

Biodiesel From Uncommon Fatty Acids

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Abstract

Ethyl esters from uncommon fatty acids, such as valproic, azelaic, and sorbic acids, were chemically synthesized and identified by gas chromatography or liquid chromatography coupled to mass spectrometry. Some properties were evaluated to determine their potential for use as biofuels or in other commercial applications. They have remarkable and pleasant odors and, in the case of ethyl ester in valproic acid, display marked resistance to clouding and crystallization.

Introduction

Two-tenths of fatty acids are the natural feedstock originating from vegetable and microorganisms oils (liquids) or animal fats (solids) for the purpose of biodiesel preparation (1). All them have a single carboxyl group (R-COOH), but they may have short, medium, or long chain lengths with the extreme examples being butyric acid (C4:0; butanoic; C₄H₈O₂) and nervonic acid (C24:1; *cis*-15-tetracosanoic; C₂₄H₄₆O₂). Also, they may be either saturated or unsaturated. Important fatty acids include the series oleic acid (C18:1; *cis*-9-octadecenoic; C₁₈H₃₄O₂), linoleic acid (C18:2; *cis*-9, *cis*-12-octadecadienoic; C₁₈H₃₂O₂), and linolenic acid (C18:3; *cis*-9, *cis*-12, *cis*-15-octadecatrienoic; C₁₈H₃₀O₂). Soy, sunflower, cotton, and *Jatropha* crude oils contain over 50% linoleic acid followed by lower contents of oleic acid and linolenic acid. Other important fatty acids are palmitic acid (C16:0; hexadecanoic; C₁₆H₃₂O₂) and stearic acid (C18:0; octadecanoic; C₁₈H₃₆O₂), which each represent about 25% of the fatty acid content of tallow.

Biodiesel is produced from animal and vegetable oils by conversion of the fatty acids to the corresponding ethyl or methyl esters. The unsaturated fatty acids in oils from soybeans and related oleaginous plants lead to biodiesel of higher fluidity, which is liquid at room temperature (25°C). On the other hand, biodiesel from tallow and similar animal fatty sources has jellifying properties and solidifies when the temperature drops to ~ 14–18°C. These temperatures correspond to the cloud and pour points for tallow biodiesel, respectively. In comparison, the pour and cloud points for soy biodiesel are far more

favorable, being 0 and 2°C, respectively.

Due to the differential properties required for the application of biodiesel in aerial transportation, resistance to freezing deserves special attention. For instance, on February 28, 2008, a Boeing 747 of the company Virgin Atlantic undertook a pioneering flight between London and Amsterdam. The biodiesel within the kerosene (Jet fuel A) was a biodiesel blend based on babassu oil and was, therefore, rich in lauric acid methyl ester (C12+1 = C13). Blends of petrodiesel and biodiesel (mainly from soybeans and canola) are finding widespread application in the Americas and Europe. For instance, the Brazilian law for terrestrial biofuels turns mandatory B-3 in 2008-2009 (a mixture of 3% biodiesel and 97% petrodiesel), and the national production of biodiesel for this purpose is currently 1.3 billion liters per year. The goal of this paper is to investigate the potential of novel fatty acids not only for the production of biodiesel to be used in diesel blends but also for other potential industrial applications. Concerning chemical stability, methyl palmitate is far more stable than methyl linoleate because the three unsaturations in the latter are prone to oxidation by oxygen, generating the respective peroxides. However, both molecules are easily degraded by soil or water microorganisms, which cause esters to be hydrolyzed to free fatty acids and alcohol by esterases and lipases.

