# Biodiesel Fuel from Connecticut Oilseed


**Walter J. Krol, PhD**

**Department of Analytical Chemistry**

**The Connecticut Agricultural Experiment Station**

**(203) 974-8456**

**Walter.krol@po.state.ct.us**


**Connecticut Agricultural Experiment Station:**
http://www.ct.gov/caes

**Connecticut DEP Biodiesel Links:**
http://ct.gov/dep/cwp/view.asp?a=2708&q=323870&depNav_GID=1763

**Making Biodiesel Online Tutorial:**
http://www.biodieselcommunity.org/makingasmallbatch/

# Biodiesel Fuel

- Recycling of used waste vegetable oils UCONN – Dorm Fryers to Transportation

- Renewable resource from oilseed crops such as canola, soybean, sunflower, castor bean and flax
- Triglyceride oils converted to fatty acid methyl esters

Environmentally Friendly

Reduce $CO_2$, CO, S, N and soot emissions

- High temperature / pressure catalytic de-polymerization of animals, plastics, oils

www.caes.state.ct.us

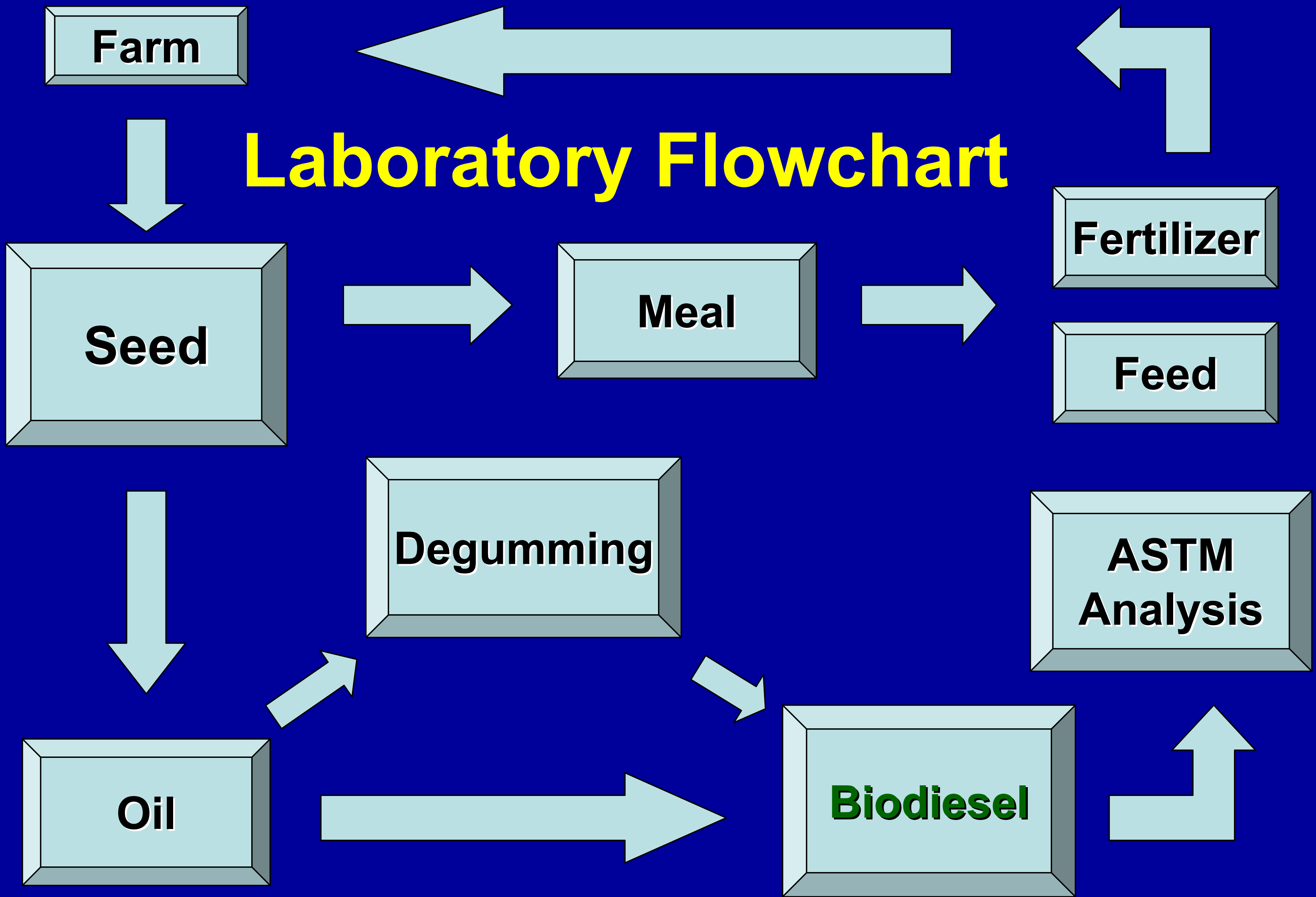
# Original Project and Goals (Spring 2006)

- In 2006, canola and soybean cultivars grown to evaluate their adaptability to Connecticut
  - Fall harvest – conventional farming
  - Spring harvest – over wintering (European)
- Seed and oil yield and quality to be determined and oil will be used to produce biodiesel fuel
- Meal to be evaluated for use as fertilizer or feedstock

Added Value Extra's (Integrated Pest Management):

- Canola contains glucosinolates which breakdown to isothiocyanates (fungicide / nematacide)
- Soybeans are legumes which fix nitrogen to the soil

# Laboratory Flowchart




www.caes.state.ct.us

# 2006 Field Studies (Feedstock)

- 2006 Crops grown at Lockwood and Windsor farms

## Canola

| | lb/acre | bu/acre |
|---|---|---|
| Hyola 357 Magnum | 1356 | 22.6 |
| Dekalb 38-25 | 1319 | 22.0 |

