

Utilisation of Extractives



Bjarne Holmbom

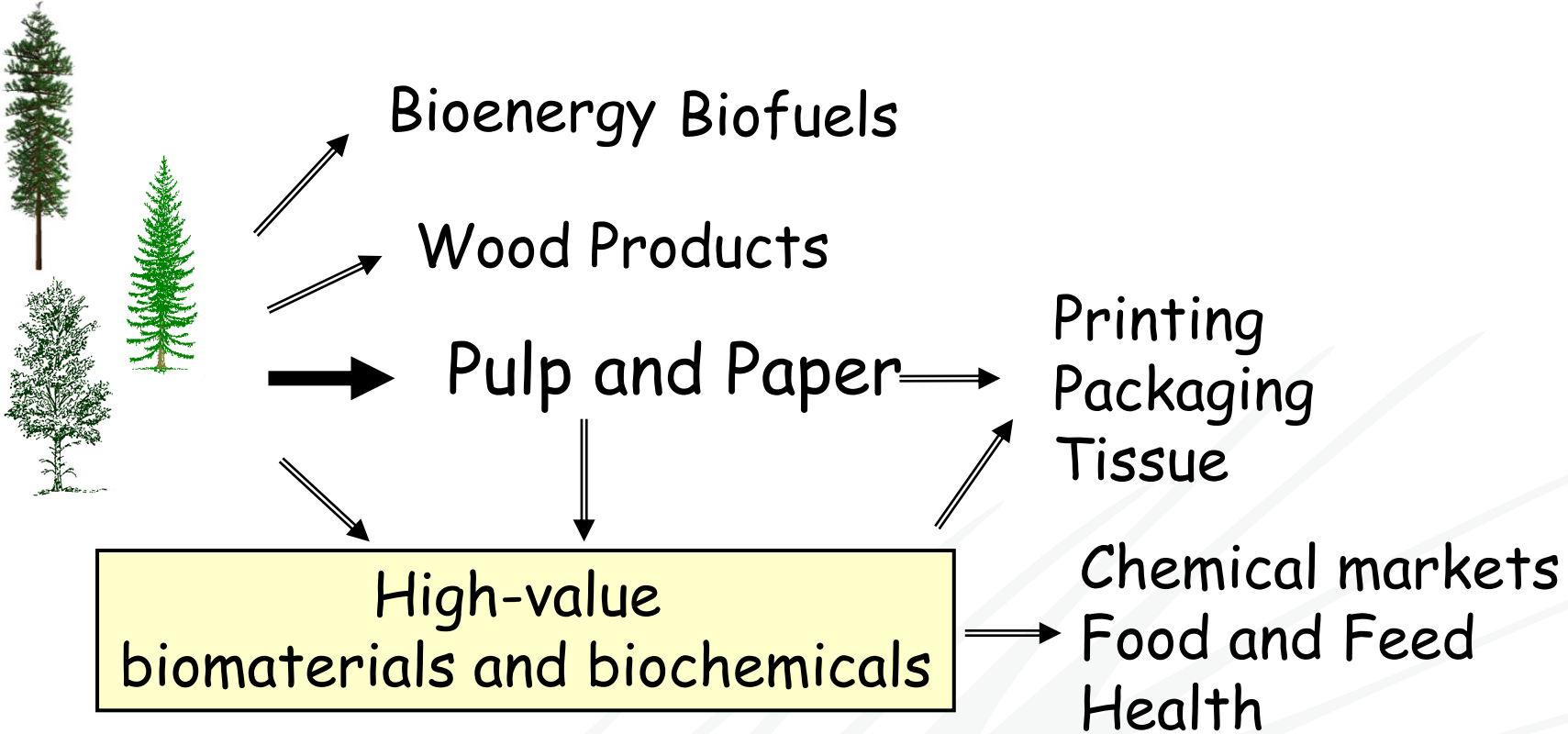
Åbo Akademi



Course "The Forest-based Biorefinery -
Chemical and Engineering Challenges and Opportunities"

ÅA/PCC 5.5. 2010

Forest Biorefineries



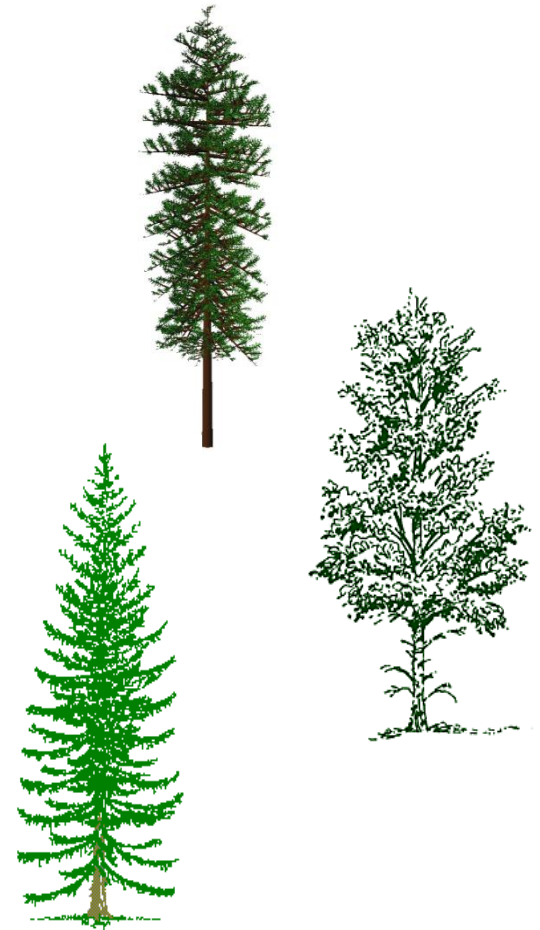
More value from the forest resources

Forest Biomass

- ☺ Grows by itself, from year to year, naturally
- ☺ No fertilisers, little maintenance
- ☺ Harvested all year round - steady flow
- ☺ Harvesting and transport already in place
- ☺ No competition with food use
- ☺ Richer in bioactive compounds than annual plants

Trees are very special plants

- Live very long
- Through evolution during millions of years → → → → → efficient chemical defense systems (mostly extractives)
- Richer in unique, bioactive compounds than annual plants



Contents

- Extractives - occurrence and chemistry
- Traditional products
 - Wood and bark tars and resins
 - Turpentine
 - Tall oil products
- More recent products based on
 - Sterols
 - Lignans
 - Flavonoids
 - Stilbenes
 - Tannins
- Opportunities and Challenges

Extractives

- Extractable with solvents, from non-polar solvents to water
- Non-structural components in trees
- All kind of components in addition to the structural polymers
 - Cellulose
 - Hemicelluloses
 - Lignin

Wood Extractives

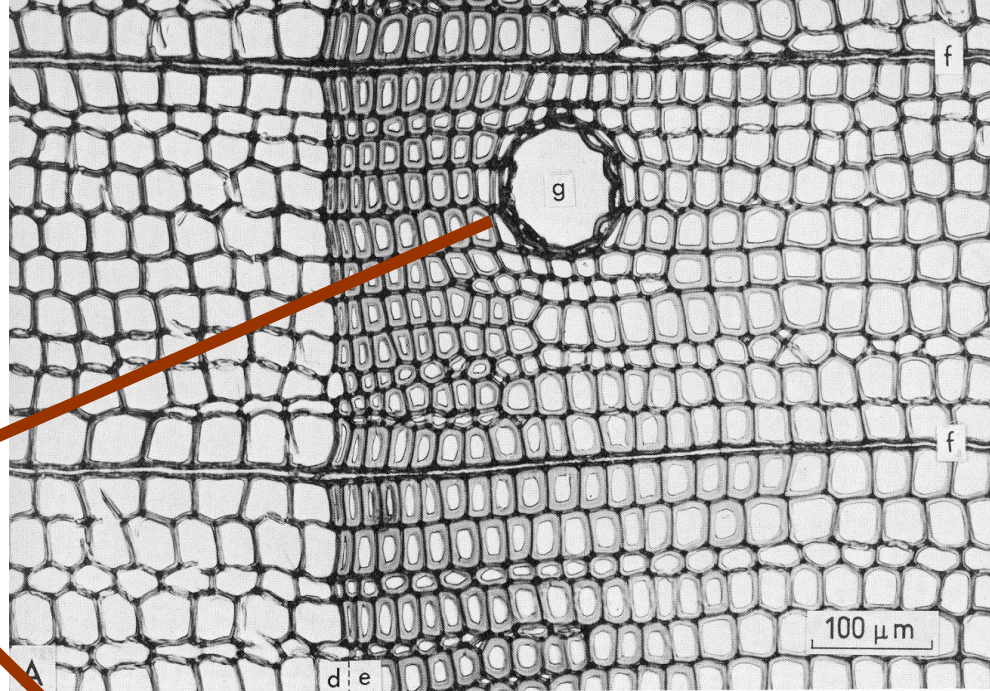
1. **Lipophilic**, insoluble in water “Pitch” “Resin”

Oleo-resin: resin acids, terpenes

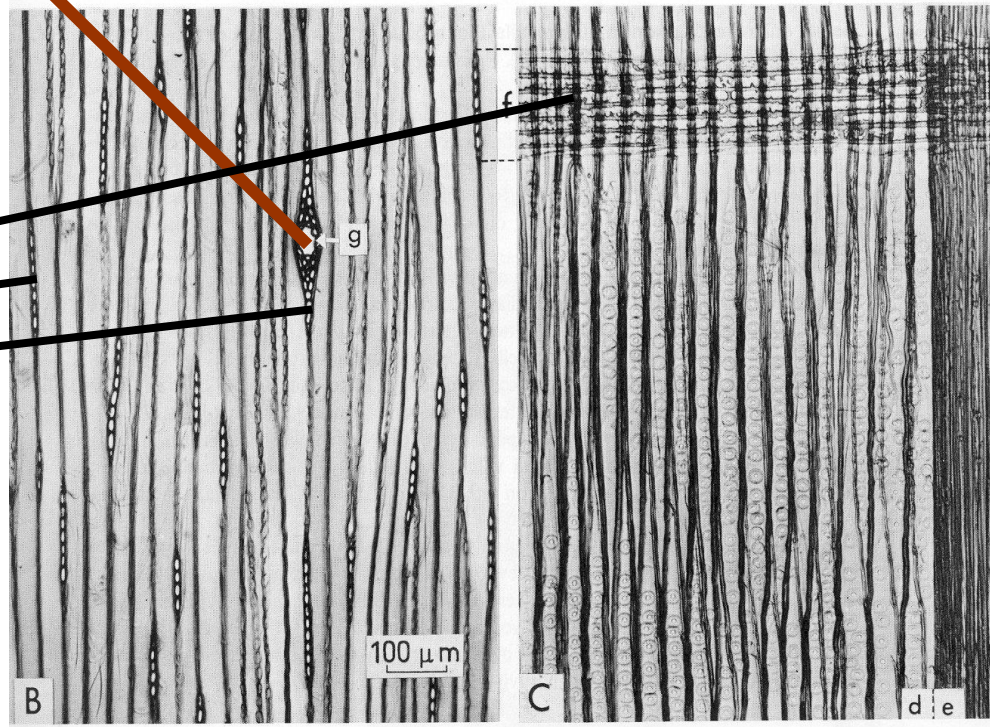
Fats: triglycerides, fatty acids, sterols, sterol esters, other alcohols, hydrocarbons

2. **Hydrophilic**, soluble in polar solvents: phenolic acids, lignans, stilbenes, flavonoids, tannins, etc.

