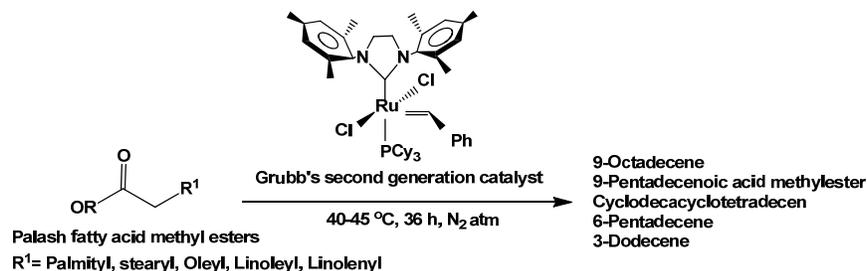
1. Introduction

With the depletion of fossil fuels and increasing emission of greenhouse gases, the importance of renewable raw materials is increasing day by day. Renewable raw materials significantly contribute to a sustainable development and further utilization can meet the principles of green chemistry such as built-in design for degradation or low toxicity of the resulting products [1]. Unsaturated fatty acids and fatty oils form promising, cheaper feed stocks for generating a number of oleochemicals [2,3].

One of the most modern synthetic routes for generating organic intermediates is metathesis of unsaturated fatty acids. The approach contributes to a sustainable development and reduction in CO₂ emissions as the raw materials employed are safer, and less toxic. Metathesis is a redistribution of fragments of alkenes by scission and regeneration of carbon-carbon double bonds. Olefin metathesis between two similar molecules is termed as self-metathesis. Self olefin metathesis which involves carbon-carbon bond formation, results in a family of important organic intermediates useful for synthesis [4]. Some of the important intermediates generated during self-metathesis of unsaturated fatty acid methyl esters are aliphatic dicarboxylic acids which serve as organic intermediates in the synthesis of biodegradable polymers [5]. Short chain linear α,ω -dicarboxylic acids such as suberic acid (C₈), azelaic acid

(C₉), or sebaucic acid (C₁₀), which are used as building blocks for the synthesis of commercially important materials such as nylon, cosmetics, plasticizers, lubricants and greases [5]. Most common and efficient method used for generating some of the organic intermediates from unsaturated fatty acids is self-metathesis of fatty acid esters or vegetable oils, catalysed by Grubb's first and second generation catalysts. Grubb's catalysts are a logically good choice due to their relatively high tolerance for polar organic functional groups compared to the classical ill-olefin metathesis catalysts [6]. Grubb's first and second generation catalysts are used in organic synthesis as the first generation catalysts, but generally with higher activity. This catalyst is stable towards moisture and air, thus is easier to handle in the lab. A variety of vegetable oils were employed by the researchers to produce organic intermediates employing metathesis routes [7,8].

Self-metathesis of a mixture of sunflower fatty acids resulted in cyclo-hexa-1,4-diene, alkenes mono and dicarboxylic acids [9,10]. Soybean oil subjected to self-metathesis resulted in polycondensation that lead to branching, with increased molecular weight, thereby the viscosity and drying properties. Heterogeneous catalysts, Re₂O₇/SiO₂, Al₂O₃/SnBu₄ catalysts, were employed for the metathesis of different fatty acid esters of South African Sunflower which resulted in alkene, mono and diesters of varied chain lengths [11].



Scheme 1

Other unsaturated fatty acids namely oleic, ricinoleic, and undecenoic acids were also found to undergo self-metathesis employing second generation Grubb's catalysts to obtain α,ω -dicarboxylic acids [4,5] in good conversions. Metathesis of soy, rapeseed, tall and linseed oil fatty acids also resulted in a variety of large number of products [4] for varied applications.