Esters typically have rich odors. They confer pleasant aromas,

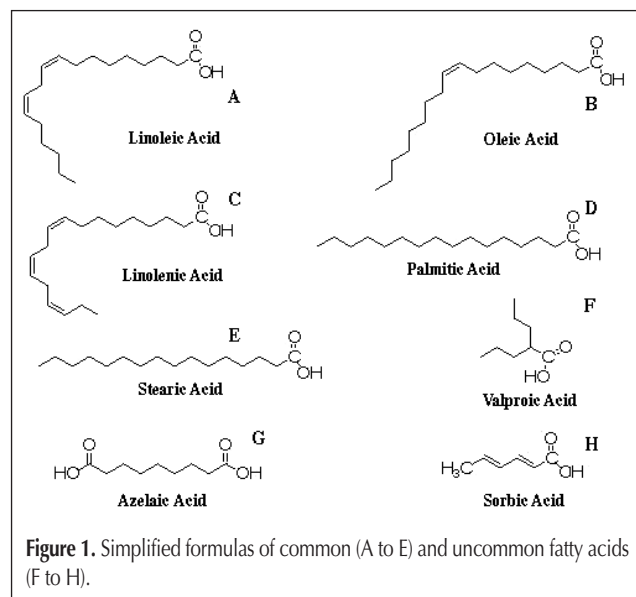


Figure 1. Simplified formulas of common (A to E) and uncommon fatty acids (F to H).

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tastes, and flavors on edible commodities, including beverages such as wines and foods such as fruits, and on non-edible commodities such as perfumes. For example, the characteristic odor of pineapple is due to propyl valerate ($C_8H_{16}O_2$) (2) while that of apple corresponds to ethyl butyrate ($C_6H_{12}O_2$). In fact, several natural triglycerides have easily recognizable odors without any need for the fatty acid to be present in the free form. For example, tributyrin is responsible for the odor of butter while trilaurin is responsible for that of coconut and babassu.

Experimental

Materials

Three uncommon fatty acids were selected for direct esterification via acid catalysis: valproic (C8, propyl-valeric), azelaic (C9, nonadioic), and sorbic (C6:2, hexadienoic). They were obtained from Sigma Aldrich (St. Louis, MO) and Eastman Kodak (Rochester, NY).

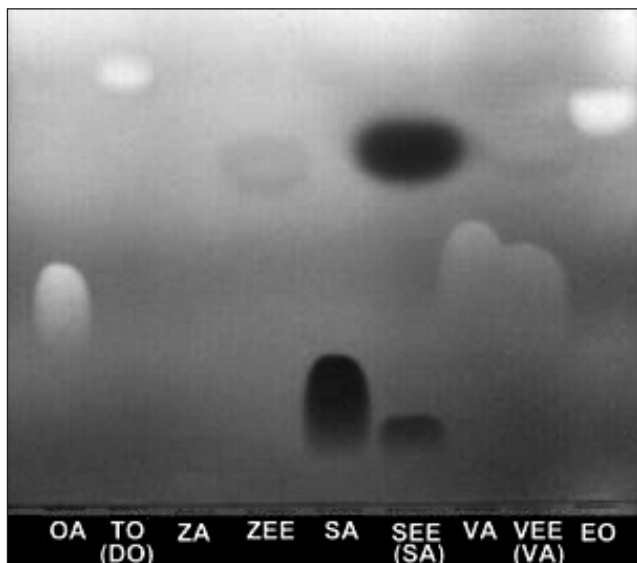


Figure 2. TLC of the parent fatty acids and their ethyl esters.

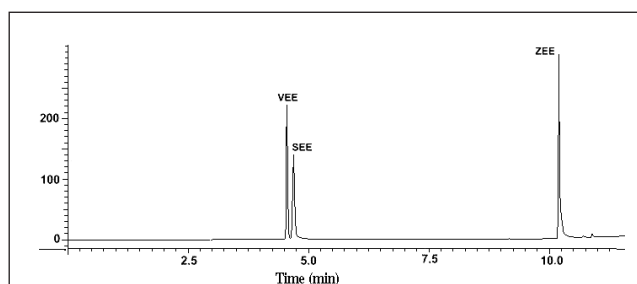


Figure 3. Gas chromatogram of the ethyl esters from valproic acid (VEE), sorbic acid (SEE) and azelaic acid (ZEE) in a CP-SIL 8 CB Low Bleed/MS (Varian) capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). Starting temperature was 100°C (hold 7 min) and further increased until 300°C ($50^\circ\text{C}/\text{min}$; hold 5 min). Helium was utilized as carrier gas at $1\text{ mL}/\text{min}$. VEE, SEE, and ZEE = ethyl esters of valproic, sorbic, and azelaic acids.

