

Succinate Ester Solvents for Fragrance

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INTRODUCTION

BioAmber is a next generation chemicals company, with a portfolio of renewable chemicals; a C4 Platform, based on bio-based succinic acid and its derivatives, and a C6 Platform, which includes bio-based adipic acid and other bio-based C6 chemicals. BioAmber was first to market with commercial scale bio-based succinic acid, and is currently serving customers from a toll manufacturing plant in France. Based on growing market demand for bio-based chemicals, BioAmber is constructing a large-scale plant in Ontario, Canada, to supply industrial scale bio-based succinic acid. As a platform chemical, bio-based succinic acid has a wide range of applications, including as an intermediate for natural ester solvents.

Bio-based succinic acid is a natural raw material, made from plants, which can be used to produce a wide range of personal care ingredients including ester solvents, emollient esters, and surfactants. Bio-based succinic acid can be reacted with natural alcohols to produce bio-based esters with up to 100% renewable content. C2-C5 succinate esters have been shown to be excellent solvents for personal care applications including fragrance carriers and nail enamel removers. While this paper will focus on the performance of selected diester solvents, C8-C18 esters have been shown to exhibit unique emollient properties for skin and hair care. Additionally, bio-based succinic acid is an effective preservative and effervescent agent, making it a versatile natural intermediate for the personal care industry.

In this study, three succinate esters were synthesized and evaluated as carriers for fragrances. The effects of the succinate esters on the odor notes of the fragrance were tested and compared to the neat fragrances, as well as to the fragrance blended with a diethyl phthalate benchmark. While many regions have moved away from phthalates as fragrance carriers and fixatives, use of diethyl phthalate is still common in some regions. Diethyl succinate, diamyl succinate, and diisooamyl succinate were investigated as solvents for neat fragrances, perfumery fragrance blends, and carriers for fragrance blends into cosmetic formulations. In addition, the succinate esters were evaluated for their performance in an incense application, Aggarbatiis, used frequently in Asia. In this case, the fragrance was evaluated upon burning.

The succinate esters showed good solvency for the fragrance compositions, with diethyl succinate demonstrating the highest solvency. In many cases, the succinate esters impart additional notes to the fragrance or fragrance blends. While this may be undesirable for some applications, it may allow for the succinate esters to be considered part of the fragrance rather than as a carrier solvent. Additionally, the succinate ester imparted pleasant, mild sweet notes which may be beneficial for some applications. Finally, the diester succinate solvents can be up to 100% natural when natural alcohols are used in ester synthesis, giving a natural solvent with good carrier properties for incorporation of fragrance into cosmetic product formulations.

In addition to the potential for a natural, bio-based solvent, BioAmber's bio-based succinic acid is carbon neutral at industrial capacity. The Sarnia, Ontario plant will generate a savings of >100% greenhouse gas emissions, and uses 60.9% less energy compared to petrochemical production of adipic acid kilogram per kilogram.¹ Also, BioAmber's bio-based succinic acid can be used to make natural succinate esters that can be formulated into Personal Care applications that are 100% natural and non-GMO. The use of bio-based succinic acid from BioAmber immediately reduces the overall footprint of any product, when used as a direct replacement for energy and carbon intensive petrochemicals.

EXPERIMENTAL

Synthesis of diesters

Diethyl Succinate: A four necked dry flask equipped with a reflux condenser, thermometer and guard tube was charged with BioAmber bio succinic acid (1Kg, 8.47 mol), dry ethanol (2.0L), and concentrated H₂SO₄ (110 mL). The reaction was allowed to reflux for 2 hours, followed by removal of ethanol by rotary evaporator under vacuum. The resulting mixture was cooled to room temperature, and was neutralized with a saturated aqueous solution of Na₂CO₃ (138g in 346 mL of

water) to reach a pH of 7. The crude diethyl succinate was separated, dried over anhydrous sodium sulfate, and purified by vacuum distillation (1 mm of Hg, bp 95-98 °C). GC Purity > 99.98%.

Diamyl Succinate: A four necked dry flask equipped with a reflux condenser, thermometer and guard tube was charged with BioAmber bio succinic acid (1Kg, 8.47 mol), dry amyl alcohol (2.2L), and concentrated H₂SO₄ (90 mL). The mixture was heated to 100 °C, and allowed to react for 2 hours. The resulting reaction mixture was cooled to room temperature, upon which two layers were observed. The aqueous layer was separated from the organic layer, and the organic layer was washed with a saturated aqueous solution of Na₂CO₃ (33g in 82 mL of water) to a pH of 7. Crude diamyl succinate was dried on anhydrous sodium sulfate and purified by vacuum distillation (1 mm Hg, bp 140-142 °C). GC Purity > 99.98%.

Diisoamyl Succinate: A four necked dry flask equipped with a reflux condenser, thermometer and guard tube was charged with BioAmber bio succinic acid (1Kg, 8.47 mol), dry *iso*-amyl alcohol (2.2L), and concentrated H₂SO₄ (90 mL). The mixture was heated to 100 °C, and allowed to react for 2 hours. The resulting reaction mixture was cooled to room temperature, upon which two layers were observed. The aqueous layer was separated from the organic layer, and the organic layer was washed with a saturated aqueous solution of Na₂CO₃ (33g in 82 mL of water) to a pH of 7. Crude diisoamyl succinate was dried on anhydrous sodium sulfate and purified by vacuum distillation (1 mm Hg, bp 140-142 °C). GC Purity > 99.98%.

