***Supplemental File A: Analytical Methods***

***Instrumentation:*** The analytical methodology is same as reported in Avula, 2019. [1] The liquid chromatographic system is an Agilent Series 1290 and the mass spectrometric analysis was performed with a QToF-MS/MS (Model #G6530A, Agilent Technologies, Palo Alto, CA, USA) equipped with an ESI source with Jet Stream technology. All the operations, acquisition and analysis of data were controlled by Agilent MassHunter Acquisition Software Ver. A.01.00 and operated under MassHunter Workstation software Ver. B.02.00. Each sample was analyzed in both positive and negative modes to provide abundant information for structural identification. Mass spectra are recorded across the range *m/z* = 100-1700 with accurate mass measurement of all mass peaks. Accurate mass measurements of each peak from the total ion chromatogram (TIC) were obtained by means of an automated calibrate delivery system using a dual-nebulizer ESI source that introduces a low flow (100 µL/min) of a calibrating solution (calibrant soltion A, Agilent Technologies), which contains the internal reference masses at *m/z* 121.0509 and 922.0098 in positive ion mode, while at *m/z* 112.9856 and 1033.9881 in negative ion mode. The compounds were confirmed in extracted ion chromatogram (XIC) mode. MassHunter Workstation software, including Qualitative Analysis (version B.07.00), was used for processing both raw MS and MS-MS data, including molecular feature extraction, background subtraction, data filtering, and molecular formula estimation.

MassHunter Qualitative Analysis software (Agilent Technologies, Santa Clara, CA, USA) was used for the initial data processing of the raw LC-QToF data. The data was acquired from methanolic extracts in both positive and negative ion modes, respectively, over the range of *m/z* 100-1300. The raw data were processed using the Find by Molecular Feature (MF) algorithm called Molecular Feature Extractor (MFE) within MassHunter Qualitative Analysis software. Extracted molecular features were processed to create a list of compounds.

A compound search for the non-targeted compounds were characterized by matching the experimental molecular formula in an [1] The Agilent MassHunter Forensics and Toxicology (8998 components) Personal Compound Database (PCD) [2] In-House generated library for 11000 components of medicinal plant samples. [3] In-House generated library for 65 components of ED [4] In-House generated library for 261 components of steroids/anabolic steroids. Other search engines included SciFinder (web-based version), Dictionary of Natural product (CRC, 2020), and google search engines by molecular formulae were used for the identification of “known unknowns.” These approaches have been utilized to identify a wide range of components, including additives, compounds from natural products, etc. In-house library includes the compound name, molecular formula, exact mass, CAS #, and structure of each compound. From the possible positive hits, the results were compared with MS-MS experiments and to those available in literature. All compounds either generated a high-abundance [M-H]− ion in negative mode or a high-abundance [M+H]+ ion in positive mode, therefore, the [M-H]− or [M+H]+ ions of each compound were selected as the precursor ions for subsequent MS-MS experiments to give more fragment ions. The generation of diagnostic fragment ions provided information concerning the core skeleton and nature of the substituents.

1. Avula B, Chittiboyina AG, Bae JY, et al. The power of hyphenated chromatography-Time of flight mass spectrometry for unequivocal identification of spirostanes in bodybuilding dietary supplements. Journal of pharmaceutical and biomedical analysis. 2019 Apr 15;167:74-82. doi: 10.1016/j.jpba.2018.12.045. PubMed PMID: 30753977; eng.