## Soybean

| | lb/acre | bu/acre |
|---|---|---|
| 6193 RR 1-9 Maturity | 3695 | 61.6 |

Valley Labs
Windsor, CT
Crop Yields

# Whole Seed Characterization

| | Canola | | | | Soybean |
|---|---|---|---|---|---|
| | Lockwood | | Windsor | | Windsor |
| | Dekalb | Hyola | Dekalb | Hyola | 6193 RR |
| **% Oil** | **29.5** | **28.7** | **28.4** | **25.5** | **10.2** |
| **% Nitrogen** | **3.1** | **3.0** | **3.4** | **3.4** | **6.6** |
| **% Protein** | **19.4** | **18.7** | **21.2** | **21.6** | **41.5** |
| **% Fiber** | **30** | **24** | **24** | **27** | **8.3** |
| **% Moisture** | **6.8** | **6.2** | **9.2** | **8.3** | **7.6** |

# Oil (Feedstock) Extraction

## Täby Type 20 oilseed press (Electrolux®)

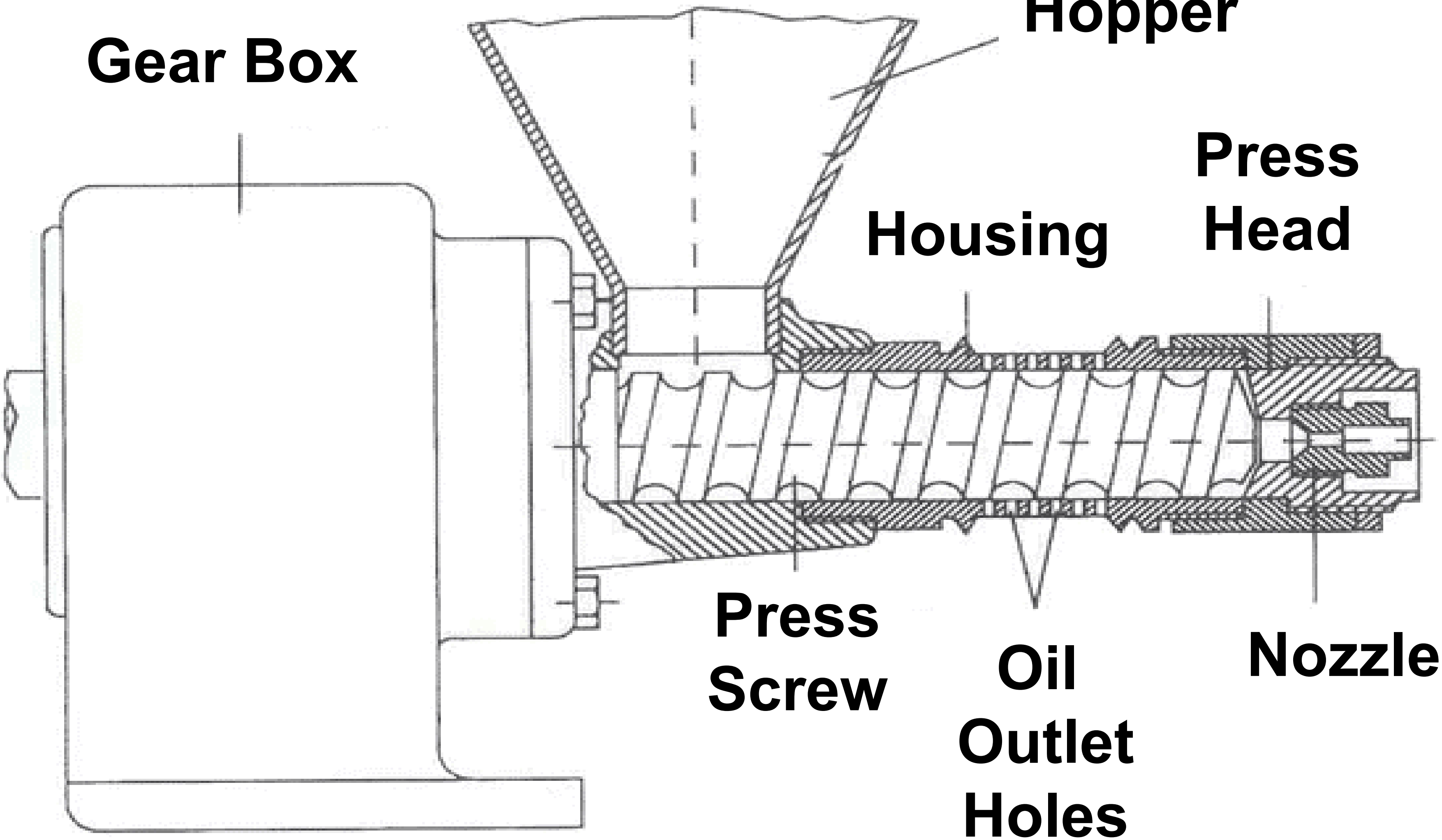
| Canola | Wt % Oil |
|---|---|
| Hyola 357 Magnum | 28.7 |
| Dekalb 38-25 | 28.4 |
| **Soybean** | |
| 6193 RR 1-9 Maturity | 10.2 |


Hyola 357 Magnum (1356 * 0.287) / 7.7 lb/gal = 50.6 gal/acre
Dekalb 38-25 (1319 * 0.284) / 7.7 lb/gal = 47.0 gal/acre

6193 RR 1-9 Maturity (3695 * 0.102) / 7.7 lb/gal = 49.0 gal/acre

www.caes.state.ct.us

# Schematic View of Oil Press



# Seed Oil Pressing Components

# Meal Byproduct

| | Canola | | | | Soybean |
|---|---|---|---|---|---|
| | Lockwood | | Windsor | | Windsor |
| **Fertilizer value:** | Dekalb | Hyola | Dekalb | Hyola | 6193 RR |
| % Nitrogen | 4.4 | 3.7 | 4.4 | 4.7 | 6.8 |
| % Phosphorous | 1.2 | 0.9 | 2.2 | 1.3 | 0.7 |
| % K, Potassium | 1.8 | 1.2 | 1.8 | 1.5 | 2.3 |
| **Feed value:** | | | | | |
| % Protein | 27.4 | 23.4 | 27.2 | 29.3 | 48.1 |
| % Fat | 14 | 17 | 16 | 15 | 1.4 |
| % Fiber | 13 | 18 | 12 | 12 | 3.8 |