Thin layer chromatography

Thin layer chromatography (TLC) were run on silica gel 60 chromatoplates from Merck (Whitehouse Station, NJ) with hexane–chloroform–acetone (15:12:1, v/v/v) and visualized under UV light (365 nm) after nebulization with ethanolic rhodamine and then fluorescein, both at 50 mg%.

Gas chromatography–mass spectrometry

Gas chromatography–mass spectrometry (GC–MS) of the ethyl esters from valproic, sorbic, and azelaic acids was carried out in a CP-Sil 8 CB Low Bleed/MS (Varian, Palo Alto, CA) capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). Starting temperature was 100°C (hold 7 min) and further increased until 300°C ($50^\circ\text{C}/\text{min}$; hold 5 min). Helium (He) was utilized as the carrier gas at $1\text{ mL}/\text{min}$. Acetonitrile was used for chemical ionization.

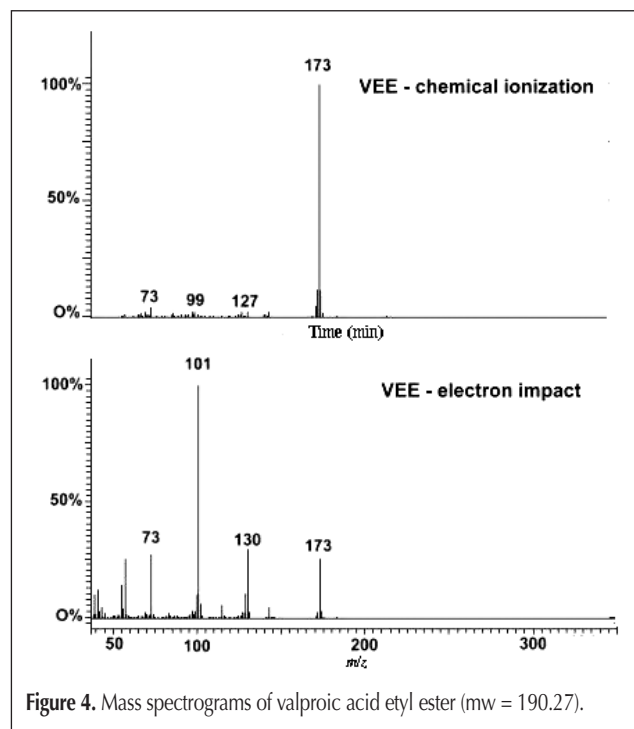


Figure 4. Mass spectrograms of valproic acid ethyl ester ($\text{mw} = 190.27$).

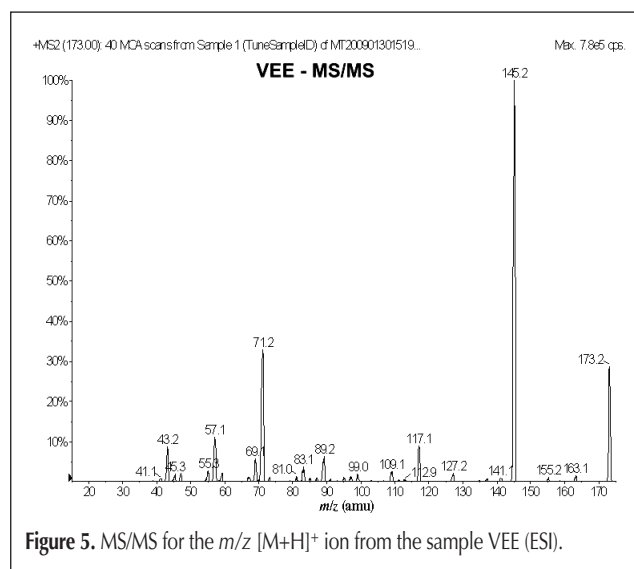


Figure 5. MS/MS for the m/z $[M+H]^+$ ion from the sample VEE (ESI).