Resin canals
Oleoresin



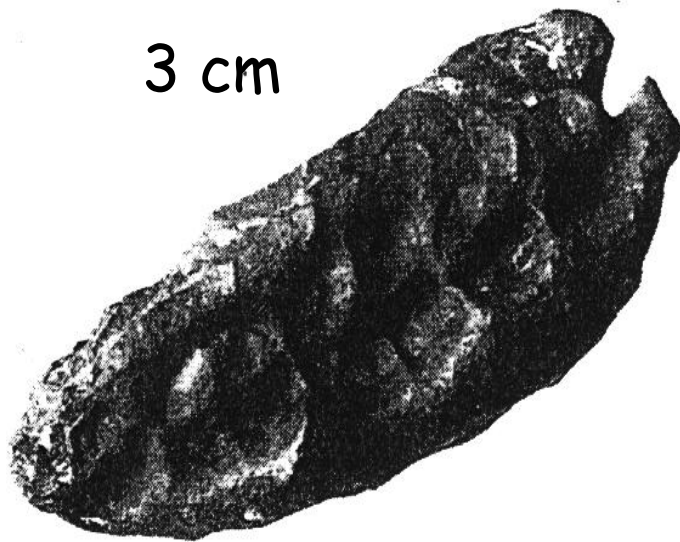
Parenchyma cells
Fats



Functions of extractives

- Protection against attacks by, e.g., bacteria, fungi, insects, plant-eating animals (terpenes, resin acids, phenolic substances)
- Physiological (fats, sterols)

Already during the Stone Age



3 cm

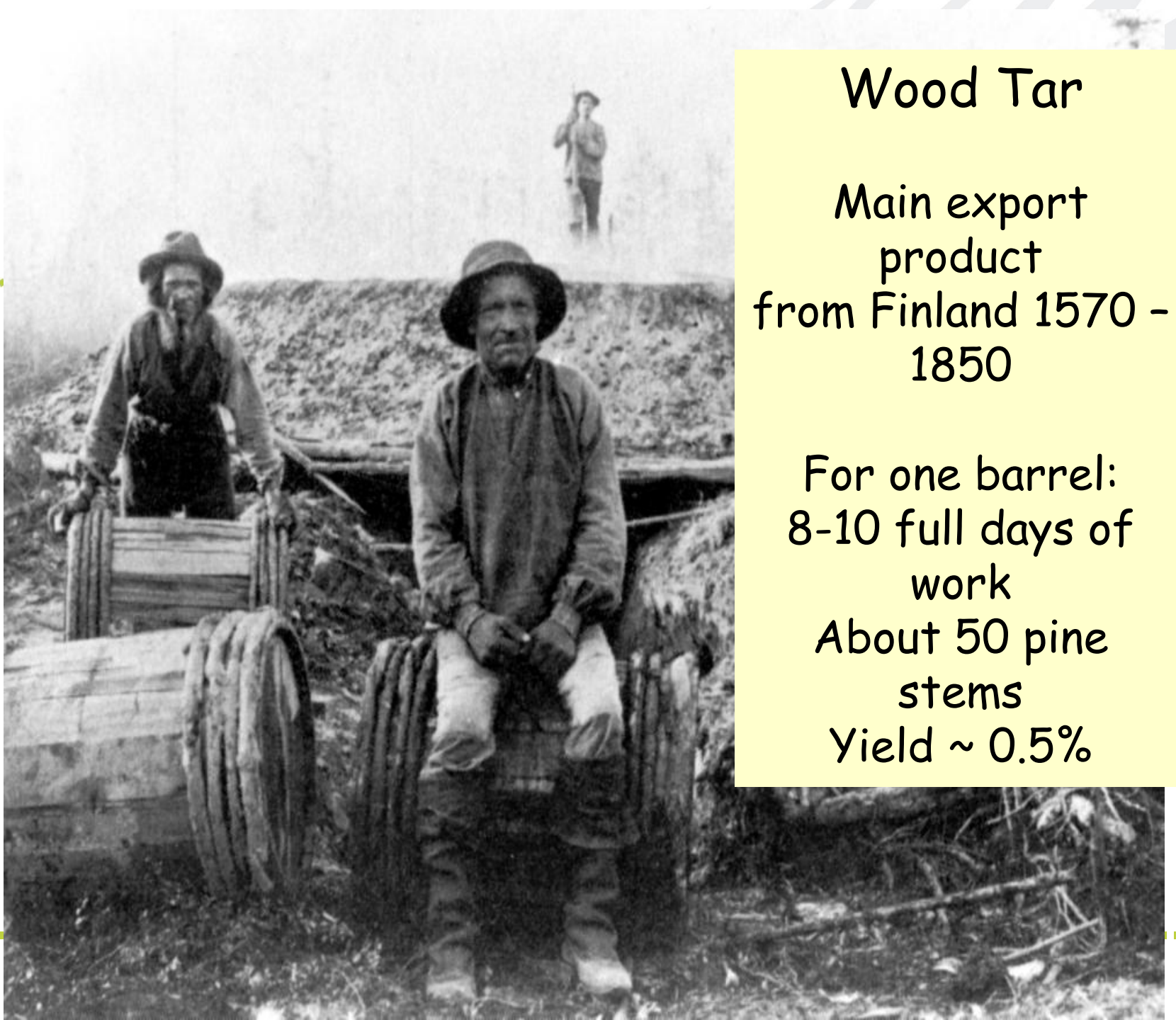
Board of Antiquities
Kerimäki, Finland
7000 B.C.

GC - MS

Manufactured from birch outer bark

Birch bark tar "Tökötti"

The first technochemical product (?)



Wood Tar

Main export
product
from Finland 1570 -
1850

For one barrel:
8-10 full days of
work
About 50 pine
stems
Yield ~ 0.5%

"Jos ei sauna, terva ja viina auta, niin tauti on kuolemaksi."

"If sauna, tar and vodka do not cure your disease, then you will die"

Suomalaisessa kansanparannuksessa terva on ollut tärkeä rohto, jota on käytetty antiseptisenä aineena tulehduksia vastaan niin ihmisten kuin eläintenkin vaivojen hoitoon. Täitä hävitettiin hiuksista tervaa sisältävällä seoksella.

Tervavettä käytettiin rohtona rokkoja ja muita tartuntatauteja vastaan.

Kemia-Kemi 33 (2006) nr 8, p. 40

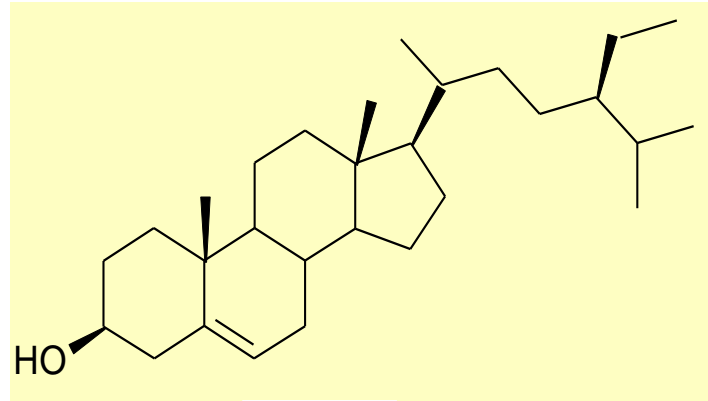
"Tuggkåda"

Nordisk Familjebok 1892

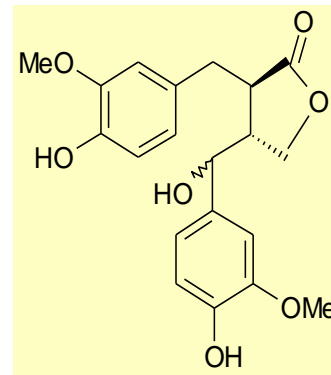
- Ett af allmogen i Dalarna till tuggning användt, af grankåda bestående njutningsmedel
- Smaken är icke obehaglig, och i den finns inblandat ett stick, som erinrar om muskott
- Det är sannolikt, att den kan vara gangnelig för tänderna, i flyktiga oljan är ett gift för bakterier i munhålan
- Dalarnas allmoge har också vanligen sina tänder i förträffligt skick