- **High Protein / Low Fat & Fiber Desirable**

# Vegetable Oil Characterization

- Six metals with ASTM Biodiesel specifications

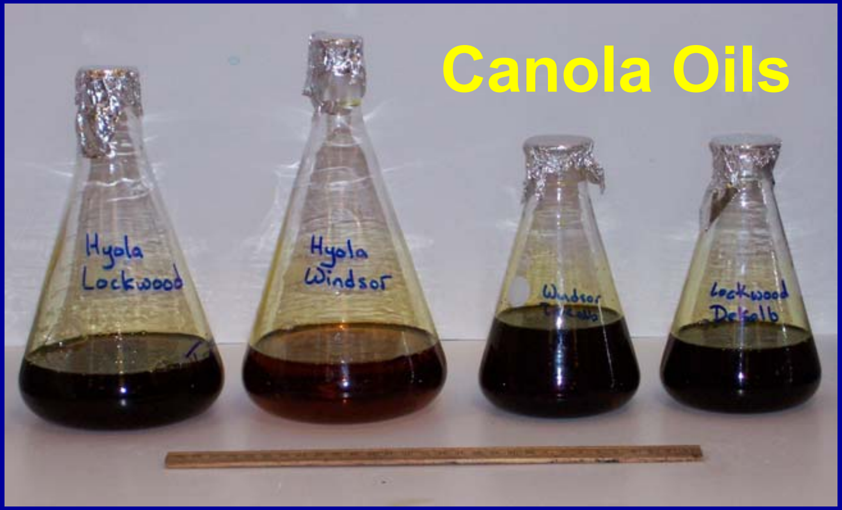
All values in mg/kg (ppm)

| | | Canola | | | | Soybean |
|---|---|---|---|---|---|---|
| | | Lockwood | | Windsor | | Windsor |
| | | Dekalb | Hyola | Dekalb | Hyola | 6193 RR |
| Na | Sodium | <2 | <2 | <2 | <2 | <2 |
| K | Potassium | <40 | 125 | 265 | <40 | 26 |
| P | Phosphorous | 51 | 300 | 601 | 30 | 182 |
| S | Sulfur | 9 | 7 | 8 | 6 | <6 |
| Mg | Magnesium | 13 | 57 | 180 | 9 | 26 |
| Ca | Calcium | 47 | 95 | 316 | 27 | 30 |

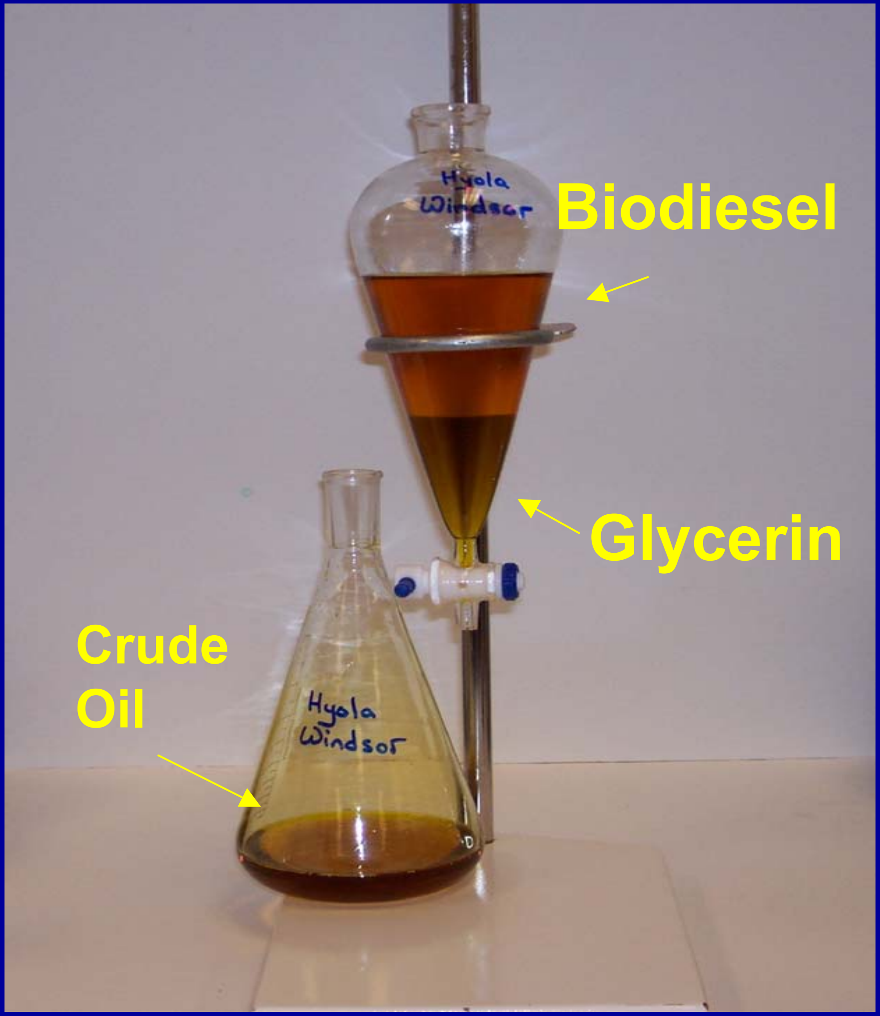
ASTM – American Society for Testing and Materials