However, most of the vegetable oils employed were from edible source or from unusual fatty acids containing non-edible oils [1,12]. On the other hand India is importing 10.3 million tons, 2013 of edible oil for domestic purpose, hence cannot afford to use edible oils for non-edible applications. In this context, palash seed oil, a non-edible tree borne oil widely grown throughout the country in grass or water logged lands, black cotton and saline soils was exploited for the study. Palash seed oil is hard oil, suitable for soap making, replacing tallow. The tree is suitable for planting in garden and parks and in reclaiming of saline oil. Since India is short of high titer natural oils, the potential of palash is to some extent tapped as a ready source of hard oil particularly for the small scale industry. It is a tribal wealth, not much utilized. However, palash oil was chosen for the study, as the oil is rich in unsaturation (65.1%), can be subjected to self-metathesis by employing Grubb's second generation catalyst to prepare a variety of platform chemicals. Also, there exists no systematic study on the possible routes involved in the formation of different metathesized products. Since the use of Grubb's second generation catalyst involves cost, the study also optimizes the catalyst concentration and the temperature of operation. Overall the study involves the self-metathesis of palash oil, optimization of catalyst concentration and the temperature of the reaction required for maximum yield of the metathesized products. The study also explains the possible routes and the molecules involved in the formation of metathesized products.

2. Experimental

2.1. Materials

Palash (*Butea monosperma*) seeds were purchased from M/S Sanjeevani Herbal Health Society, Hyderabad, Ltd. Tricyclohexylphosphine[1, 3-bis(2, 4, 6-trimethylphenyl)-4, 5-dihydroimidazol-2-ylidene benzylidene ruthenium (IV) dichloride (Grubb's second generation catalyst-II), sulfuric acid, dry methanol, dry dichloromethane (99.9%) were purchased from M/s Sigma Aldrich Chemical Co, Hyderabad.

2.2. Methods

2.2.1. Gas Chromatography analysis of palash fatty acid methyl esters and their self-metathesized products

The fatty acid composition of palash fatty acid methyl esters and the products obtained after self-metathesis were analysed using an Agilent 6890 Gas Chromatograph (Agilent Technologies, Palo Alto, CA, USA) fitted with an FID detector and split/split less injector. A non-bonded cyano silicone

column (DB-225, 30 m x 0.32 i.d., J&W Scientific, USA) was employed for Gas Chromatography analysis. The column temperature was initially maintained at 60 °C for 2 min, increased to 300 °C for a hold time of 20 min with a flow rate of 10 °C/min. The injector and detector temperatures were set at 250 °C. Chemstation software was used for the data analysis

2.2.2. GC-MS analysis of palash self-metathesized products

The structure of the products obtained by self-metathesis of palash methyl ester was analyzed using an Agilent 6890 N (Agilent Technologies, Palo Alto, CA, USA) Series equipped with an DB-225 Column (30 m x 0.25 mm i.d) series Gas Chromatograph connected to an Agilent 5973. Mass Spectrometer operating in the EI mode (70 eV; m/z 50-550; source temperature 230 °C and a quadrupole temperature 150 °C). The column temperature was initially maintained at 100 °C for 2 min, increased to 300 °C at 10 °C/min with a hold time of 20 min at 300 °C. The inlet temperature was maintained at 300 °C and split ratio of 50:1. Structural assignments were based on interpretation of mass spectrometric fragmentation and confirmed by comparison of retention times as well as fragmentation pattern of authentic compounds and the spectral data obtained from the Wiley and NIST libraries.

2.2.3. Soxhlet extraction of palash seed oil

The dried kernels were finely powdered and the powder (500 g) was Soxhlet extracted using hexane (2000 mL) as solvent for 8 h. After 8 h, the solvent was removed using a rotary evaporator and dried under reduced pressure to obtain palash oil (65 g, 13% yield).

2.2.4. Typical procedure for the preparation of palash fatty acid methyl esters

Fatty acid methyl esters of the palash oil were prepared by refluxing the oil at 70 °C for 4 h in 2% sulphuric acid in methanol. The esters were extracted into ethyl acetate, washed until acid free and passed over anhydrous sodium sulphate. The sample was further concentrated using rotary evaporator to obtain fatty acid methyl esters (99% yield). The converted fatty acid methyl esters were analysed for its fatty acid composition (wt%) using Gas Chromatography.

