

# COLLISION STIMULATED RELEASE OF FATTY ACIDS FROM ACYLGLYCERIDES BY ELECTROSPRAY IONISATION FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY

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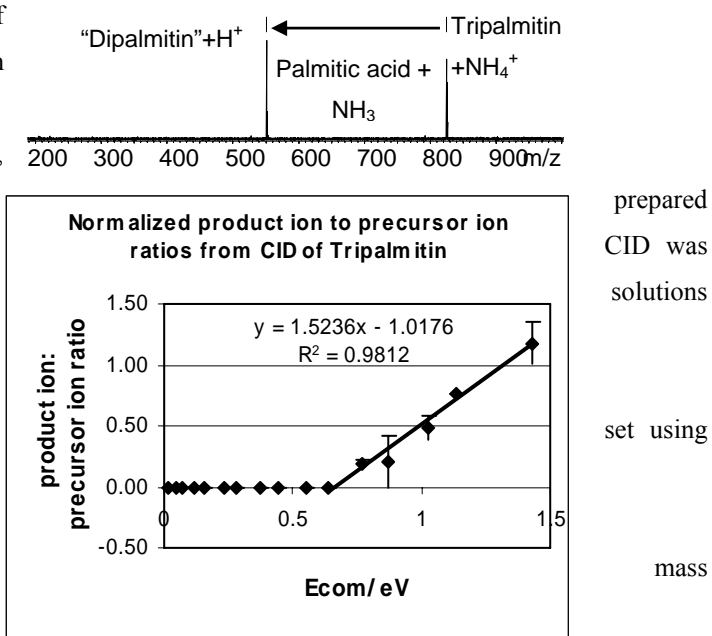
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**Introduction.** The rate of adsorption and metabolism of triacylglycerides is affected by its stereochemical configuration, which is linked to obesity, heart disease and diabetes. The position of the fatty acid acyl side chains on the glycerol backbone is important as those on the *sn*-1 and *sn*-3 position are the first to be digested by lipases. CID has been used to study the structure of triacylglycerides with Li<sup>+</sup> and NH<sub>4</sub><sup>+</sup> attachment.<sup>1</sup> The mechanism for the CID process differs with the type of cation used in the ESI ion formation. Here, we determine the activation energy for the fragmentation process of a series of triacylglycerides and use DFT quantum calculations to model the reaction mechanism.

**Experimental.** Solutions of trilaurin, trimyristin, tripalmitin and tristearate (10<sup>-5</sup> M) were in MeOH:Toluene (10:1) containing NH<sub>4</sub>OAc. CID was performed on the NH<sub>4</sub><sup>+</sup> adducts from all by positive-ion ESI FTICR-MS (Bruker BioApex-IIe 7 T). DFT calculations were performed at B3LYP level using a 6-31G basis Gaussian 03.

**Results and discussion.** CID of triacylglycerides was successful on a FTICR spectrometer (Figure 1). This enables the identification of at least one fatty acid side

from triacylglycerides in complex lipid mixtures. The variation of the ion activation pulse length allows calculation of the energy of activation by measuring the on-set of fragmentation shown in figure 2 where E<sub>com(threshold)</sub> for tripalmitin by losing a palmitic acid molecule is 0.56 ± 0.01 eV. DFT modelling of the reaction mechanism is presented and measured activation energy compared with the calculated results.



**Figure 2** On-set of fragmentation of tripalmitin

1. McAnoy, A. M. et al. *J. Am. Soc. Mass Spectrom.* **2005**, 16, (9), 1498-1509.