www.caes.state.ct.us

# Laboratory Hydrolysis

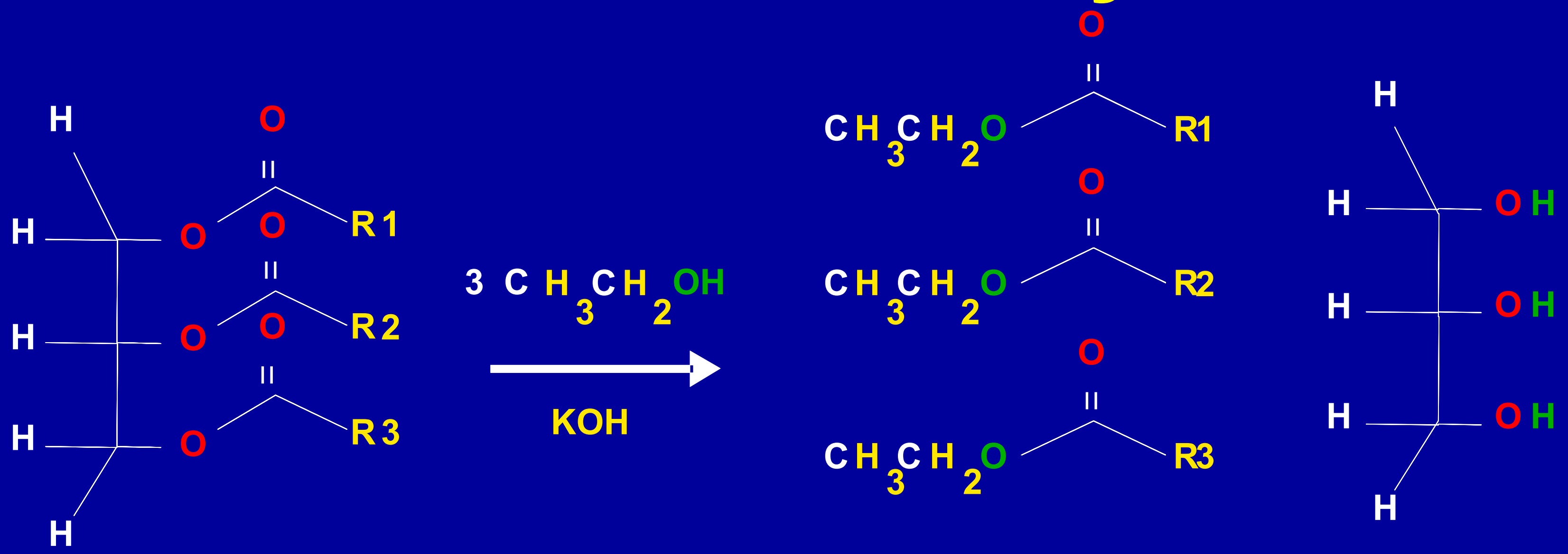







www.caes.state.ct.us

# Oil Chemistry




| | R= | Canola | Soybean | Sunflower |
|---|---|---|---|---|
| Unsaturated | | | | |
| **Palmitic** | C16:0 | 4 | 11 | 7 |
| **Stearic** | C18:0 | 2 | 4 | 5 |
| Monounsaturated | | | | |
| **Oleic** | C18:1 | 62 | 24 | 19 |
| Polyunsaturated | | | | |
| **Linoleic ω6** | C18:2 | 22 | 54 | 68 |
| **alpha Linoleic ω3** | C18:3 | 10 | 7 | 1 |

www.caes.state.ct.us

# ICP AES (ASTM D4951)

- Current ASTM method is used only for Phosphorous analysis

- We intend to analyze:
  - Phosphorous P
  - Magnesium Mg
  - Calcium Ca
  - Sodium Na
  - Potassium K
  - Sulfur S

  and study other metals


- Corrosive to engine parts; detrimental to environment

# ASTM Critical Metals (mg/kg)

| | Na | K | Mg | Ca | P | S |
|---|---|---|---|---|---|---|
| Limit | Combined Na / K = 5 | | Combined Mg / Ca = 5 | | 10 | 15 |
| Lockwood Soil | | 516 | 2589 | 1977 | 1164 | 146 |
| Windsor Soil | | 412 | 1783 | 1458 | 989 | 87 |
| **Canola** | | | | | | |
| Harvested Seed | <4 | 11832 | 4627 | 4535 | 8737 | |
| Seed Cake | | 15698 | 5792 | 4838 | 12203 | |
| Oil | <2 | 19 | 18 | 69 | 72 | <40 |
| Biodiesel | <2 | 25 | 9 | 54 | <3 | <40 |
| **Soybean** | | | | | | |
| Harvested Seed | <4 | 18720 | 3539 | 3119 | 6189 | 3161 |
| Seed Cake | <4 | 21261 | 3918 | 3319 | 7702 | 3775 |
| Oil | <2 | 62 | 17 | 38 | 137 | <40 |
| Biodiesel | <2 | 6 | <2 | 16 | <3 | <40 |

*Blank spaces denote NDA*

www.caes.state.ct.us

# Oilseed Crops – IPM Research

-Identify high yielding high oil content cvs.
- adapted soybean, canola, millets

-Value-added meals, soil quality, pest mgmt.

-Winter canola / rapeseed crops.
- reduce host effect, increase IPM efficacy.
- better fit for growers, double crop?

# Oilseed Crops – IPM Research

## ~120 glucosinolates (30 - 40 in *Brassica* spp.)

-Develop profiles for cultivars, plants vs meals.

-Activity vs pathogens, nematodes & weeds.

-Compare to discover type and amount of glucosinolate(s) associated with efficacy.

