Digging of Phytochemicals using Mass Spectrometric Machines

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Historically Important Natural Products from Plants

**Quinine**
Anti-malarial
*Cinchona succirubra* Pav.
Isolation: 1820, Pelletier et al.
Synthesis: 1944, Woodward

**Morphine**
Painkiller
*Papaver somniferum* L.
Isolation: 1806, Sertürner
Synthesis: 1954, Ginsberg

**Arteether**
Antimalarial drugs
*Artemisia annua*

**Salcin**
*Salix alba* L.
Structure and synthesis: 1906, Irvine

**Paclitaxel (Taxol®)**
Breast cancer drug
*Taxus brevifolia*
Isolation: 1971, Wani et al.

**Strychnine**
Pesticide
*Strychnos nux-vomica*
Isolation: 1818, Pelletier et al.
Synthesis: 1954, Woodward
Historically Important Natural Products from Plants

1. **Prostratin**
   - Used for the treatment of (AIDS)
   - *Homalanthus nutans*

2. **(-)-Littoralisone**
   - Neurotrophic Growth Factor
   - *Verbena littoralis L*
   - Isolation and structure: 2001, Li
   - Synthesis: 2005, Mangion

3. **Dynemicin A**
   - Antibiotic
   - *Micromonospora chersina*
   - Structure: 1989, Matsumoto et al
   - Synthesis: 1991, Nicolau

4. **(+)–Absinthin**
   - Anti-inflammatory Agent
   - *Artemisia absinthium L*
   - Isolation: 1953, Herout
   - Synthesis: 2004, Zhang

5. **Cocaine**
   - Appetite Suppressant
   - *Erythroxylon coca*
   - Isolation: 1859, Niemann
   - Synthesis: 1923: Willstätter

6. **Ephedrin**
   - Decongestant
   - *Ephedra equisetrina*
   - Structure and synthesis: 1920, Späth and Göring
LDI Analysis of Plant Powdered Materials

Solvent Effect: LDI-MS Analysis

Figure 1. Graph between solvents of various polarities (decreasing order) and the intensity of TOF-MS ions of selected withanolides found in *Withania somnifera* leaf.

Solvent Effect: SEM Analysis

Figure 2. SEM Images of *Withania somnifera* plant material passed through 50 μm mesh sieves treated with different solvents

Effect of Plant Parts: SEM Analysis

Figure 3. SEM Images of ≤50 μm mesh particles of various parts of *Withania somnifera* treated with CHCl₃ solvent.

Effect of Plant Particle Size

Figure 7. Microscopic images of MALDI plate spotted with Withania somnifera plant material after passing through sieves of different mesh sizes.

Screening of various Plants Species

**Fig.**: TOF-MS Spectra of selected plants screened after treatment with different solvents.

Fig: TOF-MS Spectra of selected plants screened after treatment with different solvents.

Characterization of Plant Metabolites

Fig. A) MALDI-TOF-MS spectrum of *Nicotiana tabacum* leaves powder. B) Product ion spectrum of ion at $m/z$ 163. C) Product ion spectrum of nicotine standard solution.

Characterization of Plant Metabolites in various Plants Species

<table>
<thead>
<tr>
<th>No.</th>
<th>Observed m/z</th>
<th>Adduct ion</th>
<th>Plant analyzed</th>
<th>Proposed Metabolite</th>
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<tbody>
<tr>
<td>1</td>
<td>163</td>
<td>H^+</td>
<td><em>Nicotiana tabacum</em></td>
<td>Cotinine</td>
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<tr>
<td>2</td>
<td>177</td>
<td>H^+</td>
<td><em>Nicotiana tabacum</em></td>
<td>Nicotine</td>
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<td>3</td>
<td>493</td>
<td>Na^+</td>
<td><em>Withania coagulans</em></td>
<td>Coagulin R/ Coagulin J</td>
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<tr>
<td>4</td>
<td>463</td>
<td>H^+</td>
<td><em>Physallis minima</em></td>
<td>Withaphysalin A/ Withaphysalin D</td>
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<tr>
<td>5</td>
<td>165</td>
<td>H^+</td>
<td><em>Ricinus communis</em></td>
<td>Recinine</td>
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<tr>
<td>6</td>
<td>303</td>
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<td><em>Ricinus communis</em></td>
<td>19-Hydroxy-3,7,11-casbatrien-5-one</td>
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<tr>
<td>7</td>
<td>339</td>
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<td><em>Catharanthus roseus</em></td>
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<tr>
<td>8</td>
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<tr>
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<td>809</td>
<td>H^+</td>
<td><em>Catharanthus roseus</em></td>
<td>Vincathicine/ Leurosine</td>
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<td>10</td>
<td>393</td>
<td>Na^+</td>
<td><em>Nerium oleander</em></td>
<td>Δ^{16}-Dehydroadynerigenin</td>
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<tr>
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<tr>
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<tr>
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<td>474</td>
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<td><em>Datura alba</em></td>
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<tr>
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<td>Daturametelin J</td>
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<td><em>Buxus papillosa</em></td>
<td>Buxanoldine</td>
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Laser Desorption Ionization Method for Plant powder analysis

- LC-ESI-MS/MS analysis

- Quantitative Analysis based on LC-MS/MS analysis