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Research Article

Identification of Modified and Unmodified Lipophilic B-Diketones Using Electrospray Ionisation Mass Spectrum (Esi-Ms)

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Abstract

Identification of modified and unmodified lipophilic β-dketone was carried out successfully using positive ion mode of ESI-MS. The ESI-MS spectra were obtained using LC - Agilent 1260 Infinity with MS - Bruker micro OF time of flight MS in mass range of m/z 200-900, capillary voltage 4500V, nebuliser pressure 21.8 psi, dry gas flow 8L/min and dry gas temp 433K. Potassium adduct ion 503.4437m/z was found for the 14,16-Hentriacontanedione (Htd); whereas, the itaconate modified Htd (Ita) gave a confirmatory sodium species 645.5051m/z. The ion 589.4794 m/z was for potassium species of the singly added acrylate modified Htd (Mas). Meanwhile, the doubly added acrylate modified Htd (Mad) formed the potassium adduct ion of 675.5179m/z. However, protonated species for these molecules were not obtained.

Keywords: Electrospray ionisation mass spectrum (ESI-MS); Modified and unmodified lipophilic β-diketone

Introduction

Electrospray ionization mass spectroscopic technique (ESI-MS) has already been established as a powerful tool in the characterization of small and large molecules [1]. ESI concept was firstly introduced in 1968 by Dole [2]. It is a less energetic ionization technique, where a sample is protonated in gas phase to form cationic species; not radical (as is the case of impact ionization approach), [3] thus causing little or no fragmentation of the parent compound. It is pertinent to make do with ESI-MS because, in some cases, the column in GC is not suitable for detecting very high molecular weight organic compounds. Literature report has it that, ESI-MS method is reliable, robust and much less time consuming than the GC methods [4]. Importantly, ESI-MS is simple, fast, accurate, sensitive and straightforward technique for the analyzing compounds [5,6]. Alternative techniques for analyses of compounds such as NMR need further processing and requisite expertise to enable the identification of a compound.

Thus, the interfacing of electrospray ionization with modern mass spectrometers has been applied to estimating the molecular weights of many compounds [6]. It is useful to determine molecular weight of organic molecules even at femtomole level. Hence, Knepper [4] also reported electrospray mass spectrometry as a simple, sensitive and quick method for the determination of polar organic traces in water samples without derivatization. Electrospray ionization mass spectrometry was used to develop a rapid, sensitive and accurate method for determination and identification of hepatotoxic microcystins, cyanobacterial cyclic heptapeptides [5]. Poon [6] reported a simple, fast and sensitive way of identification of anticancer drugs and their analogues consisting of organic and organometallic compounds using ESI-MS. The studies suggested that ESI-MS is an effective technique for identification of organometallic and small organic compounds [6] Loss of fragments were observed from the ESI-MS spectra of the anticancer drugs. Kaltashov [7] investigated the structure, dynamics and function of metalloproteins with ESI-MS.

This method has also been used to identify major phenolic compounds present in strawberry fruits [8]. Sun [9] reported the application of ESI–MS in the identification of non-phenolic compounds in red wines as well. Phenolic compounds profile in wild edible greens was also detected with ESI-MS as reported by Barros [10] Identification of phenolic compounds in rapeseed meals were ascertained with ESI-MS [11]. In this studies, the molecular weight were predominantly detected in the form of $[M+H]^+$ [11]. ESI-MS was also applied successfully for the qualitative analysis of green tea extract [12]. Quantitative analysis of docetaxel in polymeric matrices of poly (lactide-co-glycolide) and poly (lactide-co-glycolide)- poly (ethylene glycol) nanoparticles has been reported using ESI-MS [13]. It was observed that there was more intense formation of $[M+H]^+$ than $[M+Na]^+$ [13]. In as much as ESI-MS has become a global method for qualitative and quantitative analyses, there are no literature on the ESI-MS analyses of lipophilic β-diketones and there derivatives. Hence, this paper reports the identification of 14, 16-hentriacontanedione (Htd), acrylate modified Htd (Ma) and itaconate modified Htd (Ita) for the first time.

Material and Methods

About 20 mg of each sample was prepared in methanol: water (1:1). Their ESI-MS spectra were obtained using LC - Agilent 1260 Infinity with MS - Bruker micrOTOF time of flight MS in mass range of m/z 200-900 positive ion mode, capillary voltage 4500V, nebuliser pressure 21.8 psi, dry gas flow 8 L/min and dry gas temp 433K. The following chemicals in Figure 1 whose ESI-MS spectra were studied were prepared and purified prior to these studies.

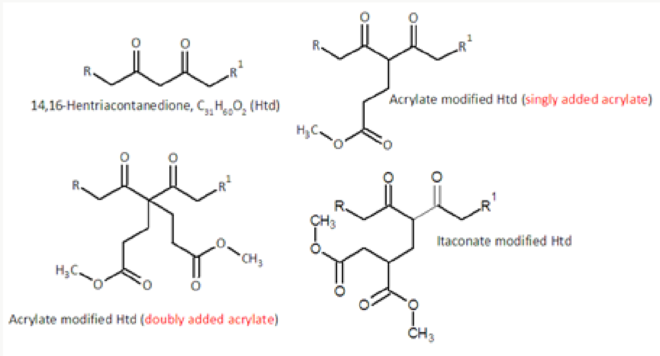

Figure 1: The lipophilic β-diketone and its derivatives.