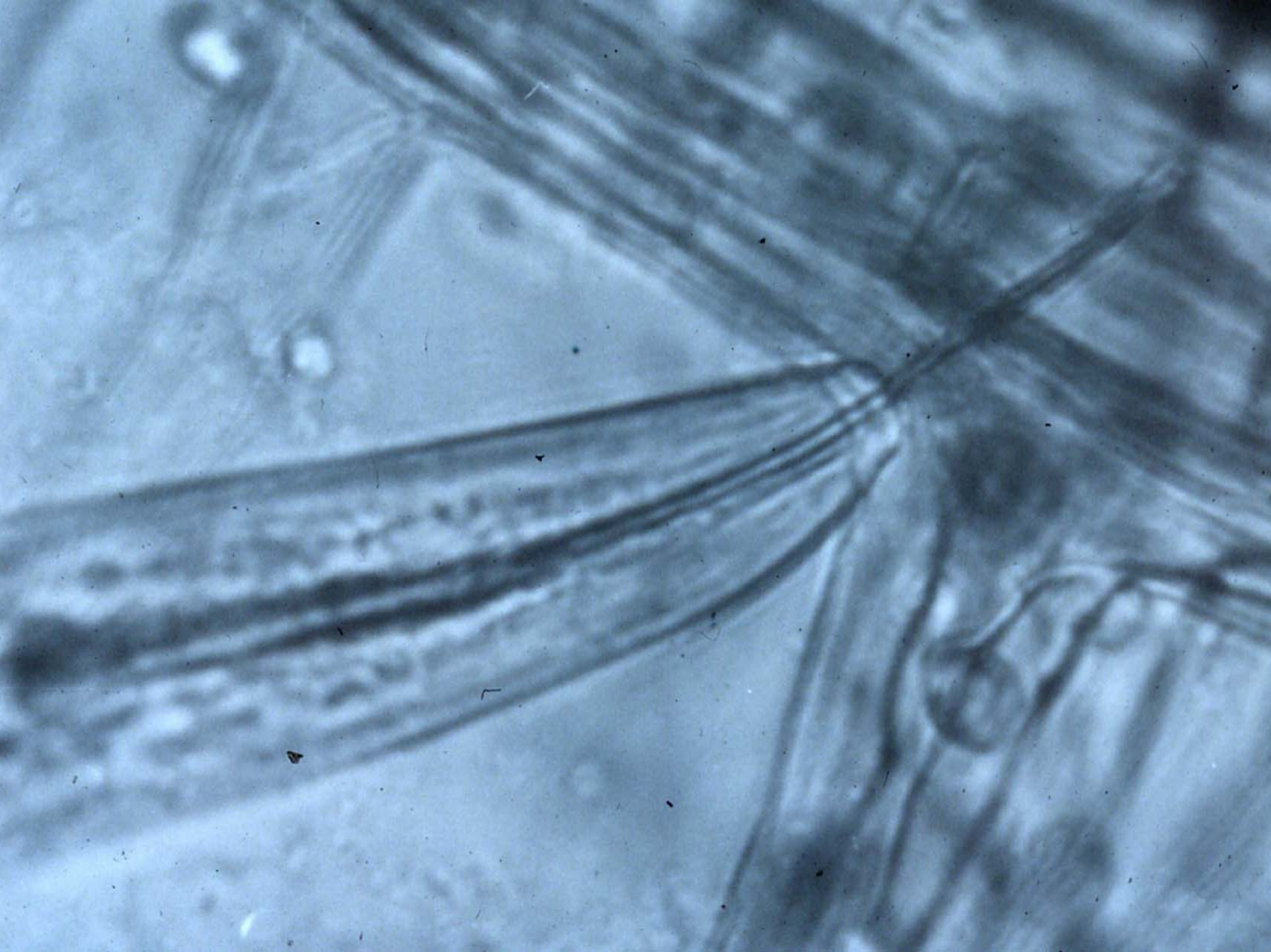
-Necessary for breeding and bioengineering.

# Plant parasitic  Nematodes

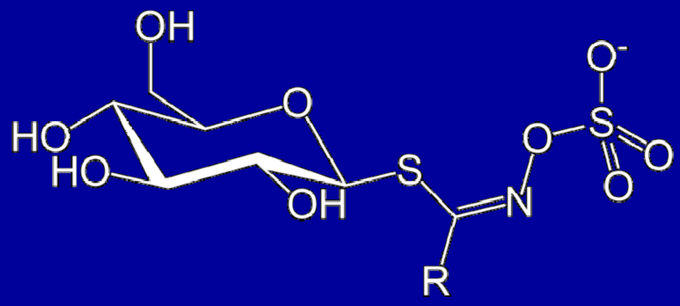
Lesion: *Pratylenchus* spp.

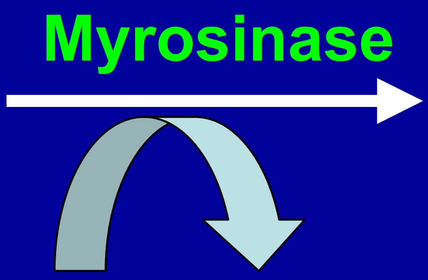
Root-Knot: *Meloidogyne hapla*

Dagger: *Xiphinema* spp.