Wood extractives products today

- Tall oil and turpentine since the 1910's
- Sitosterol since 1995



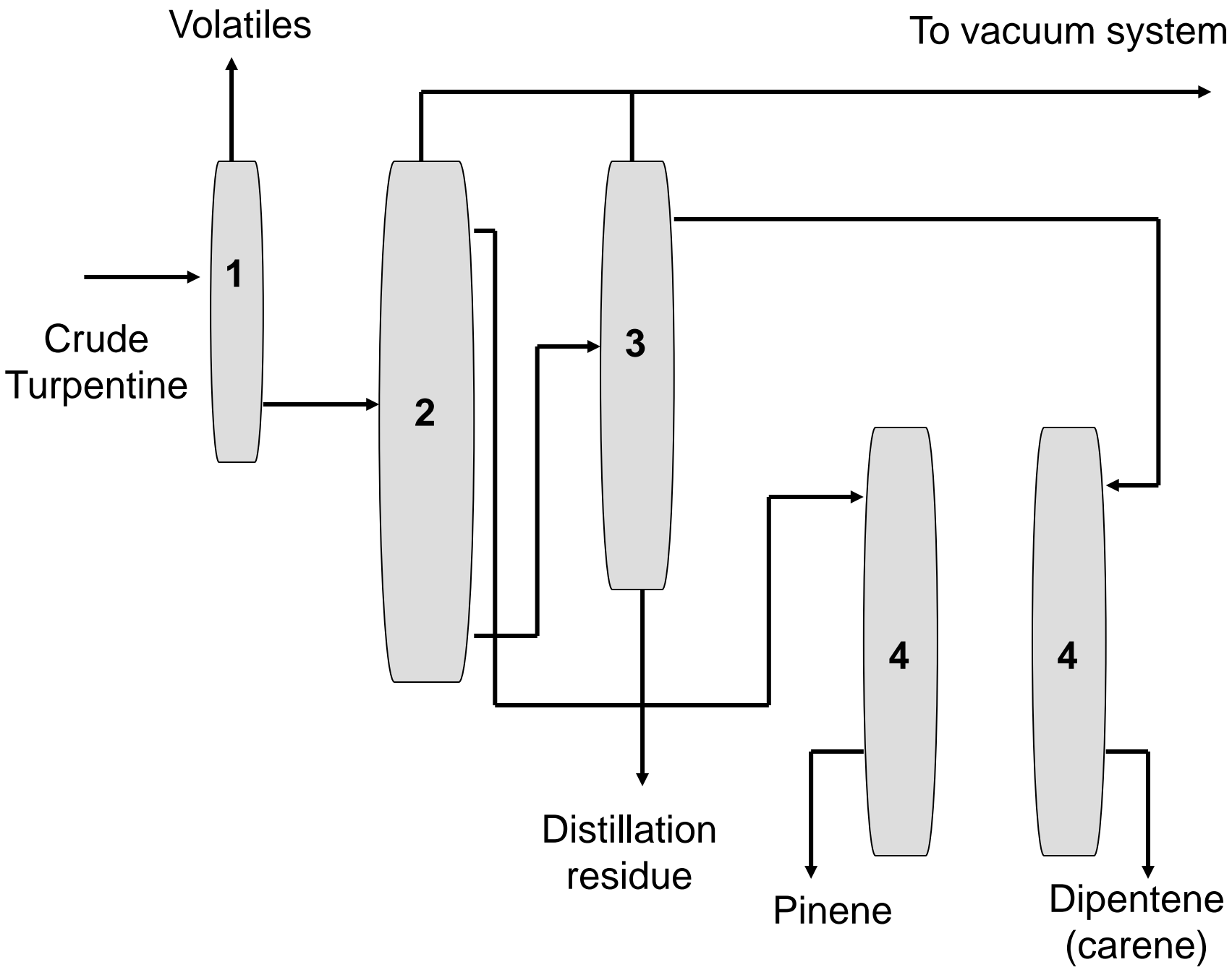
- HMR Lignan since 2006



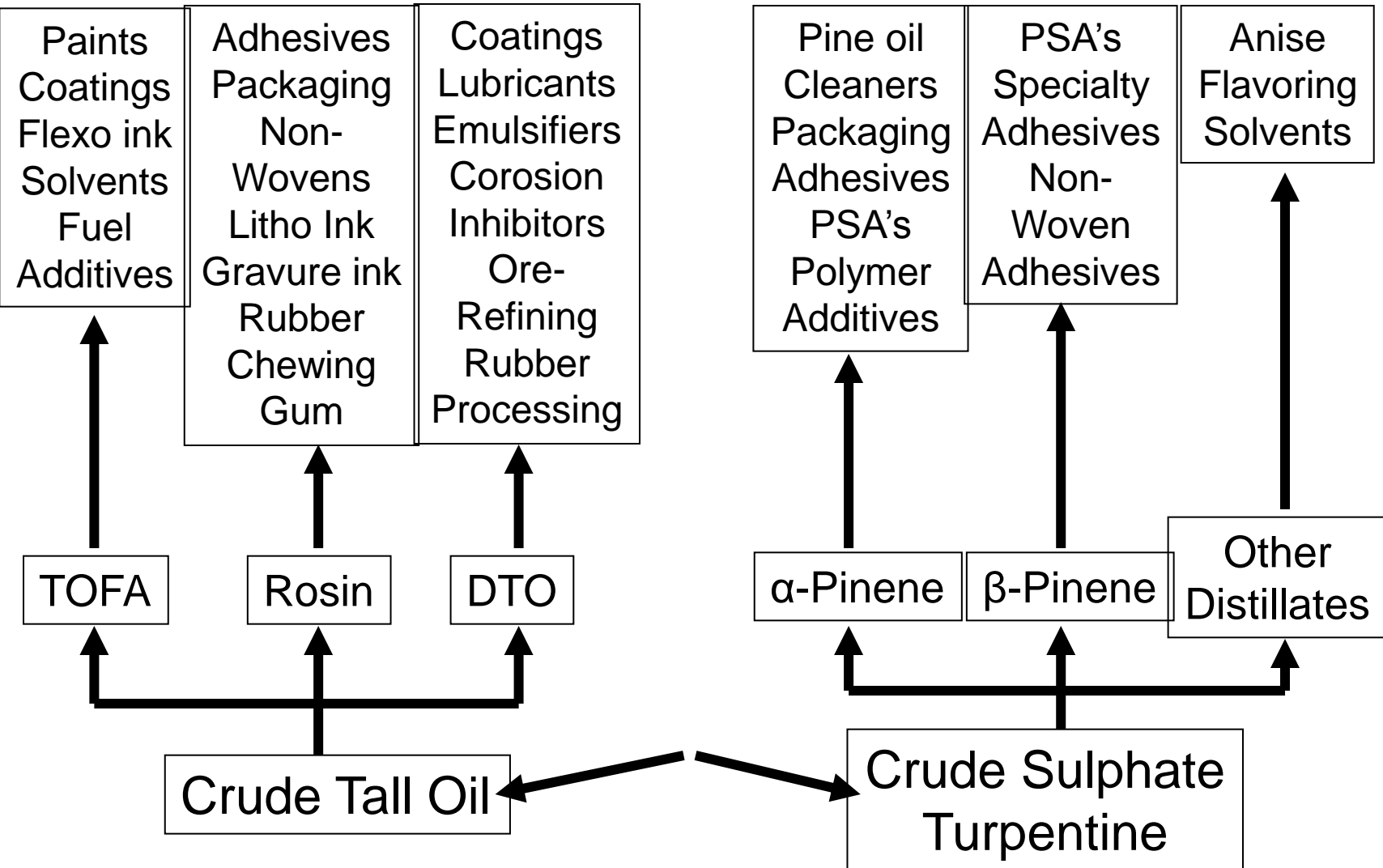
- Emerging products ?

Turpentine

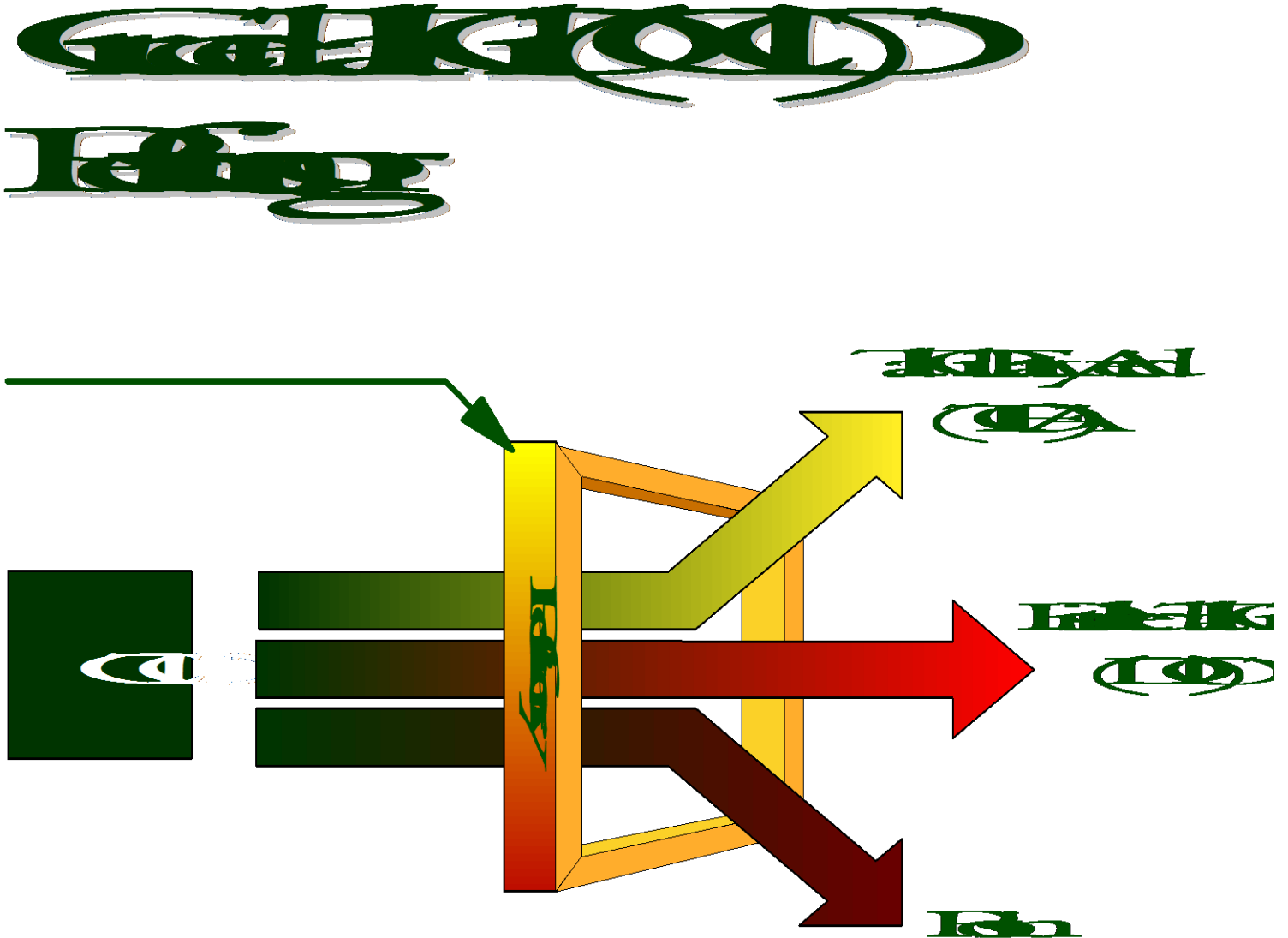
- Consists of the monoterpenes from oleoresin
- Recovered by condensation of digester relief (crude turpentine)
- Purified by distillation
 - X α -pinene fraction (96% α -pinene)
 - X dipentene fraction (60% D³-carene + dipentene)