Results and Discussion

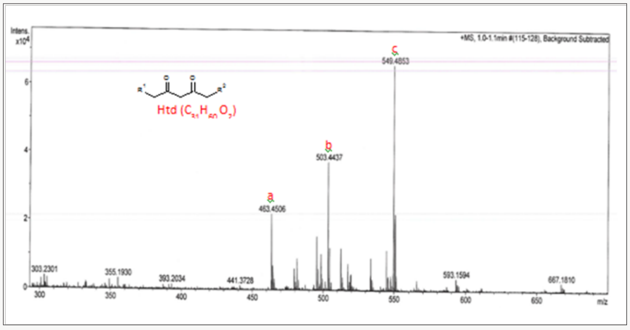

Figure 2: ESI-MS(+) for the Htd.

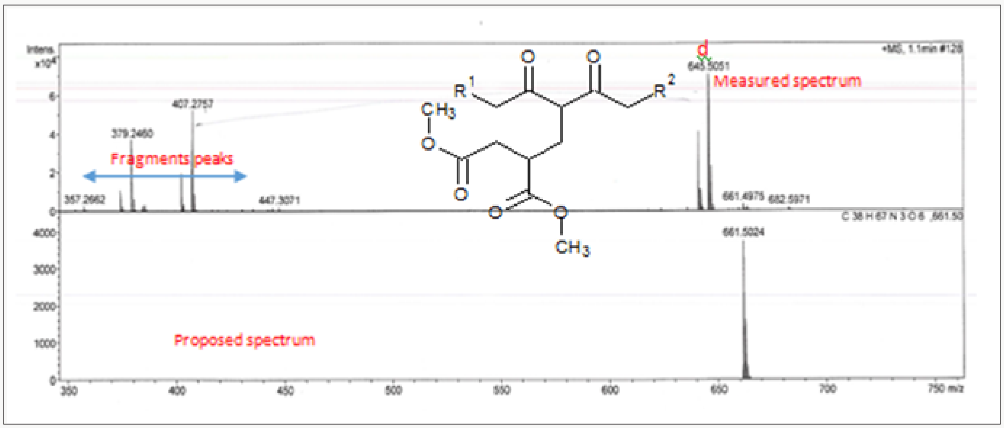

Figure 3: ESI(+)-MS of Ita.

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The unmodified Htd was firstly identified using the ESI-MS technique. Proton, potassium and copper adduct species of the Htd have been identified in the ESI-MS spectrum shown in Figure 2 and further described in Table 1 below. Copper is accounted for in this spectrum since it comes from the cuprous acetate used to isolate the long chain Htd. Aravindhan [14] reported Na species of the metal and azo-metals complexes of embelin in their ESI-MS analysis [14]. In a similar vein, the modified Htd were identified with this technique. The ESI (+)-MS of the itaconate modified Htd obtained is presented in Figure 3 and the peaks are interpreted/ assigned in Table 2. The ESI (+)-MS of this itaconate modified 14,16-hentriacontanedione (Ita) had minor peaks (i.e. less intense peaks), 407.2757 m/z and 379.2460 m/z in addition to the major sodium adduct peak, 645.5051m/z $(M+Na)^+$. The 407.2757 m/z ion is due to loss of 239 ($C_{16}H3_{10}$) from the product peak (645.5051m/z). However, if the loss of C16H31O occasioned from the parent molecule of Ita (622m/z), then 383m/z will be produced. This fragment 383 m/z would have combined with Na^+ to produce 407.2757m/z. Then, 379.2460m/z may have come from losses of 211 ($C_{15}H_{31}$) and 32 (MeOH) from the Ita (622m/z). Alternatively, loss of CO (28) from the 407.2757m/z ion could also form 379.2460m/z. Loss of CO in such compounds has been previously reported by Brent [15] see Figure 4 which describes the possible fragmentation pattern of the lipophilic β-diketone derivatives.

Table1: ESI-MS(+) interpretation of the Htd.

Sample	m/z peak	Interpretation
14,16-hentriacontanedione (C31H60O2)	464 (a)	[M]+
	503.4437 (b)	[M+K]+
	549.4853 (c)	[(Htd-Cu)+ + Na - H]+

Table 2: The major ESI-MS peaks and interpretation for the Ma and Ita.