2.2.5. Typical procedure for self-metathesis of palash fatty acid methyl esters

Palash fatty acid methyl esters (2 g, 6.8 mM) dissolved in dry DCM 20 mL was taken into a two necked round bottom flask under N_2 atmosphere. Grubb's second generation catalyst (25 mg, 0.03 mM) taken in dry DCM was added to the methyl esters using a 20 mL syringe. The contents were heated at 40-45 °C for 36 h (Scheme 1). The reaction was monitored hourly using TLC eluted with hexane:ethyl acetate (90:10, v:v).

The contents were washed with ethyl acetate and passed over anhydrous sodium sulphate. The solvent was removed using rotary evaporator and dried under reduced pressure (2-5 mmHg) to obtain metathesized products (1.6 g, 80% yield). The products were qualitatively and quantitatively identified using GC and GC-MS.

3. Results and discussion

The present study involves self-metathesis of unsaturated rich, non-edible tree borne oil, palash with fatty acid composition palmitic, 19.6%; heptadecenoic, 0.15%; stearic, 6.3%; oleic, 24.26%; linoleic, 27.7%; linolenic, 0.3%; arachidic, 2.0%; gondoic, 12.9%; erucic, 0.2%; nervonic, 5.6% (Figure 1) acids employing Grubb's second generation catalyst (Scheme 1). The optimized conditions to obtain 98% yield of the metathesized products was carried out varying the concentration of catalyst from 0.03-0.05 mM, (Figure 2) temperature 45-65 °C (Figure 3) and sampling hourly. The metathesized products were monitored using GC-MS (Figure 4) and the percentage of the products obtained using GC (Figure 5). It was observed that the maximum yield (98%) of metathesized products was obtained by taking Grubb's second generation catalyst, 0.03 mM at 45 °C for 36 h (Figure 2 and 3). Complete conversion of the methyl esters to the metathesized products was observed by employing 0.03 mM of the catalyst unlike other reports, where self-metathesis of vegetable oil methyl esters was carried out using higher concentrations of the catalyst [5,11].

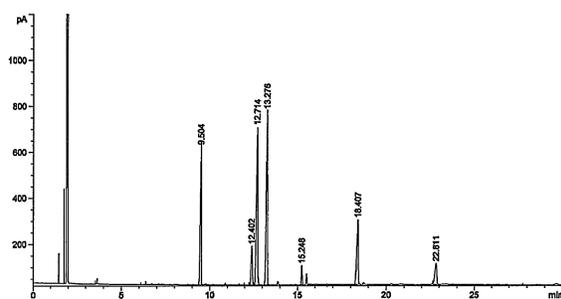


Figure 1. GC analysis of palash fatty acid methyl esters.

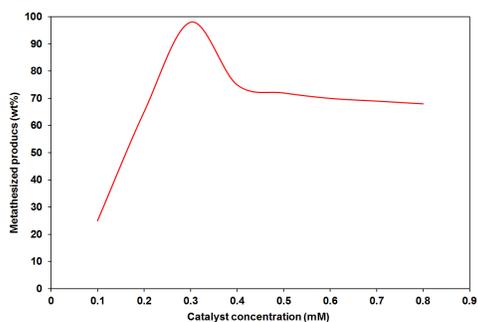


Figure 2. Optimization of catalyst concentration (mM) at 45 °C.