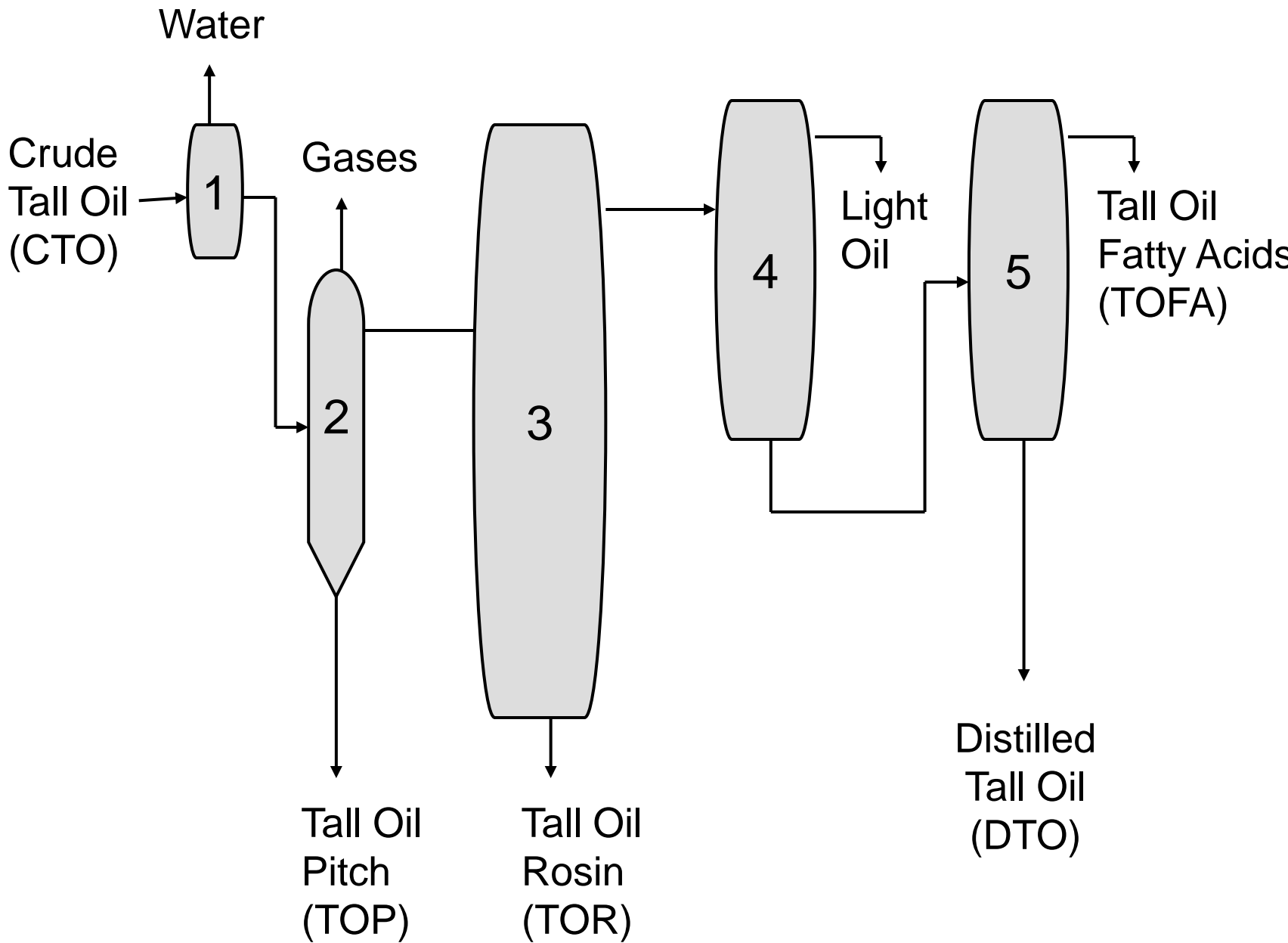
Value From The Tree



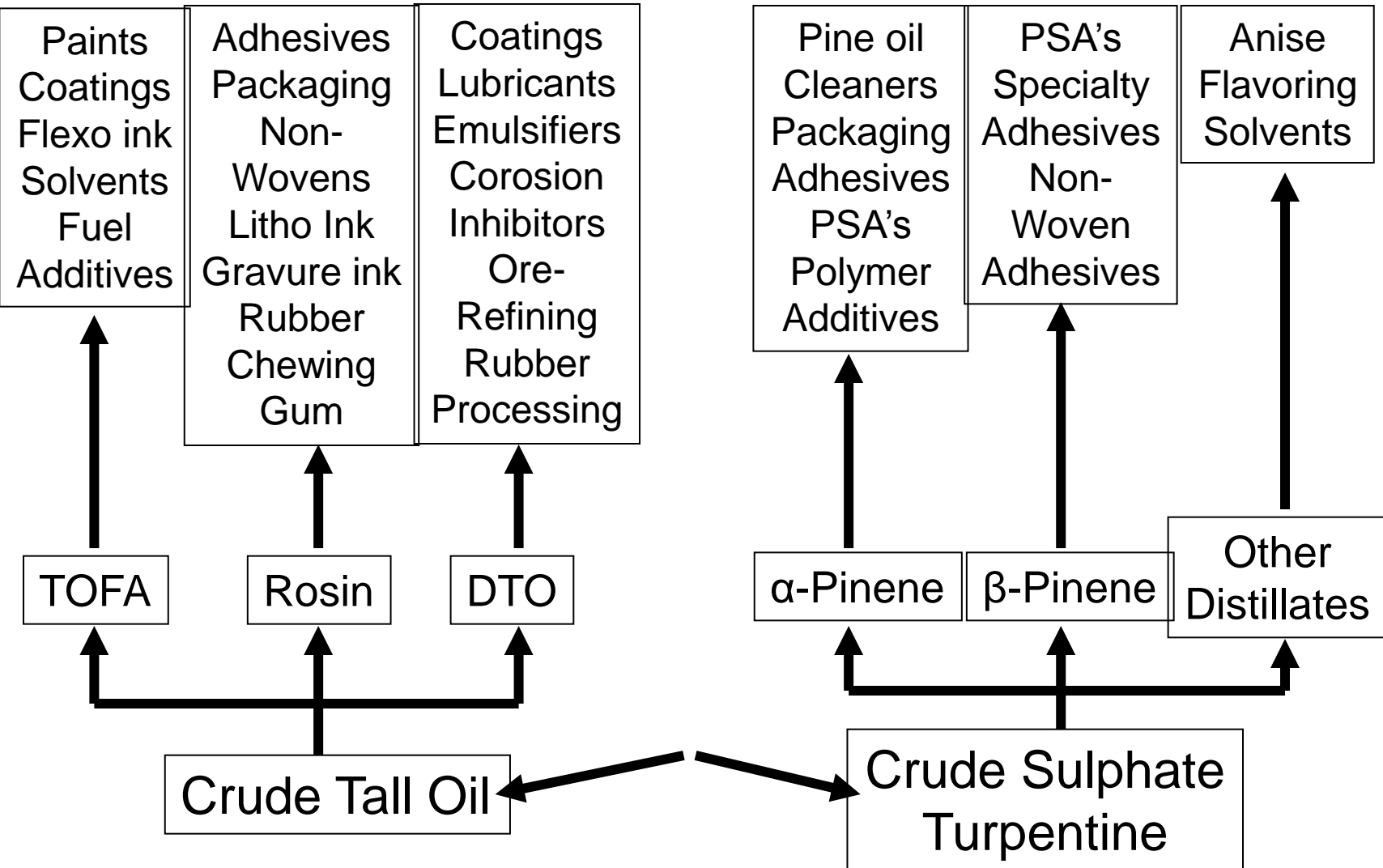
Crude Tall Oil Distillation since 1913

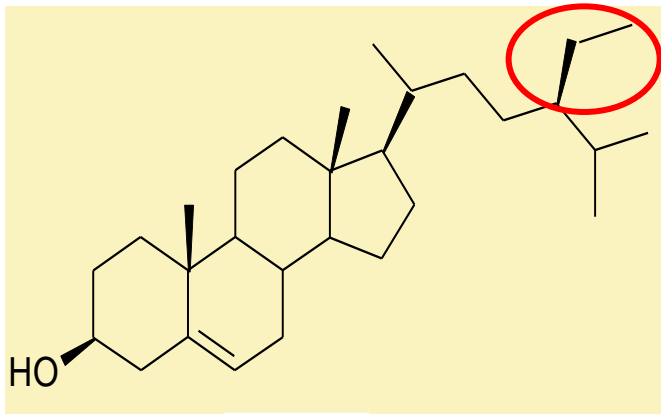


Sitosterol from Tall Oil Pitch

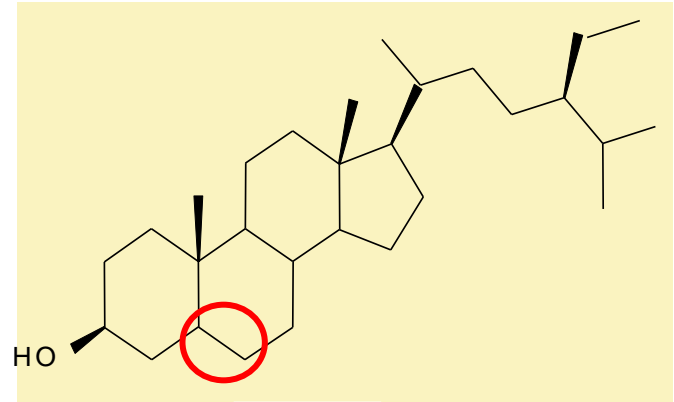


Value From The Tree

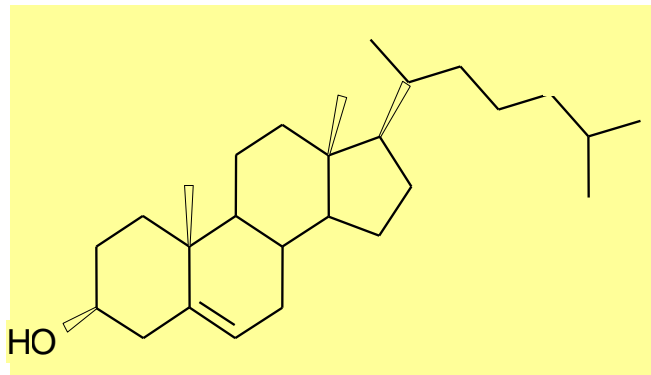




Sitosterol



Sitostanol



Cholesterol



Blood and heart

Sitosterol production

- From tall oil soap at pulp mills or pitch at tall oil distillation plants
- Plant in Kaukas 1977 - 2005
- Also from soybeans
- Global production now about 5000 t/a
- New sitosterol plant producing 4000 t/a in Rauma announced in 2006 (company Forchem) - but not yet built

Many sitosterol products

- Raisio Group
- Unilever: Becel pro-active
- Teriaka: Diminicol
- and other ---



Raisio Group
1995 -



Conjugated Linoleic Acids (CLA's)