Cationic species	Peaks (m/z)	Molecular weight	Interpretation	Cross Ref.
		464(M)	Htd	
[Ms + K]+	589.4794	550	singly added acrylate – Mas	Figure 5(c)
[Md + K]+	675.5179	636	doubly added acrylate – Mad	Figure 5(a)
[Md + Na]+	659.5216	636	doubly added acrylate – Mad	Figure 5(b)
[M + Na]+	645.5051	622	singly added of itaconate-Ita	Figure 3(d)

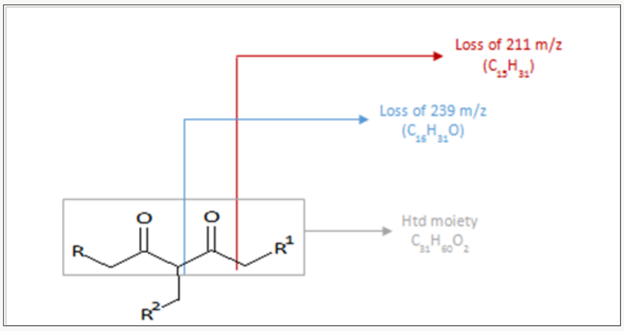

Figure 4: Proposed dissociation (fragmentation) of Htd derivatives as found in ESI-MS(+).

Similarly, sodium and potassium adducts were seen in the ESI-MS of the acrylate modified β-diketone (Ma) as presented in ESI-MS of Figure 5. The ESI (+)-MS spectrum of Ma had major peaks; 589.4794m/z and 675.5179m/z for potassium adducts of singly [Ms+K]+ and doubly $[Md+K]^+$ added acrylate products respectively; then 659.5216m/z as sodium species of doubly added methyl acrylate product. Please refer to Table 2 for detail descriptions. The minor peaks 421.2924m/z, 449.3213m/z and 479.2984m/z in the ESI-MS of the Ma are likely due to formation of these species; $[M_d\text{-}239+Na]^+$, $[M_d\text{-}211+Na]^+$ and [M_d- 239+2Na+K-2H]+. In all these spectra, protonated species $[M+H]^+$ common in ESI(+)- MS were absent as it has been similarly reported [16] Although other researchers have confirmed predominant formation of protonated species in such studies [11,13]. Furthermore, Ramaroson-Raonizafinimanana [17] had also observed similar fragmentation of such lipophilic β-diketones as it was found in the mass spectrum of 2,4-diketone silyl ether derivatives described in Figure 6. According to Leenheer [16] the ESI (+)-MS of fulvic acid has been shown to loss CO, COO, H_2O, carbon and proton. Furthermore, Brent [15] reported losses of COO (m/z 44), H_2O (m/z 18), CO (m/z 28) or combinations

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of losses CO and $_{H2}$O (m/z 46), COO and H_2O (m/z 62) in coupled IC/ESI-MS/MS characterization of branched aliphatic monoacids, branched and straight chain aliphatic diacids. These show that group of atoms could be lost even from soft ESI-MS technique. Thus in addition to the to the product peaks, 407.2757 m/z and 379.2460 m/z; 421.2924 m/z, 449.3213 m/z and 479.2984 m/z were observed in the Ita and Ma molecules respectively.

Figure 5: ESI (+)-MS of the Ma.

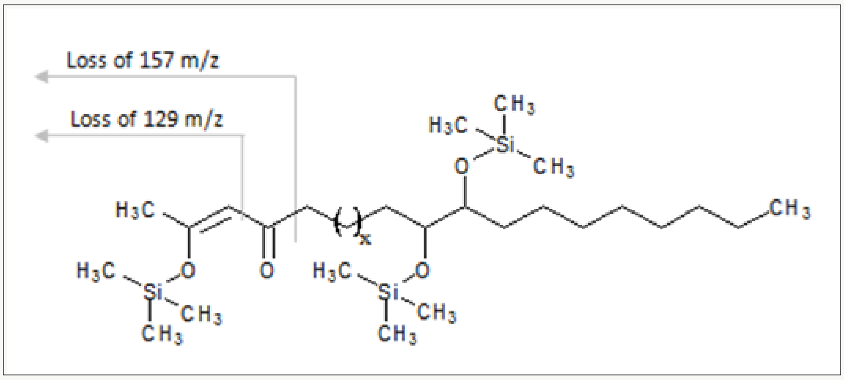

Figure 6: Fragmentation of long chain 2,4-diketone silyl ether derivatives.

Conclusion

Identification of modified and unmodified lipophilic β-dketone was carried out successfully using positive ion mode of ESI-MS. Potassium adduct ion 503.4437m/z $[M+K]^+$ was found for the 14,16-Hentriacontanedione (Htd); the itaconate modified Htd (Ita) gave a confirmatory sodium species 645.5051m/z $[M + Na]^+$. The ion 589.4794m/z $[Ms + K]^+$ was for potassium species of the singly added acrylate modified Htd (Mas). Meanwhile, the doubly added acrylate modified Htd (Mad) formed the potassium adduct of 675.5179m/z $[M_d+K]^+$. However, protonated species for these molecules were not obtained.

Acknowledgements

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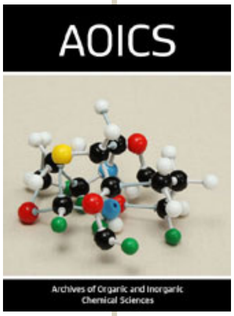

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