Research Open

Nanotechnology and Advanced Material Science

Volume 2 Issue 4

Opinion Article

# Structural Elucidation of Natural Polymeric Materials Treated by Ball Milling: A Mass Spectrometrist View

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**Received:** November 04, 2019; **Accepted:** November 20, 2019; **Published:** November 25, 2019

It is well known to synthetic organic chemists that ball milling can be used for the synthesis of new compounds [1]. On the other hand, it is well known that ball milling of complex natural materials such as lignin and pollen grains can lead to alteration of their original structure and may produce new compounds that originally do not exist [2]. For example, Milled wood Lignin (MWL) contains more hydroxyl groups than the native one due to the extensive depolymerization during the ball milling process [2]. The presence of more hydroxyl groups indicated the homolytic bond cleavage between lignin monomers, which in turn produce reactive radicals that can create new compounds [2].

It is well known that sporopollenin is composed of carbon, hydrogen, and oxygen in the form of a cross-linked polymer that is amazingly stable [3]. It makes up the outer wall of pollen grains, and when extracted it is in the form of an empty exine or microcapsule [3]. During the late past century sporopollenin exine resistance against chemical treatments has been well documented [3]. It was found that the rigidity of sporopollenin restricted its practical analytical analysis to a limited number of techniques, such as Fourier transform infrared (FTIR) spectroscopy and analytical pyrolysis combined with gas chromatography–electron ionization-mass spectrometry (GC–EI-MS) [4,5]. Based on those outdated and old studies, there is still the belief that sporopollenin contains an aromatic identified as *p*-coumaric acid and, to a lesser extent, ferulic acid [4,5]. Some recent studies, which still champion this outdated theory was published in nature plants implying a resemblance between sporopollenin and lignin. In this study, Li *et al.*[6] reported the structure elucidation of sporopollenin extracted from ball-milled pollen grains. It should be noted that in 1966, Gordon Shaw, one of the earliest pioneers in sporopollenin, withdraw his proposal that sporopollenin contains lignin because it does not give any positive test for lignin's [7].

Needless to say that the pollen grain contains proteins and genetic material that is enclosed by the intine composed of carbohydrates followed by the exine composed of sporopollenin [8]. Logically, high energy ball milling of the pollen grains could produce new artefactual compounds through the reaction between all these pollen grains components together, which in turn could alter the structure of the studied target material sporopollenin.

The effect of ball milling on the structure of these complex natural polymeric biomaterials is perhaps comparable to using specifically pyrolysis GC-MS for their structural analysis [9,10]. Pyrolysis GC-Ms can lead to the identification of compounds that initially does not exist in your sample [9,10]. As an example, pyrolysis GC-MS of unsaturated fatty acids leads to the production of aromatic compounds and, even linear saturated polymers such as polyethylene can produce aromatics during pyrolysis GC-MS analysis [9,10]. Overall, as a mass spectrometrist, firstly, it is recommended to avoid any procedures that could alter the structure of these complex natural materials before using any mass spectrometric techniques for structure elucidation and/or sequencing purposes. Secondly, using soft ionization methods such as electrospray ionization (ESI-MS) and matrix-assisted laser desorption/ionization (MALDI-MS) is more advantageous than pyrolysis GC-MS. The use of these soft ionization methods allows the analysis of the native form of these complex materials without any alteration in their structure that could lead to misleading results [4,5,9,10]. We are in the process of reporting new finding on the structure of the hollow empty clean sporopollenin exine using state of the art analytical experiments, such as high-resolution X-ray-photoelectron spectroscopy, TOF-SIMS, TOF-SIMS, MALDI-TOF-MS, OF-SIMS (FIB) MALDI-Tandem Mass spectrometry analysis and Solid-State $^{1}$H and $^{13}$C-NMR (1D and 2D experiments) [11]. We can state that sporopollenin exine does not contain any aromatics and bear no resemblance to lignin [11].

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**Citation:**
Joseph Banoub, Abanoub Mikhael (2019) Structural Elucidation of Natural Polymeric Materials Treated by Ball Milling: A Mass Spectrometrist View. *Nanotechnol Adv Mater Sci* Volume 2(4): 1–2.