Liquid chromatography–mass spectrometry

Low-resolution electrospray ionization (ESI)-MS and ESI-MS-MS data were acquired using an API 3200 of Applied Biosystems instrument (Foster City, CA) equipped with an ESI and atmospheric pressure ionization (APCI) source. A TurboIonSpray (ESI) probe positive ion mode was utilized in these experiments. Full-scan mass spectra and products ion scan spectra for compounds were obtained by direct infusion into the mass spectrometer diluted in methanol containing 5 mM ammonium formate. The typical ion source parameters were: declustering potential (DP): 20 V (ethyl esters from sorbic acid, SEE, and valproic acid, VEE), 50 V (ethyl esters from azelaic acid, ZEE), and 5500 V (IS); collision energy (CE): 20 eV (SEE), 20 eV (VEE), 15 eV (ZEE); entrance potential (EP) 10 V; collision cell exit potential (CXP) 3.8 V; spray voltage, 5500 V. Nebulizer gas (NEB), curtain gas (CUR) and collision gas (CAD) were set to 40, 10, 5 psi, respectively. Nitrogen gas was used for CUR, CAD, NEB.

Acid-mediated esterification

Alkaline and acid catalysis are used to produce biodiesel from triacylglycerols (1), but with free fatty acids as the substrate, only acid catalysis is applicable. One-tenth of a mole of each acid was mixed with five-tenths of a mole of ethanol containing 2% sulphuric acid (referred to the weight of free fatty acid). The mixture was refluxed for 1 h, cooled, and then carefully alkalized with sodium hydroxide to pH 9 in order to convert any residual fatty acid into the corresponding sodium soap. One volume of hexane-ethyl acetate was then added to the mixture in order to extract the desired ester(s). The organic phase was then removed and the solvents were evaporated, leaving an oily mixture of esters. Yield(s), as evaluated by gravimetry and chromatography, were 80–90%.

Pour point determination

A MiniPour/Cloud Point Tester from Tanaka Scientific (Tokyo, Japan) was used to determine the pour points of the ethyl esters of valproic and azelaic acids until a local operational limit of -56°C . The analysis was done by Dr. Luiz P. Ramos from the Applied Chemistry Laboratory of the Federal University of Paraná (UFPR).

Determination of the higher heating value

The higher heating value (HHV) of VEE was determined in an adiabatic “Julius Perter” bomb calorimeter based on the Berthelot method, following the guidelines of ASTM-D-240-50. The analyses were carried out by Dr. Dimas A. da Silva from the Biomass Energy Laboratory (UFPR).

Results

Chromatographic analysis

The TLC profiles of the VEE, SEE, and ZEE are shown in Figure 2. The parent fatty acids and their ethyl esters can be distinguished based on their colors and their chromatographic migrations (Rf). The standard compounds oleic acid, triolein,

and ethyl oleate displayed Rf values of 0.39, 0.84, and 0.74. The Rf(s) of the parent azelaic, sorbic, and valproic acids were 0.04, 0.22, and 0.47, respectively, while those of their corresponding ethyl esters were 0.66, 0.69, and 0.71, respectively. It should be noted that the derivative of azelaic acid is a diester. The strongest colors were observed for sorbic acid and its ethyl ester, both derived from the unsaturated chain.

Figure 3 show the GC analysis for the ethyl derivatives of valproic ($t_R = 4.6$ min), sorbic ($t_R = 4.75$ min), and azelaic acids ($t_R = 10.25$ min). The higher t_R observed for azelaic acid ethyl ester is due to the double substitution with ethanol.