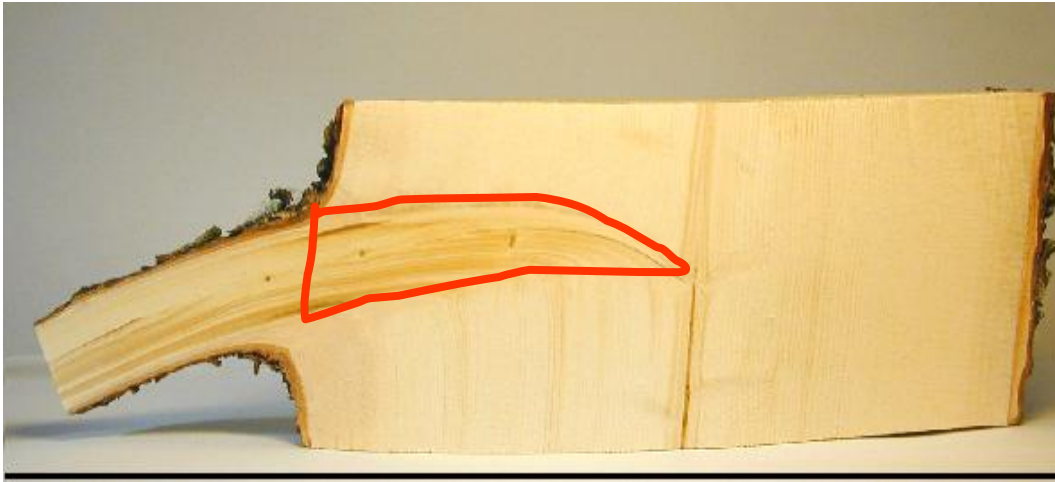
- Linoleic acid 9 cis, 12 cis - 18:2 (40-50% of TOFA)
- CLA's 9 cis, 11 trans
10 trans, 12 cis
- Conjugation by catalytic transformation
- Occurs partly also in kraft pulping

- Various antioxidant and antitumor properties
- Marketed as dietary supplements



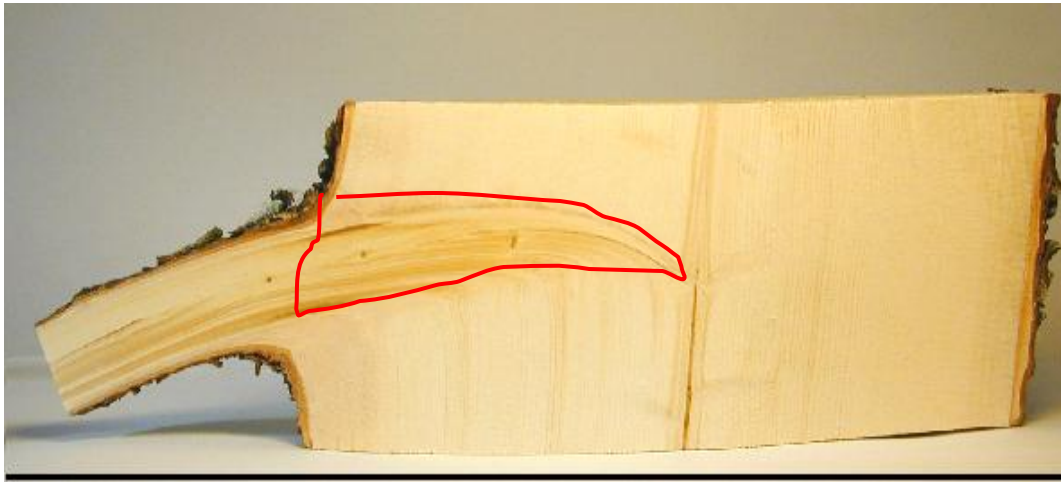
1998

A crooked spruce tree was cut down
A knot was sawn out



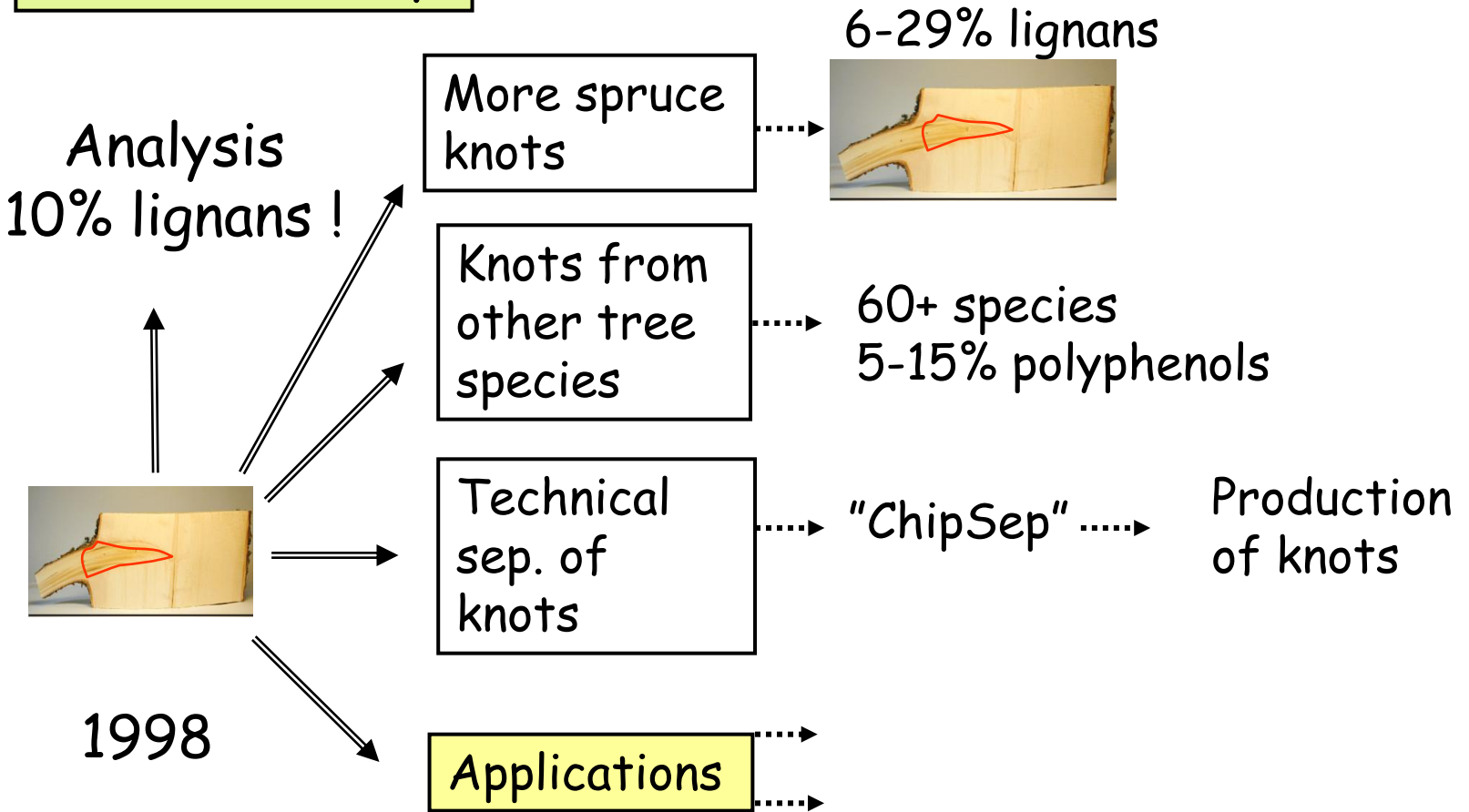
Analysis: it contained 10% of lignans !

The start for extensive research on knots



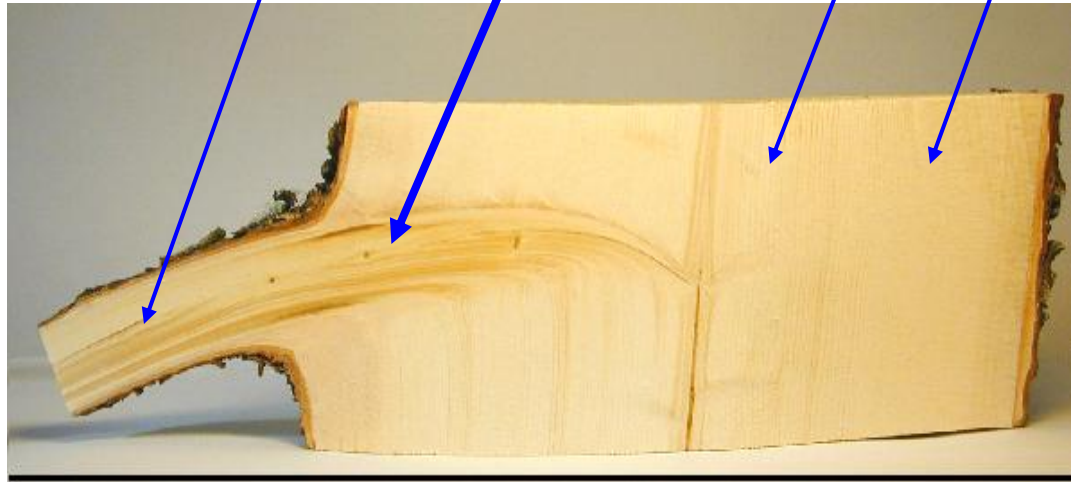
- Detrimental in pulping
- Should be removed
- Can be removed from chips