Fragrance Solvent Evaluations

The esters were evaluated for their physical properties including density, viscosity, color and basic odor. The esters were then incorporated into three perfumery raw materials, menthol, ethyl vanillin and Helional. These perfumery materials were selected due to their characteristic range of odors, namely sharpness, smoothness and freshness. Additionally, the esters were incorporated into two fragrance blends, Amanat (SHK) and SHK C151. All combinations were evaluated for odor characteristics and compared to diethyl phthalate controls. In addition, fragrance blends with succinate esters were also incorporated into personal care formulations including shampoo, cream base, astringent and Aggarbatiis. These product formulations were tested for initial odor both before and after application. The formulations were also subjected to 5 freeze thaw cycles and reevaluated for odor characteristics.

Odor Evaluations

The succinate esters were mixed with raw perfumery materials in 20% dilution and then tested by 10 trained panelists. The evaluation was done using Magnitude estimation method, which is a procedure where the intensity of one odor is compared to the control odor.

RESULTS AND DISCUSSION

Diethyl succinate, diamyl succinate and diisoamyl succinate were tested for basic physical properties such as density, color, odor, texture on the skin and solubilizing efficiency. All succinate esters were transparent and colorless. In addition, all of the succinate esters gave similar feel on the skin, imparting a glossy film with a texture lighter than water. Table 1 summarizes the performance of the bio based succinate ester solvents.

| <i>Table 1. Properties of Bio Based Succinate Esters</i> | | | |
|--|------------------|--|---------------------------------|
| Succinate ester | Relative Density | Odor | Solubilizing Efficiency* |
| Diethyl succinate | 1.04 | Very mild sweet, powdery, citrusy, green notes | Quickly solubilizes |
| Diisoamyl succinate | 0.96 | Strong gourmet, edible notes | Slow solubilizing (3 min) |
| Diamyl succinate | 0.96 | Mild fruity chemical note | Moderate solubilizing (1.5 min) |

*20% solution of perfumery raw materials

Evaluations with neat fragrance

The succinate esters were evaluated for the intensity of their odor performance at a 20% dilution of the fragrance compared to the neat fragrance control. Neat fragrances used for this study include Ethyl Vanillin, Helional, or Menthol. The impact of the esters on the fragrance odors was the same regardless of the fragrance used and is summarized in Table 2. In general, DES imparts a fatty note that interferes with the original note of the neat fragrance. DIAS imparts a sweet gourmet edible note which also interferes with the original note of the neat fragrance. DAS imparts similar notes as the neat fragrance, but imparts an additional mild sweet odor.

| <i>Table2. Odor Properties of Succinate Esters with Neat Fragrance</i> | | |
|--|---|----------|
| Ester | Difference | Strength |
| Diethyl succinate | Rancid coconut note, fatty oily note which is an off note | 2 |
| Diisoamyl succinate | Sugary sweet and dry powdery notes | 3 |
| Diamyl succinate | Closest to neat fragrance | 4 |
| Diethyl phthalate | Less powdery character but close to neat fragrance | 5 |

Evaluations with perfumery blends

The succinate esters were evaluated for the intensity of their odor performance at 20% dilution of fragrance compared to the original fragrance blend composition. Fragrance blends for this evaluation included SHK Amanat and SHK C1511. Results for the succinate esters were similar regardless of the fragrance blend used. Table 3 summarizes the performance of the fragrance blends with succinate esters compared to the neat fragrance blends and the diethyl phthalate benchmark. The DES imparted a fatty note that interfered with the original notes of the fragrance blend. The DIAS imparted a sweet gourmet edible note which also interfered with the original notes of the fragrance blends. DAS gave similar notes as the neat fragrance blends, but did impart a mild additional sweet odor.

| <i>Table3. Odor Properties of Succinate Esters with Perfumery Blends</i> | | |
|--|---|----------|
| Ester | Difference | Strength |
| Diethyl succinate | Rancid coconut note, fatty oily note which is an off note | 2 |
| Diisoamyl succinate | Sugary sweet and dry powdery notes | 3 |
| Diamyl succinate | Closest to neat fragrance blend | 4 |
| Diethyl phthalate | Less powdery character but close to neat fragrance blend | 5 |

Evaluations with Cosmetic Products

The bio-based succinate esters were evaluated with SHK Lilac fragrance blend at a ratio of 1:3, fragrance to ester. This diluted fragrance mixture was incorporated into an emulsion based cream at 0.4%, a shampoo base at 0.5%, and an astringent at 1.0%. The finished formulations were evaluated for odor at point of purchase (POP) and upon application. The succinate ester fragrance mixtures performed the same regardless of the cosmetic base used, and had the same odor performance both before and after application to the skin. Table 4 summarizes the performance of the bio based succinate esters compared to the undiluted fragrance. DES gave the basic notes of the fragrance blend, with slight additional sweet notes. Diffusion with DES was lower than DEP, but was the best of the succinate esters. DIAS changed the fragrance notes to edible chocolaty notes. DAS added powdery strong notes to the formulations.