The study also describes the possible routes and the molecules involved in the formation of the metathesized products. Further, the unsaturated products obtained were of *trans* isomers, as they are thermodynamically more stable. Palash oil methyl esters upon metathesis showed the formation of 9-octadecene (Ret. Time: 15.87 min, 10.9% GC; m/z 252, GC-MS) and cyclodecacyclotetradecene (Ret. Time: 22.08 min, 27% GC; m/z 286, GC-MS) as major hydrocarbons along with other hydrocarbons namely 3-dodecene (Ret. Time: 12.52 min, 3.2% GC; m/z 168, GC-MS) and 6-pentadecene (Ret. Time: 15.65 min,

3.2% GC; m/z 210, GC-MS) in minor amounts. 9-Octadecene is obtained by the reaction between two 9-octadecenoic acid methyl esters (Figure 6), a valuable product which can be dimerised and hydrogenated to give (*E*)-10,11-dioctyleicosane, a lube-oil range hydrocarbon intermediate [2,13]. The hydrocarbon plays an important role in decreasing friction between the moving parts. Most familiar applications are motor oil [1].

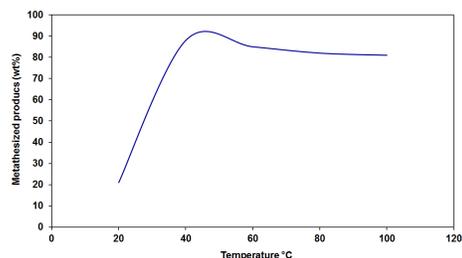


Figure 3. Optimization of temperature (°C) using Grubb's second generation catalyst 0.03 mM.

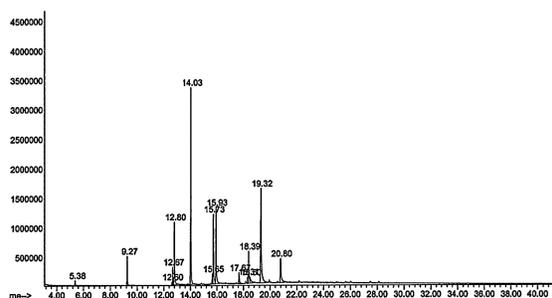


Figure 4. GC-MS of self-metathesized products of palash fatty acid methyl esters.

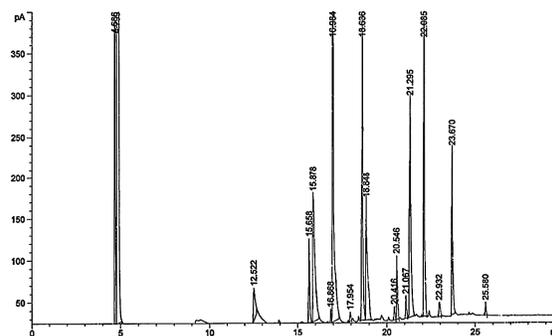


Figure 5. GC analysis of self-metathesized products of palash fatty acid methyl esters.

In addition to this another hydrocarbon, 3-dodecene was obtained in minor amounts by the reaction between 9,12,15-octadecatrienoic acid methyl ester and 9-octadecenoic acid methyl ester as shown in Figure 7. 6-Pentadecene was also found in minor amounts, obtained by the reaction between 9-octadecenoic acid methyl ester and 9,12-octadecadienoic acid methyl ester as shown in Figure 8 and is a type of alarm pheromone found in acarid mite [14].

A cyclic hydrocarbon, cyclodecacyclotetradecene was obtained by the reaction between two 9,12,15-octadecatrienoic acid methyl esters or two 9,12-octadecadienoic acid methyl esters or 9,12,15-octa decatrienoic acid methyl ester and 9,12-octadecadienoic acid methyl esters (Figure 9). This bicyclic C₂₂ ringed hydrocarbon was observed in major amounts (27%), for

the first time and may have potential applications as synthetic intermediate. However, a bicyclic hydrocarbon, C₂₀ cyclodeca cyclododecene (19%) molecule was formed using tobacco methyl esters as reported in our earlier study [16].

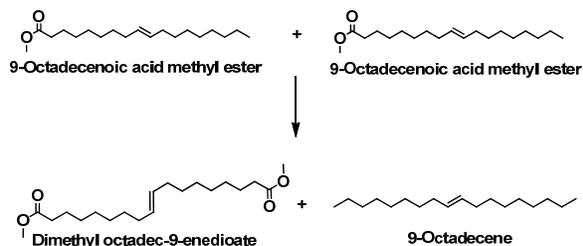


Figure 6. Formation of 9-octadecene.