The knot story

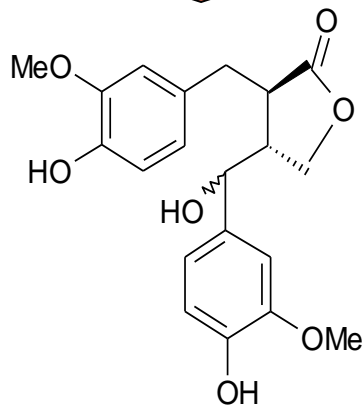


Lignans in *Picea abies*

0.1 - 5 % **6 - 29%** 0.1 % 0.0 %



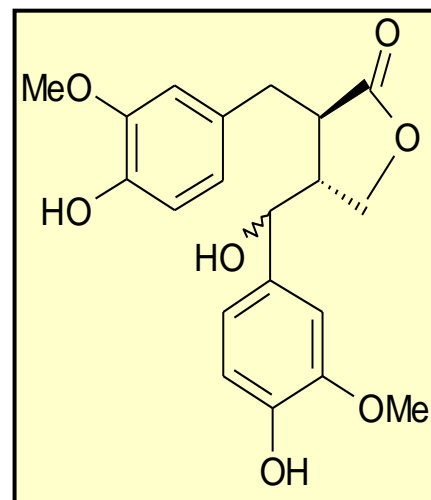
70-85% of the lignan



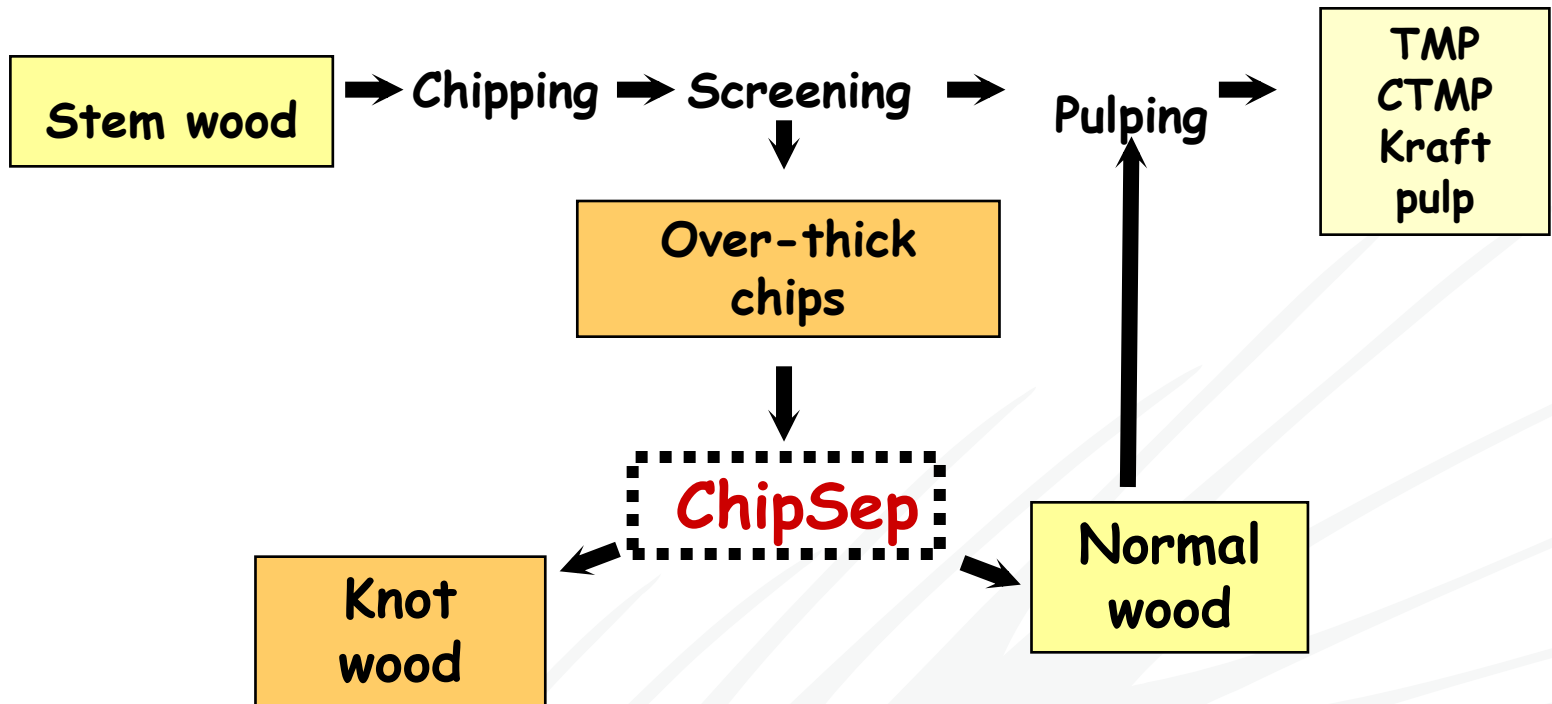
Hydroxymatairesinol (HMR)

The spruce lignan Hydroxymatairesinol (HMR)

- Strong antioxidant
- Inhibits breast cancer growth (Univ. of Turku)
- Hormos Medical Corp., Turku, product development 1997 ---
 - Clinical test on humans: no adverse effects
 - New dietary ingredient clearance from US FDA 2004
 - License Hormos → Linnea S.A. in 2005
 - HMRLignan™ on the market in 2006