| <i>Table4. Odor Performance in Cosmetic Products</i> | | |
|--|---|----------|
| Ester | POP and On Application | Strength |
| Diethyl succinate | Floral, creamy, slightly sweeter than DEP | 4 |
| Diisoamyl succinate | Edible gourmet note along with the normal notes Adds a chocolate note to the fragrance | 1 |
| Diamyl succinate | Lots of powdery and chalky notes along with the normal notes of the fragrance | 2 |
| Diethyl phthalate | Normal note of the fragrance | 5 |

Evaluations in Aggarbatiis

The effect of the succinate esters on the burning notes of the fragrance was evaluated by incorporation of the fragrance mixtures in aggarbatiis, a type of incense. The aggarbatiis was dipped in a mixture of fragrance and ester at a ratio of 1:3. The dipped aggarbatiis was dried and then burned in order to evaluate the effects of the esters on the burning notes of the fragrance. Diethyl succinate gave the basic notes of the fragrance blend, which were mild and less diffusive compared to the diethyl phthalate benchmark. DIAS gave good diffusion compared to DES, but was milder compared to DEP, and also added sweet gourmet notes to the fragrance. DAS gave the best diffusion of the succinate esters, but was slightly less diffusive than DEP. Table 5 summarizes the performance of the succinate esters in the aggarbatiis incense evaluations.

| <i>Table4. Odor Performance in Cosmetic Products</i> | | |
|--|--|----------|
| Ester | Upon Burning | Strength |
| Diethyl succinate | Lower diffusion, mild notes | 2 |
| Diisoamyl succinate | Good diffusion with addition of a sweet gourmet note | 3 |
| Diamyl succinate | Good diffusion but lower than DEP | 4 |
| Diethyl phthalate | All notes perceived with good diffusion | 5 |

CONCLUSION

Bio-based succinate ester solvents can be used as natural solvents for fragrances in both perfumery and as carriers for solvents into personal care formulations. The impact of the succinate esters on the fragrance odor was the same regardless of the fragrance used, or the cosmetic product that it was incorporated into, showing versatility of the succinate esters as solvents for fragrance. Diethyl succinate is the best candidate for a natural solvent for fragrances that are incorporated into cosmetic products like cream emulsions, shampoos, and astringents. Diamyl succinate can be used as a solvent for perfumery and aggarbatiis, as it does not interfere much with the original notes of the fragrance, with the exception of imparting a mild sweet note. Diisoamyl succinate is closer to diethyl phthalate in its base properties, but adds gourmet chocolaty notes. Overall, natural succinate esters are a versatile solvent choice for the fragrance and personal care industries.

BioAmber

BioAmber is a next generation chemicals company. Its proprietary technology platform combines industrial biotechnology, an innovative purification process and chemical catalysis to convert renewable feedstocks into chemicals for use in a wide variety of everyday products including plastics, food additives and personal care products. BioAmber produces bio-based succinic acid in what it believes to be one of the world's largest bio-based chemical manufacturing facilities. For more information visit the company's web site at www.bio-amber.com.

REFERENCES

1. "Field-to-Gate Energy and Greenhouse Gas Emissions Associated with Succinic Acid Produced At BioAmber's Facility In Samia Ontario," Riffel Consulting, March 2013

BIOGRAPHIES

Tara Mullen is the Manager of Application Engineering and Technical Support at BioAmber Inc. She received a Bachelor of Science Degree in Chemistry from St. Norbert College, and a Doctorate Degree in Polymer Science and Engineering from the University of Southern Mississippi. Prior to joining BioAmber in 2012, Tara held Application and Commercial Development roles at Segetis, and spent 5 years at GE Plastics in a Product Development role. Tara has authored numerous peer reviewed journal articles, and holds 10 U.S. patents.

Sujata V. Bhat is the head of Laboratory for Advanced Research in Natural and Synthetic Chemistry at V. G. Vaze College, Mumbai. She received a Doctor of Philosophy degree in Chemistry from National Chemical Laboratory, Pune. Prior to joining the Vaze college, she served as Professor for 18 years in the Chemistry department at the Indian Institute of Technology Bombay, Powai, Mumbai, and worked for 12 years as the Head of natural products division, Research Centre, Hoechst Pharmaceuticals Ltd. Mulund, Mumbai. She has published over 110 manuscripts in refereed journals, 6 books, 24 patents and 4 review articles. Under her guidance over 80 students have received Ph. D. and M. Sc. Degrees in Chemistry and Biotechnology.

Renuka Thergaonkar is the Head of the Department of Cosmetics and Perfumery and heads the Formulation and Research & Development lab in the Scientific Research Center at V.G. Vaze College. She holds a Bachelors and Masters in Cosmetic Technology, and is pursuing her Doctorate in Cosmetic Technology. Renuka also holds a Diploma in Business Management, and has completed 35 formulation projects with 85 marketed products in the national and international market. She holds several published papers and three patents.