Mass spectrometry fragmentation patterns were obtained in a Varian Saturn 2000 apparatus with either chemical ionization with acetonitrile (IQ) or electronic impact (IE) (Figure 4). The expected and respective peaks for valproic acid ethyl ester, as an example, were: 173, 127, 99, 73 and 173, 130, 101, 73.

Liquid chromatography coupled to MS-MS, as shown in Figure 5–7, confirmed the expected structures for the synthesized esters. The observed peaks $[M+H]^+$ for valproic, sorbic, and azelaic acid esters and their fragmented esters were 173.2 and 145.2; 141.1 and 113.2; 245.3 and 189.1, respectively.

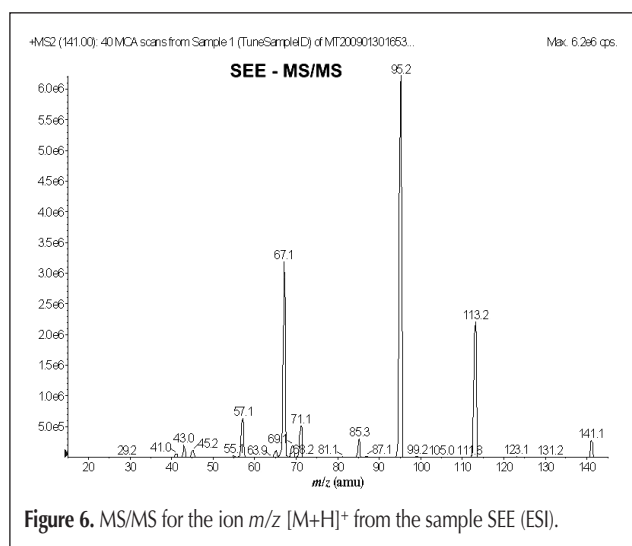


Figure 6. MS/MS for the ion m/z $[M+H]^+$ from the sample SEE (ESI).

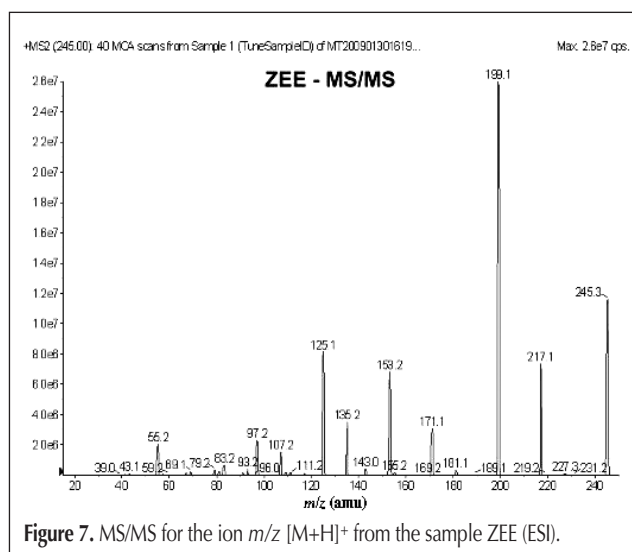


Figure 7. MS/MS for the ion m/z $[M+H]^+$ from the sample ZEE (ESI).

Table I. Properties of Uncommon Fatty Acids Ethyl Esters

Parent fatty acid → ester	Ethyl * valproate	Ethyl azelate	Ethyl sorbate
Formula	C ₁₀ H ₁₉ O ₂	C ₁₁ H ₂₀ O ₄	C ₈ H ₁₂ O ₂
Carbon Chain Characteristics	Ramified ("bifid")	2 carboxyls (2 polar "heads")	2 double conjugated links
Odor	bottom note with woody characteristic	synthetic; without specific classification	middle note with fruity characteristic
Comburent action ^{†,‡}	+ (normal) [†]	++ (increased) [‡]	+ (normal)
Parent acid physical state	Liquid	Solid	Solid
Ethyl ester physical state	Liquid	Liquid	Liquid
Pour point	< -56°C [§]	-24°C	nd
Fungistatic, bacteriostatic, algistatic activity**	?	?	+ **
Anti-acne potential bioactivity	?	+ (via skin esterases)	?
Anti-convulsant potential	+	-	-