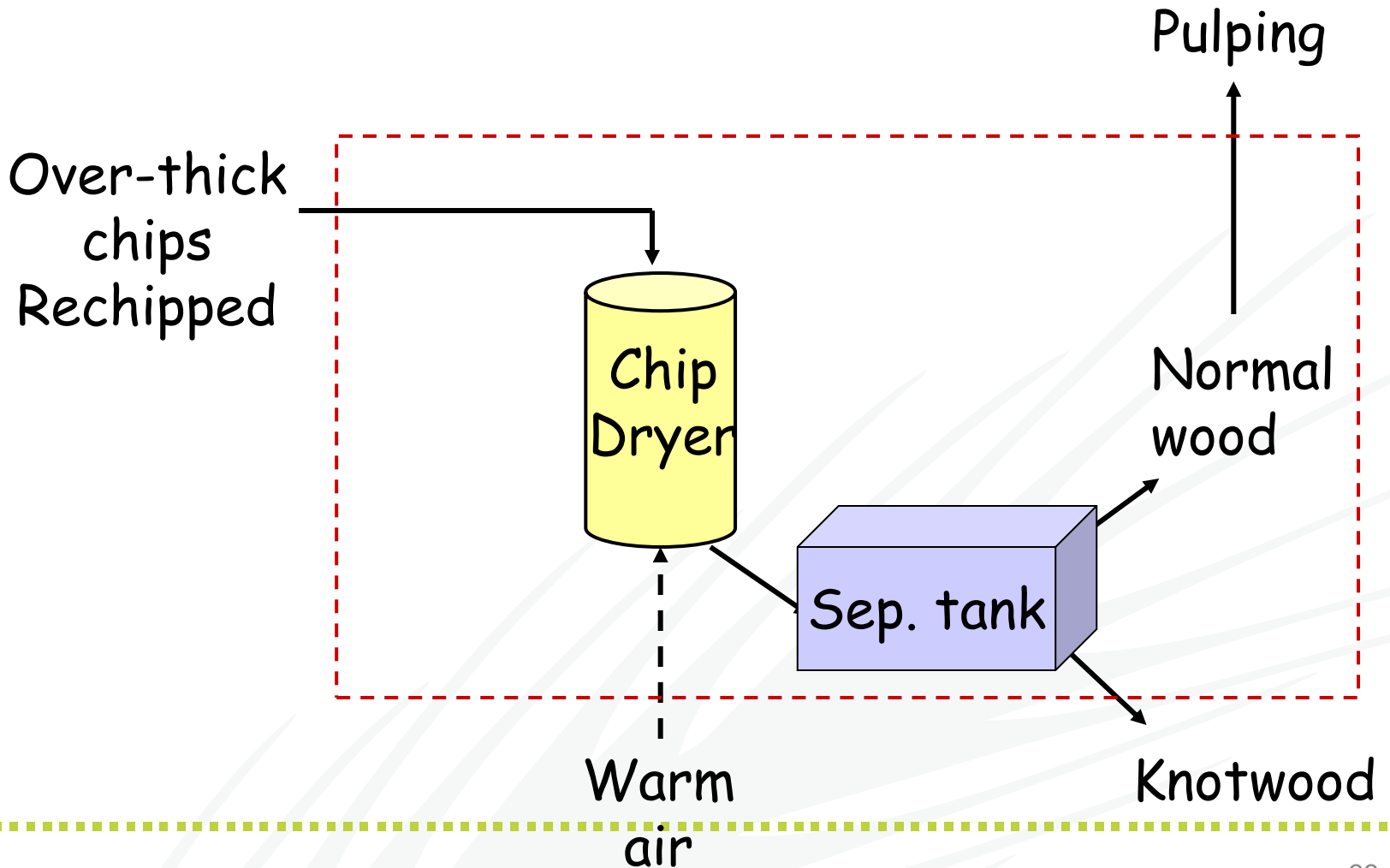


Knots can be separated from wood chips



The ChipSep Process

FI Pat Appl. Aug. 2000 by C. Eckerman and B. Holmbom



Paper mill in Northern Finland
UPM-Kymmene



Knot-rich spruce chips

Farm in Southern Finland
Separation of pure knots



Pure knot material

Linnea SA, Locarno
Extraction and purification



HMR in capsules

Dietary supplement markets

Farm production of knots 2005 - 2007

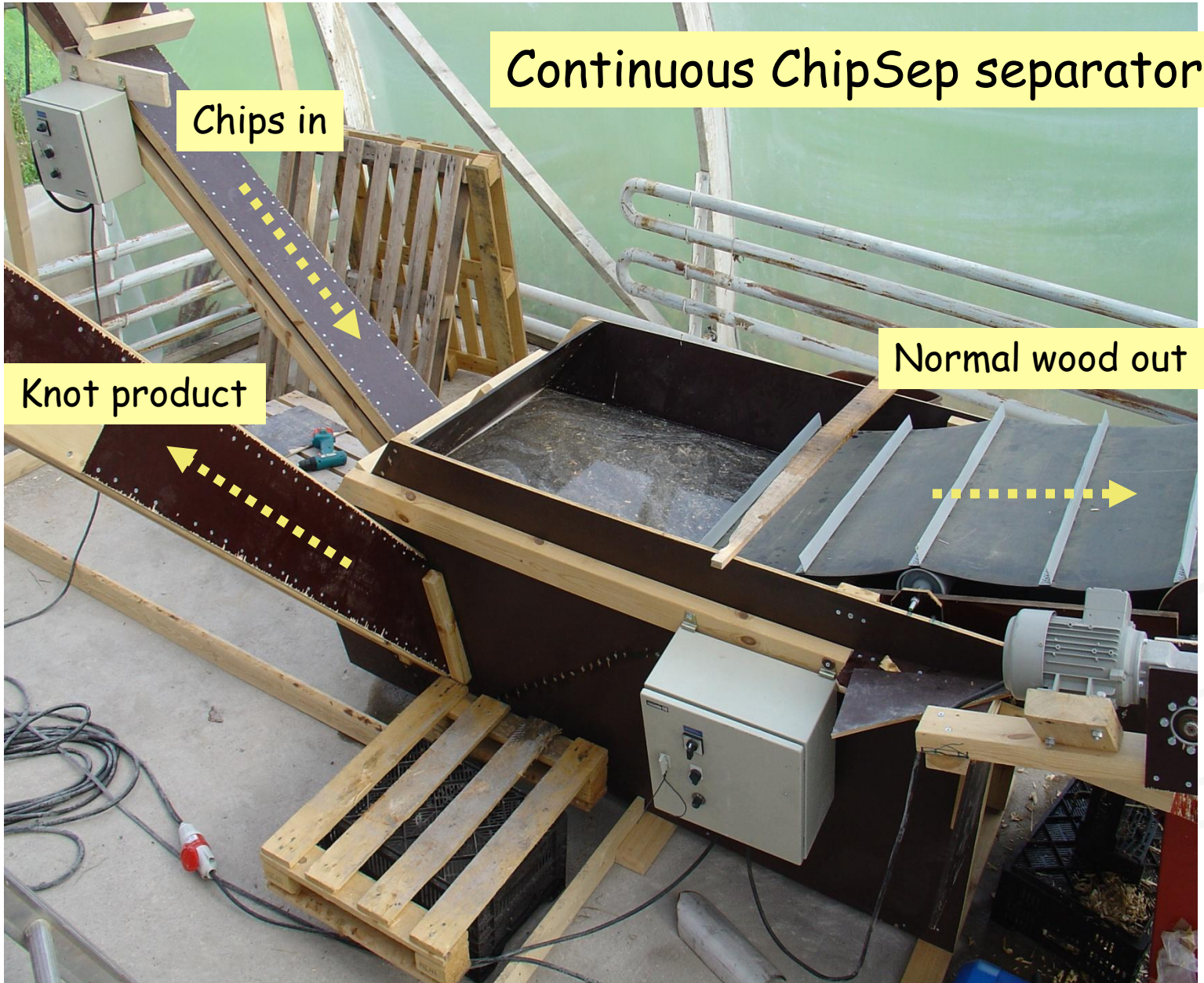


Continuous ChipSep separator

Chips in

Normal wood out

Knot product



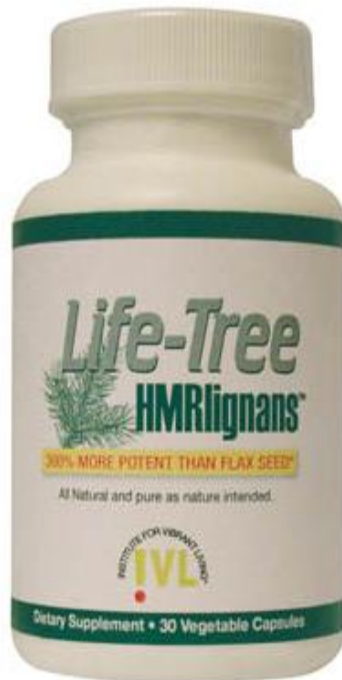




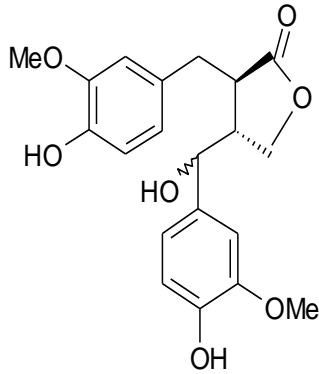
www.hmrlignan.com

Recent research has shown that plant lignans have a positive influence on the development of breast, prostate and colon cancer which rely specifically on oestrogens in order to progress.

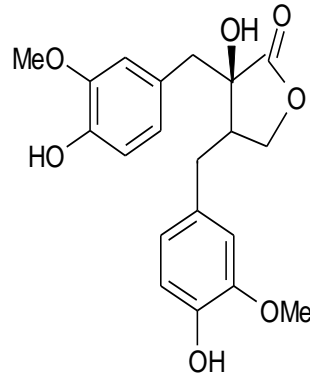
Lignans also help to maintain good cardiovascular health and to moderate other oestrogen-dependent health problems such as menopause symptoms and osteoporosis.



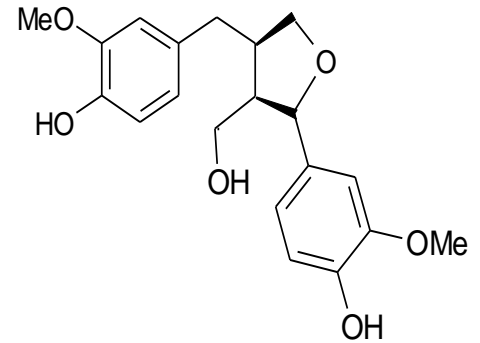
Knots: the richest source of polyphenols in nature



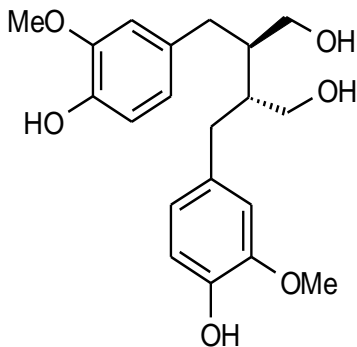
HMR



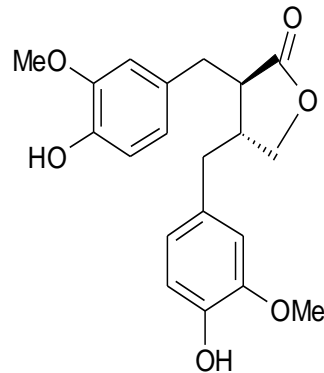
Notrachelogenin



Lariciresinol



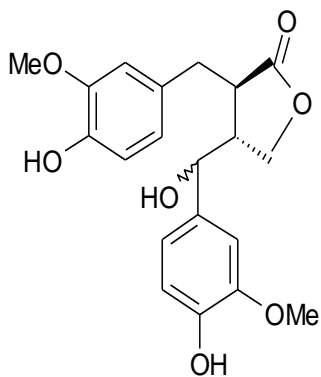
Secoisolariciresinol



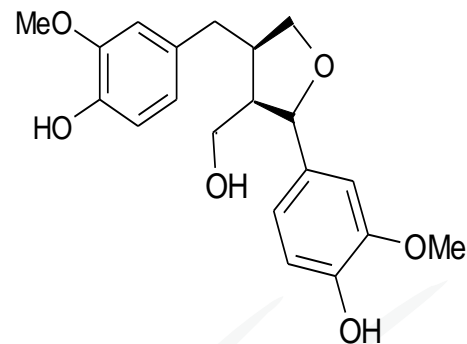
Matairesinol

In many species
also
flavonoids
and stilbenes

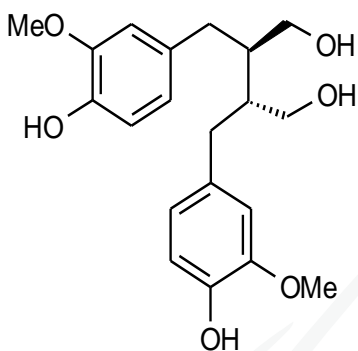
From HMR to other lignans



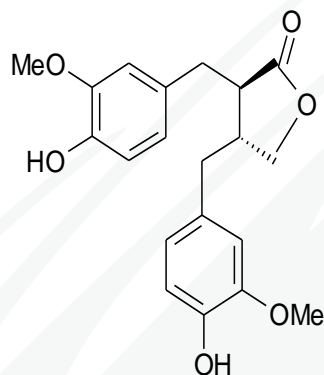
HMR



Lariciresinol



Secoisolariciresinol



Matairesinol

Next lignan products ?

- HMR in functional foods, "Novel Foods"
- Spruce knot extract in cosmetics
- Technical antioxidants
- Natural biocides

Recent products containing spruce knot extract

LUMENE 3-action
Day Treatment / Night Recovery



NATURAL
With Arctic Beauty Blend

Kuusen oksatyviuute: on vahva antioksidantti, joka suojaa ihoa ikääntymistä aiheuttavilta ulkoisilta tekijöiltä.



XZ tervashampoo tasapainottaa ja rauhoittaa hiuspohjaa sekä vähentää hilseen muodostumista.

Bioactive extractives from bark

- Tannins (*Acacia*)
- Spruce resin salve Abilar®
- Pycnogenol® from maritime pine bark
- Taxol® from yew (*Taxus*) bark or needles
- Stilbenes from spruce bark

Abilar®



Abilar pihkavoide on valmistettu puhtaasta Lapin pihkasta sekoittamalla se rasvapitoiseen salvaan. Salva sisältää 10% pihkaa.

Pressure ulcers

Burns

Wound infections

Surgical Wounds

Psoriasis

Nail fungus (onychomycosis)

Trycksår

Brännsår

Infekterade sår

Operationssår

Psoriasis

Nagelsvamp

Our products are approved by the National Agency for Medicines in Finland. The new Abilar® Resin Salve is now for sale in Finnish pharmacies (since 2008).

Repolar Ltd - science in the service of your health!