# Glucosinolates (*Brassica*)




R–N=C=S
Isothiocyanates

R–S–CN
Thiocyanates

R–CN
Nitriles

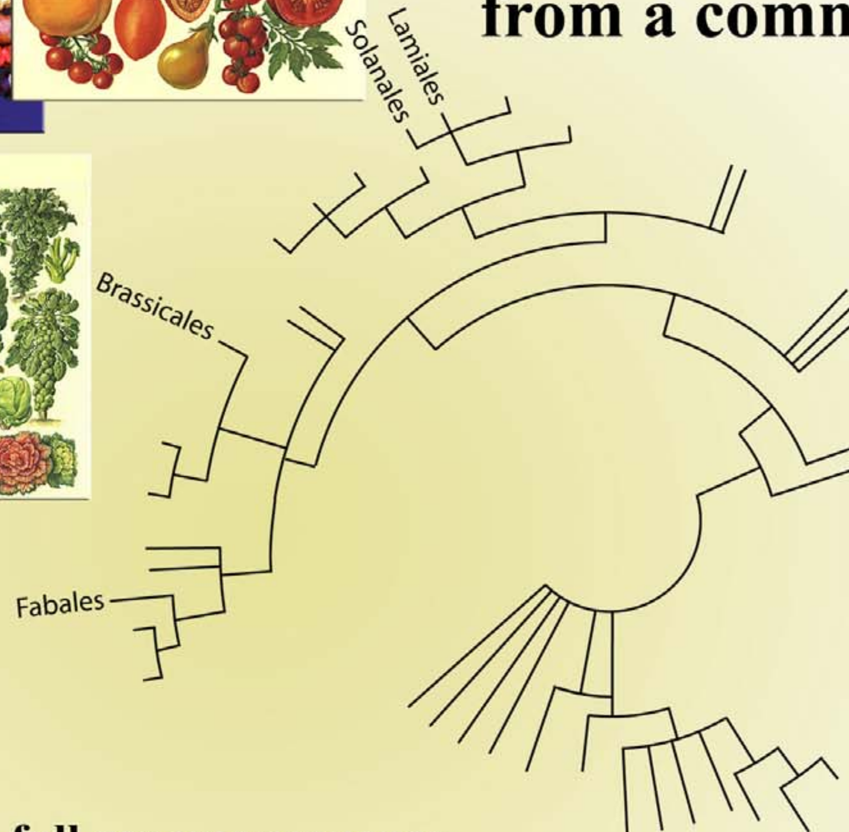
R = varied

Required stabilized cation for thiocyanates

- Glucosinolates are sulfur-rich, anionic natural products
- Amino acid derived *via* amino acid aldoximes
- Hydrolysis by myrosinases yield different products
- Products are defense compounds & attractants
- Humans take advantage of cancer-preventing agents, biopesticides, flavor compounds
- Each species produces 30 – 40 different