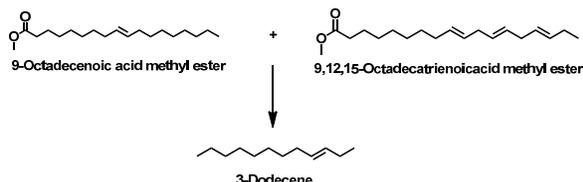


Figure 7. Formation of 3-dodecene.

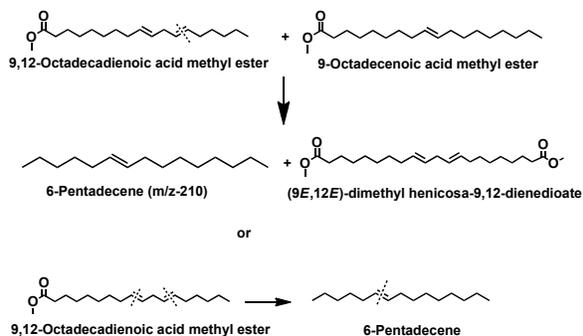


Figure 8. Formation of 6-pentadecene.

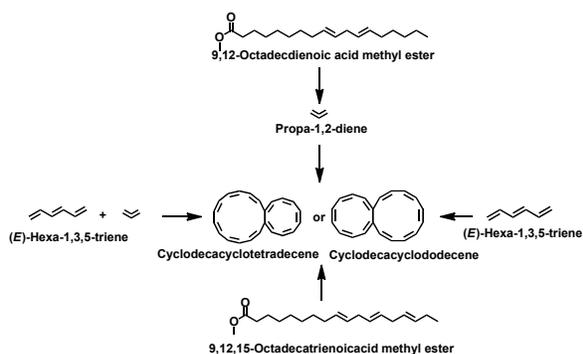


Figure 9. Formation of cyclodecacyclotetradecene.

A monoester 9-penta decenoic acid methyl ester (Ret.time: 16.9 min, 21.12% GC; *m/z* 254, GC-MS; Figure 10) was also observed, which is useful as a synthetic organic intermediate. Unlike most of the literature reports [5,11,15], no diester formation was observed, which could be due to the further reaction of diesters, to give other products (Figure 4-6).

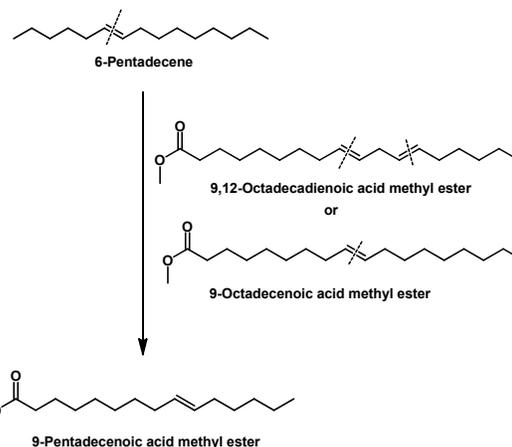


Figure 10. Formation of 9-pentadecenoic acid methyl ester.

4. Conclusions

The study describes the olefin metathesis of palash methyl esters with 65.1% unsaturation using Grubb's second generation catalysts, which resulted in organic intermediates with a variety of industrial applications. The catalyst concentration and the temperature employed for the reaction were less compared to the literature reports. Further the unsaturated products formed were of *trans* isomers as these are thermodynamically most stable. Another significance of the study is that it explains the possible routes and the molecules involved in the formation of metathesized products. Formation of cyclodecacyclotetradecene was observed for the first time and may serve as a potential synthetic intermediate. Thus the platform chemicals synthesized from the renewable resource, palash oil can replace most of the petroleum based products. If the source, palash is exploited for developing such high value intermediates, can uplift the economy of the country and also can serve in rural development.

Acknowledgements

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