SYNTHESIS AND CHARACTERISATION OF DIHYDROXYSTEARIC ACID-ESTOLIDES FROM PALM-BASED DIHYDROXYSTEARIC ACID

By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Master of Science

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Chairman : Professor Wan Md. Zin Bin Wan Yunus, PhD

Faculty : Science

Estolide is a polyfunctional oligomer that contains ester linkages on the alkyl backbone of the molecule, which is formed by the esterification reaction between fatty acids. These ester linkages are more resistant to hydrolysis than those of triglyceride. The unique structure of the estolide makes it has superior physical properties if compared to the mineral and vegetable oil in certain applications. Estolides can be potentially used in a variety of applications, such as surfactants, ingredient or additive in cosmetic and inks formulations.

An attempt was made to synthesize dihydroxystearic acid-estolides from palm-based DHSA through a condensation reaction. The hydroxyl and carboxyl groups in DHSA reacted intermolecularly to form DHSA-estolides. The synthesis of DHSA-estolides was successfully conducted *via* condensation reaction at 180^{o}C without any acid catalyst under atmospheric pressure. The condensations of DHSA at various reaction periods (2 h, 4 h, 6 h and 8 h) yield product mixtures with high saponification values but low acid values indicating

fatty acid has been successfully converted into the ester. As the reaction proceeds, the powdery DHSA changes to a sticky and hardly pourable paste. This is due to the homo-oligomerization of DHSA produces DHSA-estolide with higher molecular weight than that of the starting material. The increased average molecular weights (calculated based on the neutralization equivalent, NE and end-group analysis) of the product mixtures obtained indicate the repeating unit or molecular weight of the DHSA-estolides produced increase as the reaction period is increased. The low peroxide values of DHSA-estolides show they are oxidatively stable.

Analyses of GPC and HPLC show that the product mixtures obtained are actually mixtures of DHSA and DHSA-estolides of different repeating unit/ molecular weight. Both FT-IR and NMR analyses confirm the formation of estolide. The ester transmittance peak (1742 cm^{-1} -1733 cm^{-1}) with an acid shoulder (1716 cm^{-1} -1713 cm^{-1}) is observed in FT-IR spectrum. The ester methine signal (4.84 ppm) and 2 α-methylene protons (α-acid, 2.36 ppm; α-ester, 2.30 ppm) are the distinctive features of DHSA-estolide in ^{1}H-NMR.

These DHSA-estolides are found applicable as anti-rust additive in cutting fluid. DHSA-monoestolide and DHSA-diestolide with the acid value of 60 – 90 mgKOH/ g are found compatible in shampoo formulation and improves the performances of the shampoo. DHSA-triestolide and DHSA-pentaestolide with the acid value of 20 -40 mgKOH/ g are found fully function as emulsifier and thickener in water-in-oil emulsion for cosmetic formulations.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS DAN PENCIRIAN DIHIDROSISTERIK-ESTOLIDA DARI ASID DIHYDROKSISTERIK (DHSA) BERASASKAN SAWIT.

Oleh

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Estolida adalah sejenis oligomer pelbagai fungsi yang mempunyai ikatan-ikatan ester yang terletak di dalam rantai utama alkil molekul estolida tersebut. Ia terbentuk hasil daripada tindak balas pengesteran di antara asid lemak. Ikatan-ikatan ester ini mempunyai sifat untuk melawan daripada berlakunya tindak balas hidrolisis yang lebih baik jika dibandingkan dengan molekul trigliserida. Dengan keunikan struktur molekul ini, maka estolida mempunyai ciri-ciri fizikal yang amat baik untuk digunakan dalam sesetengah aplikasi jika dibandingkan dengan minyak-minyak mineral dan juga tumbuh-tumbuhan. Estolida mempunyai potensi dalam pelbagai aplikasi seperti sebagai agen aktif permukaan, sebagai salah satu bahan dalam pembuatan plastik, bahan pencetak dan juga dalam formulasi bahan kosmetik.

Usaha untuk menghasilkan DHSA-estolida daripada asid dihidroksistearik berasaskan sawit telah berjaya dilakukan melalui tindak balas kondensasi pada suhu 180^{o}C tanpa pemangkin di bawah tekanan atmosfera. Pembentukan DHSA-estolida ini adalah hasil tindak balas antara-molekul di antara kumpulan hidroksil dan karboksil yang terdapat dalam molekul DHSA.

Tindak balas kondensasi DHSA pada jangka masa tindak balas yang berlainan (2j, 4j, 6j dan 8j) menghasilkan hasil campuran tindak balas DHSA-estolida yang mempunyai nilai saponifikasi yang tinggi dan nilai asid yang rendah. Ini menunjukkan bahawa sebatian asid lemak berjaya ditukarkan ke sebatian ester melalui tindak balas kondensasi. DHSA yang berbentuk serbuk bertukar kepada pes yang sangat melekit apabila tindak balas diteruskan. Ini adalah disebabkan oleh tindak balas oligomerasi-homo antara molekul-molekul DHSA menghasilkan DHSA-estolida yang mempunyai jisim molekul yang lebih tinggi daripada DHSA. Jisim molekul relatif yang diperolehi daripada pengiraan berdasarkan persamaan peneutralan (*neutralization equivalent, NE*) dan juga analisis kumpulan berfungsi (*end-group analysis*) bagi hasil campuran tindak balas yang diperolehi adalah bertambah. Ini menunjukkan bahawa jisim molekul DHSA-estolida yang dihasilkan adalah bertambah apabila masa tindak balas kondensasi ditambahkan. Nilai peroksida yang rendah menunjukkan DHSA-estolida yang dihasilkan adalah stabil terhadap tindak balas pengoksidaan.

Analisis GPC dan HPLC menunjukkan bahawa hasil campuran tindak balas yang diperolehi terdiri daripada DHSA dan juga beberapa DHSA-estolida yang mempunyai unit ulangan yang berlainan. Pembentukan DHSA-estolida telah dibuktikan oleh penganalisaan terhadap FT-IR dan NMR. Penyerapan puncak ester (1742 cm^{-1} -1733 cm^{-1}) yang disertai dengan 1 puncak asid (1716 cm^{-1} - 1713 cm^{-1}) yang kecil dapat dilihat di dalam spektrum FT-IR. Penyerapan kumpulan ester metine (4.48 ppm) and 2 jenis proton metilin-α (α-ester, 2.36 ppm; α-asid, 2.30 ppm) merupakan ciri-ciri jelas bagi DHSA-estolida di dalam spekstroskopi ^{1}H-NMR juga

Semua DHSA-estolida yang dihasilkan didapati boleh digunakan sebagai bahan anti – pengaratan dalam minyak pelincir. Walaubagaimanapun, hanya DHSA-monoestolida dan DHSA-diestolida yang mempunyai nilai asid di antara 60 -90 mgKOH/g sahaja yang didapati sesuai digunakan dalam formulasi syampu sebagai bahan tambahan bagi mempertingkatkan prestasi penggunaan syampu. DHSA-triestolida dan DHSA-pentaestolida yang mempunyai nilai asid di antara 20-40 mgKOH/g pula didapati mampu bertindak sebagai bahan pengemulsi dan juga agen pemekat dalam formulasi kosmetik terutamanya dalam sistem emulsi air-dalam-minyak.

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I certify that an Examination Committee has met on 25th May 2006 to conduct the final examination of Aminah Bte Nor Azizan on her Master of Science thesis entitled "Synthesis and Characterisation of Dihydroxystearic Acid-Estolides from Palm-based Dihydroxystearic Acid" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

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AMINAH BTE NOR AZIZAN

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