* Also requested to the National Institute of the Industrial Property for the protection of the idea of the remaining members of the series, such as oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, and sebacic;
[†] MiniPour Tester;
[‡] Cloud Points Tester;
[§] Maximum operational limit for the apparatus MiniPour / Cloud Points Tester. When blended to diesel: (*) typical for a mono-ester (di-oxygenated); expected for a diester (tetra-oxygenated);
** Already known for a few food s [acc. (3)] but so far not yet tested when added to other biodiesel blends.

Properties of ethyl esters of uncommon fatty acids

Some of the more remarkable properties of the ethyl esters obtained from the uncommon fatty acids are shown in Table I. It is worth mentioning the remarkable negative temperature regarding the pour point for the ethyl ester of the ramified valproic acid.

Discussion

The ethyl esters of three uncommon fatty acids, namely azelaic, sorbic, and valproic acids, were chemically synthesized through acid catalysis and further characterized by TLC and GC techniques. Valproic acid ethyl ester had the most remarkable properties, with a pleasant and marked woody odor and a dramatic resistance to clouding and crystallization. The HHV obtained for valproic acid ethyl ester was 8523 kcal/kg (average superior value) with a standard error of 333 kcal/kg, whereas the reference compound, soybean ethylic biodiesel, had a HHV of 9751 kcal/kg with a standard error of 96 kcal/kg. Azelaic acid creams are extensively used for the treatment of acne, usually as

20% formulations (2,3). Its ethyl esters might find medico-pharmaceutical applications due to the natural occurrence of skin esterases (4). Either GC-MS or ESI-MS-MS confirmed the expected structures for the synthesized esters.

Conclusion

The fast-growing biodiesel industry may encompass the utilization and applications for novel biodiesel. The scent and marked-resistance to crystallization may be desirable innovations on biodiesel and ethyl esters from uncommon fatty acids, such as valproic, azelaic, and sorbic acids, may fulfill this industrial gap. There are other potential applications for these novel biodiesel, and examples are as simple additives for diesel, such as biodiesel blends and in the cosmetic industry.

Acknowledgments

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References

- G. Knothe, J. Van Gerpen, and J. Krahl. *The Biodiesel Handbook*. AOCS Catalog, p. 312, 2005.
- Y. Tokitomo, M. Steinhaus, A. Butner, and P. Schieberle. Odor-active constituents in fresh pineapple (*Ananas comosus*) by quantitative and sensory evaluation. *Biosci. Biotech. Biochem.* **69**(7): 1323–1330, (2005).
- L.C. Meher, D. V. Sagar, and S.N. Naik. Technical Aspects of biodiesel production by transesterification – a review. *Renew. Sustain. Energy Rev.* **10**: 248–268 (2006).
- G. Webster. Combination of azelaic acid therapy for acne vulgaris. *Eur. Academ. Dermatol.* **43**(2): 847–850 (2000).
- I. Fariba, A. Sadeghinia, Z. Shahmoradi, A. H. Siadat, and A. Jooya. Efficacy of topical azelaic acid gel in the treatment of mild-moderate acne vulgaris. *Indian J. Dermatol. Venereol. Leprol.* **73**(2): 94–96 (2007).
- J.J. Prusakiewicz, C. Ackerman, and R. Woorman. Comparison of skin esterase activities from different species. *Pharm. Res.* **23**(7): 1517–1524 (2006).
- J.A. Troler, & R.A. Olsen. Derivatives of sorbic acid as food. *Preservatives. J. Food Sci.* **32**(2): 228–231 (1967).

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