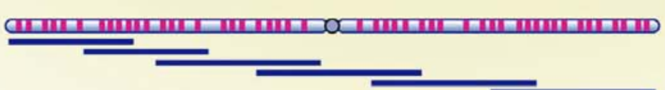
www.caes.state.ct.us

# Flowering plants evolved from a common origin

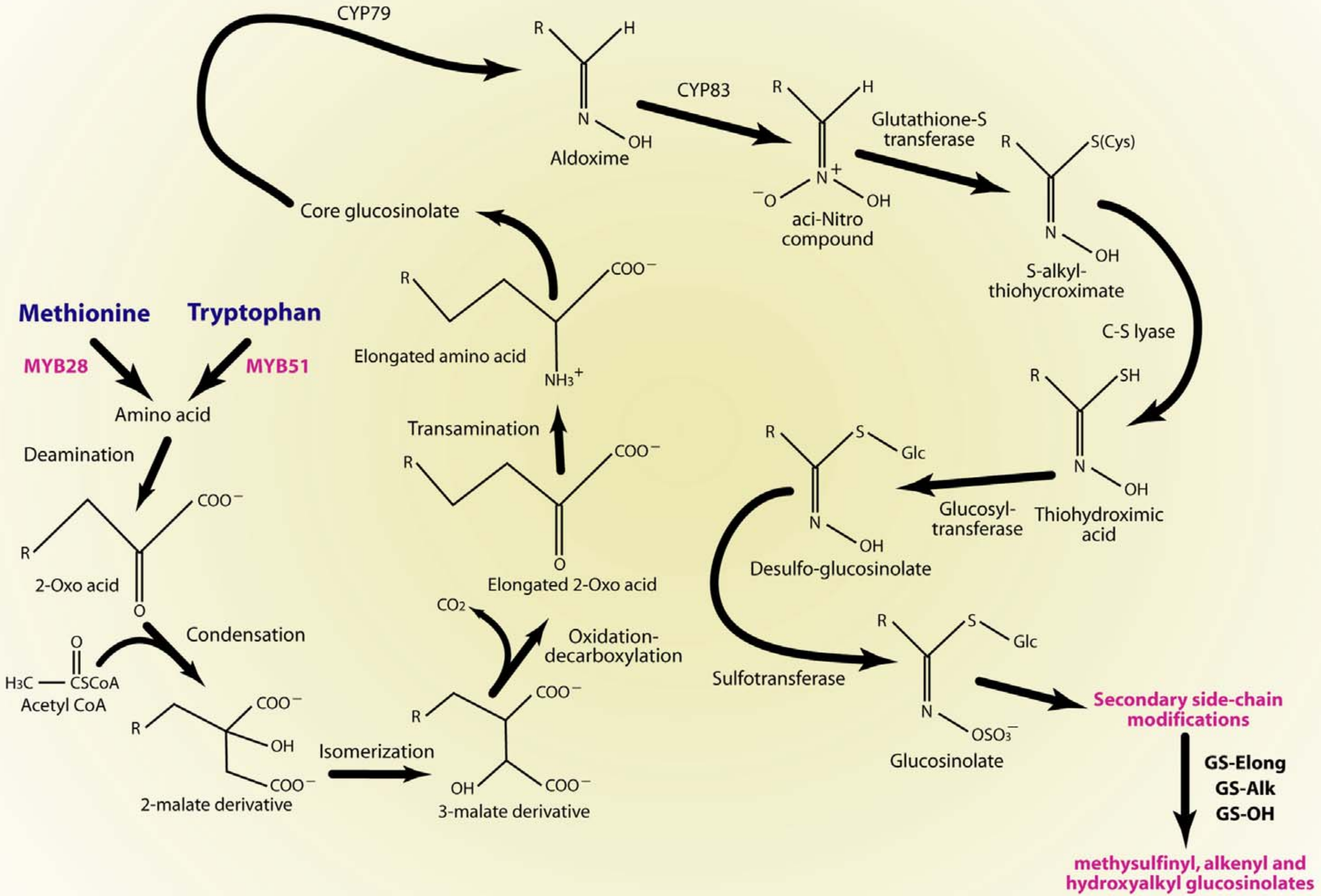



*Arabidopsis thaliana*

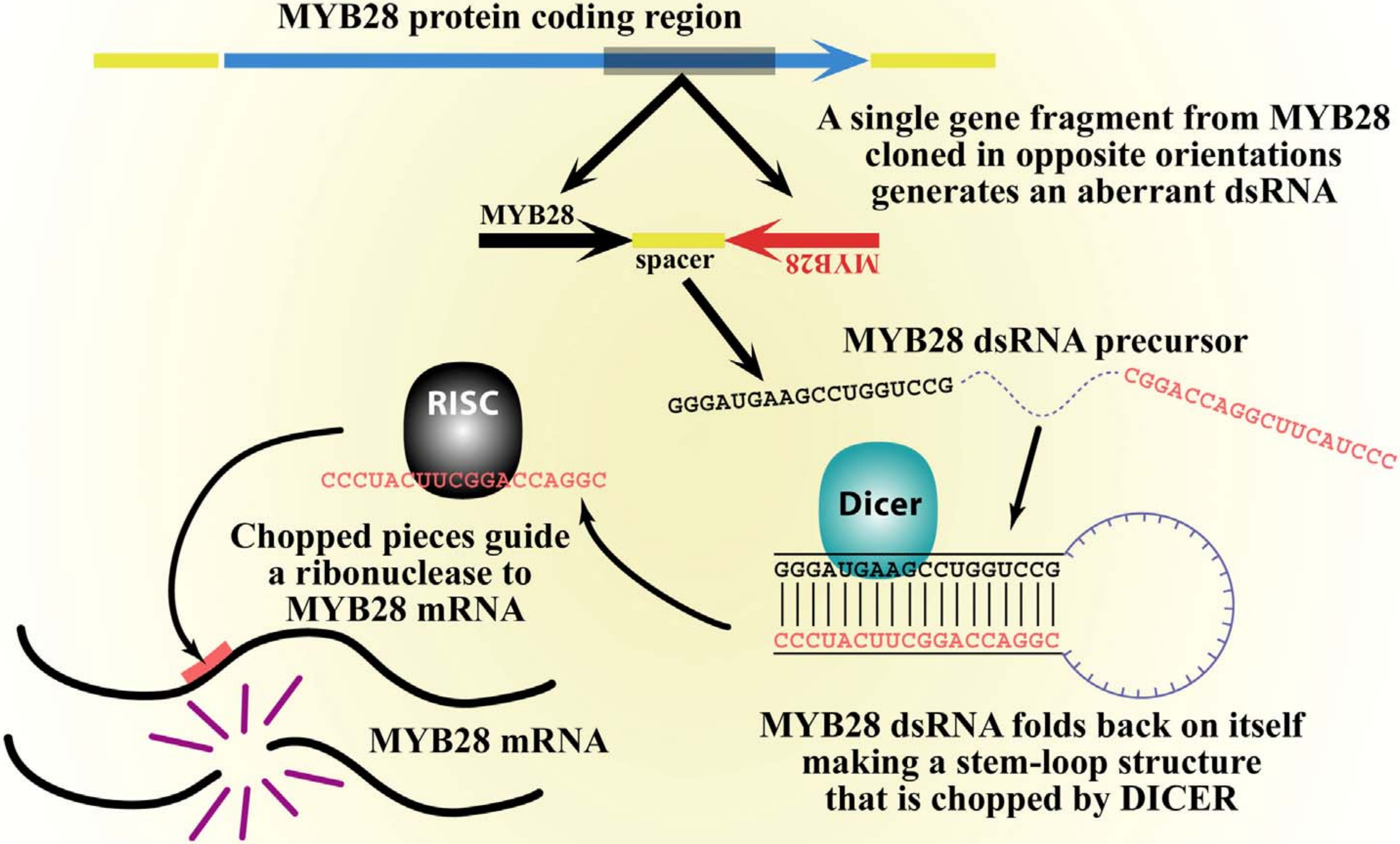
**The full genome sequence in *Arabidopsis* is a direct avenue to isolation of genes in *Brassica napus***

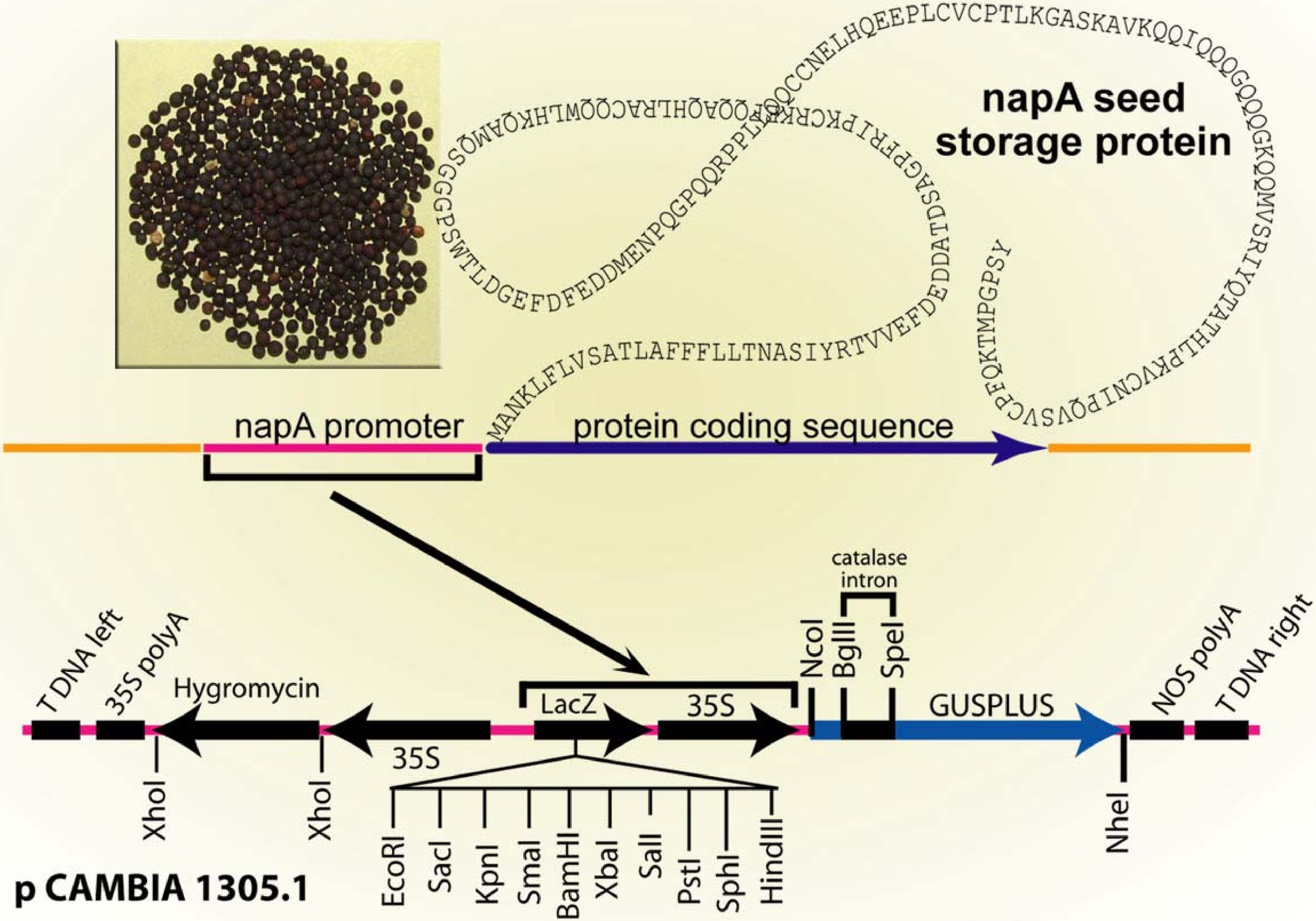
# Biosynthesis of Glucosinolates



# Silencing Expression of MYB28



# Altering Gene Expression Patterns in *Brassica napus* seeds



# 2005 – Connecticut Planting Statistics:

- **4,200 Farms Averaging 86 Acres**
- **360,000 *Total* Acres in Farms** (*Incl. Livestock Farms*)
- **Planted 271,430 Acres**

| Commodity | Harvested Acres | Yield/ Acre | Production Totals | Price | Value ($) |
|---|---|---|---|---|---|
| Hay All (*dry*) | 63,000 | 1.9 t | 118,000 t | 162 $/t | 19,153,000 |
| Hay Other (*dry*) | 55,000 | 1.8 t | 99,000 t | 157 $/t | 15,543,000 |
| Tobacco (*All*) | 2,430 | 1,674 t | 4,067,000 lb | 5.85 $/lb | 15,356,000 |
| Binder | 1,500 | 1,750 lb | 2,625,000 lb | | |
| Wrapper | 930 | 1,550 lb | 1,442,000 lb | | |
| Hay Alfalfa (*dry*) | 8,000 | 2.4 t | 19,000 t | 190 $/t | 3,610,000 |
| Silage Corn | 26,000 | 20 t | 52,000 t | | |

**117,000 All Purpose Acres** **(Grain Corn – 28,000)**
**(Alfalfa and Mixture – 2,000)** **(Field Crops/ Misc. – 87,000)**

www.caes.state.ct.us

*Source: USDA National Agricultural Statistics Survey*

# Connecticut Fuel Consumption

## Total Energy 888,663 billion BTU 0.9% (2003)

| | Barrels | US% | Period |
|---|---|---|---|
| ➢ Total Petroleum | 86,141,000 | 1.1 | 2004 |
| Gasoline | 43,740,000 | 1.3 | 2004 |
| Distillate Fuel | 28,850,000 | 1.9 | 2004 |
| Jet Fuel | 2,382,000 | 0.4 | 2004 |
| LPG | 3,057,000 | 0.4 | 2004 |
| Other | 8,112,000 | | |

1 barrel = 42 gallons

| | | | |
|---|---|---|---|
| ➢ Ethanol in Gasohol | 20,478,000 gal | 0.7 | 2003 |
| ➢ Natural Gas | 162,642,000,000 cf | 0.7 | 2004 |
| ➢ Coal | 2,076,000 st | 0.2 | 2005 |

*Energy Information Administration*
*http://www.eia.doe.gov*

# Economics

- Assume we plant *ALL* 360,000 acres of CT farmland with oilseed crop; 100% crop yield; 50 gallons oil / acre

| | Gallons | Barrels |
|---|---|---|
| ➢ Theoretical CT Yield | 18,000,000 | 428,572 |
| ➢ 2004 CT Distillate Fuel use | 1,211,700,000 | 28,850,000 |
| | 1.5% of CT Oil / Diesel Needs | |

- In 2005 US: Planted 1,153,000 acres Canola / Rapeseed
  Harvested 1,125,000 acres Canola / Rapeseed
  Yield 1,333 lb / acre (CT 1337.5)

| | | |
|---|---|---|
| ➢ 2005 Theoretical US *Canola* Biodiesel Yield | 56,250,000 | 1,339,286 |
| | 4.6% CT Requirement | |

www.caes.state.ct.us

*Source: Montana State University AMPC, Nov 2005 Briefing 60.*

# Summary

- Biodiesel is an alternative oil for use in diesel engines and home heating and is not the same as ethanol
- It is a renewable oil derived from plant material
- In 2006 many details of planting, harvesting, extracting, producing and analyzing Biodiesel have been examined in Connecticut
- Science needs to drive this work
- Future work in progress:
    - Over Wintering canola; increased oil seed yield
    - Better methods of determining metals in oils
    - Reducing metal content in Biodiesel

# Current Work Glucosinolates in Connecticut

1. **Farming Component** (Dr. James LaMondia)
   - Win over Connecticut farmers with IPM aspect
   - Evaluate oil seed crop rotation
   - Evaluate cultivars and time of planting/ harvest
   - Study agricultural value of meal produced

2. **Laboratory Component**
   - Work out details of oil extraction
   - Study the seed / oils / meals:
     nutritional value; metals; pesticides; glucosinolates
   - Study the conversion to biodiesel

3. **Regulatory Component**
   - Ensure biodiesel meets ASTM criterion
   - Establish Connecticut Biodiesel testing program
   - UCONN collaboration