ANTIOKSIDANTTI-RAVINTOLISÄ • ANTIOXIDANT-KOSTTILLSKOTT

PYCNOGENOL®

RANNIKKOMÄNNYN KUORIUUTETABLETTI
Havstalls barkextrakttablett

40 mg

STRONG



Voimakas kasviantioksidantti

Vahvistaa ihon kollageenia

Suojaa soluja ennenaikaiselta
vanhenemiselta

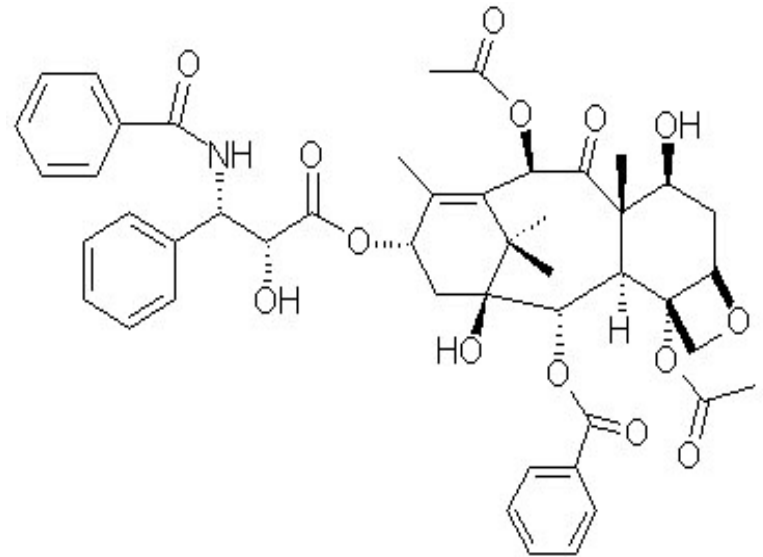
Jalkojen turvotukseen

Sydämen ja verisuonten
hyvinvointiin

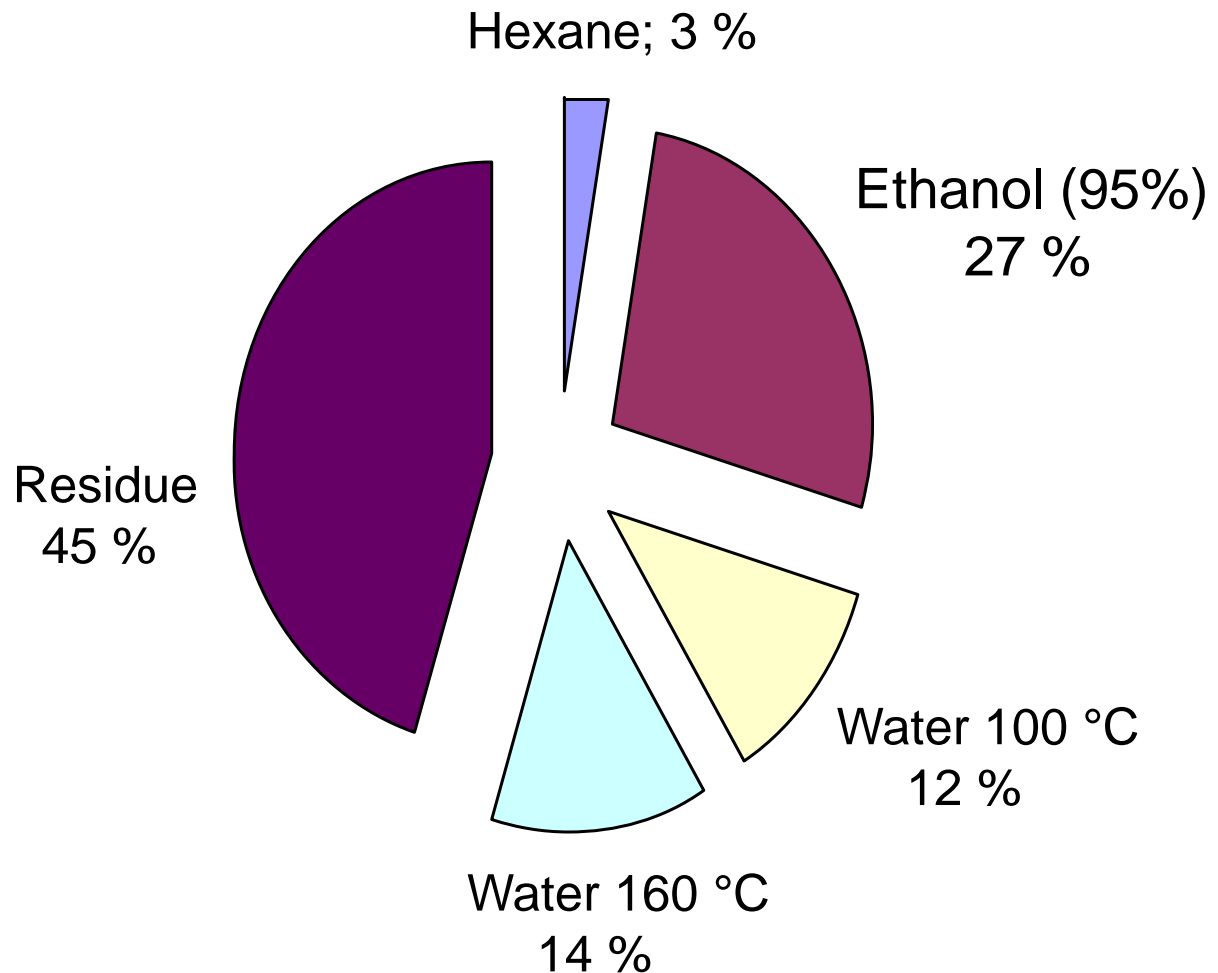
Helpottaa oloa siitepölyaikana

Paclitaxel (Taxol®)

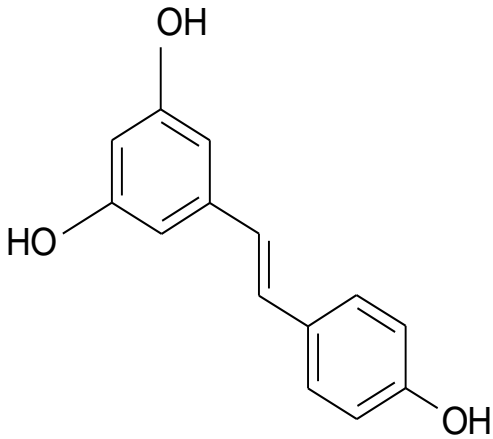
- A chemotherapy drug for treatment of ovarian, breast and lung cancer
- An alkaloid extracted from the bark and needles of the yew tree, *Taxus brevifolia*
- Approved by FDA 1992
- Competing product: Taxotere®
- The best selling anticancer drugs



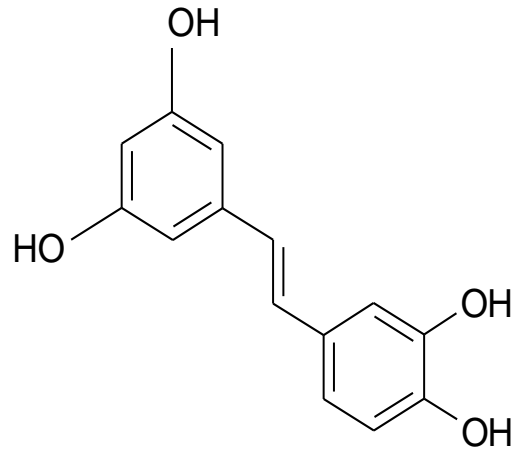
Spruce inner bark



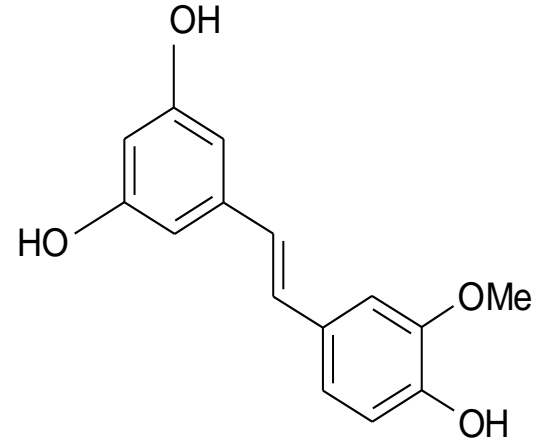
Stilbenes in spruce bark



Resveratrol
(Also in
red wine)

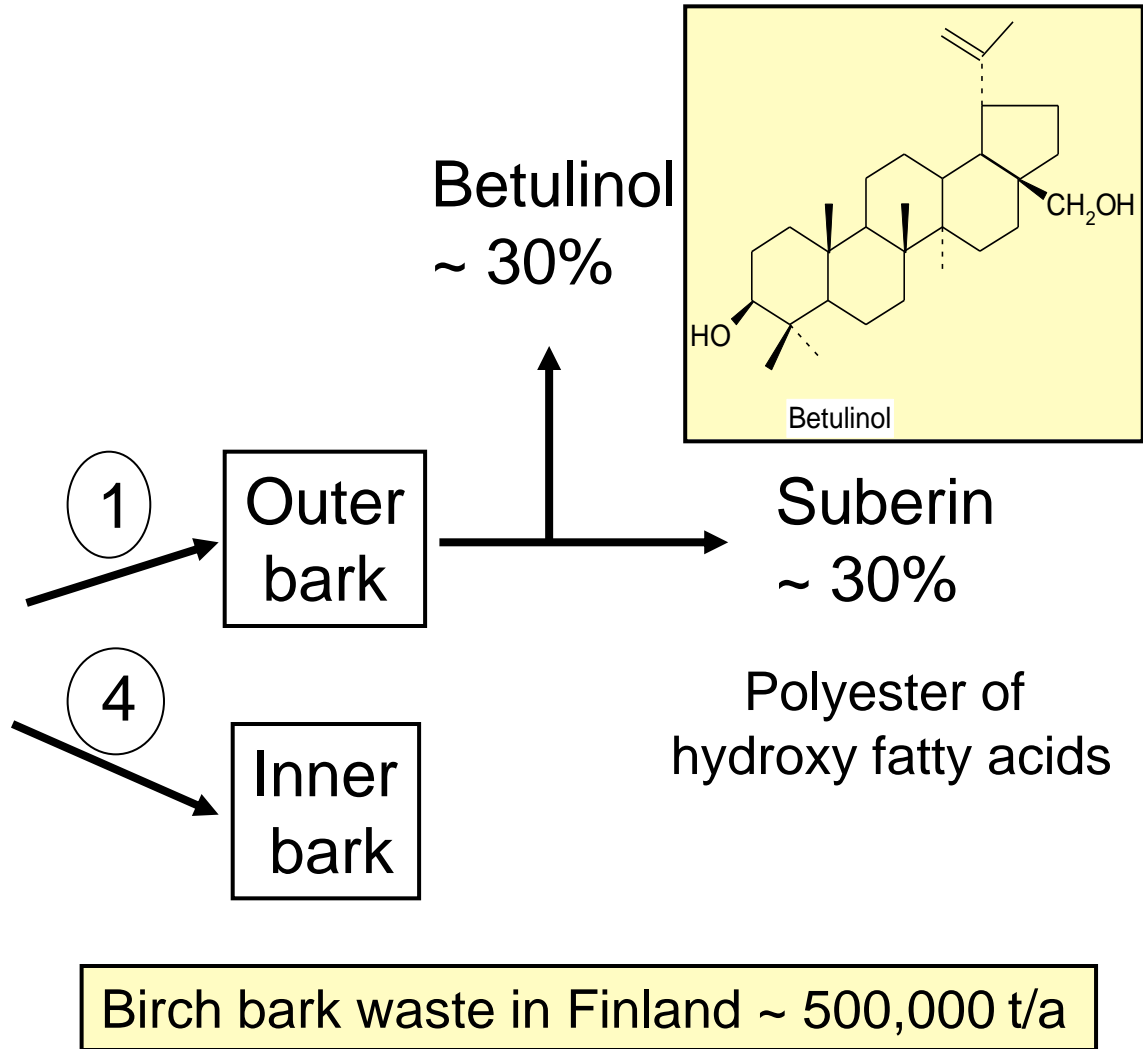


Piceatannol



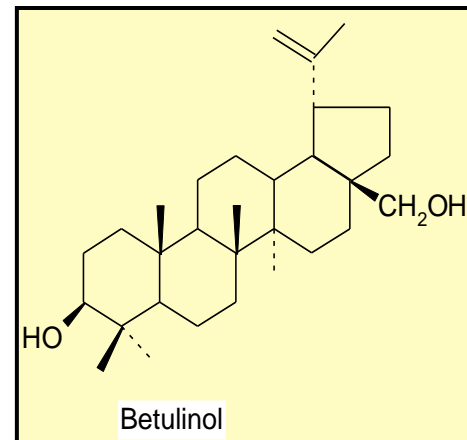
Me-Piceatannol

Birch outer bark

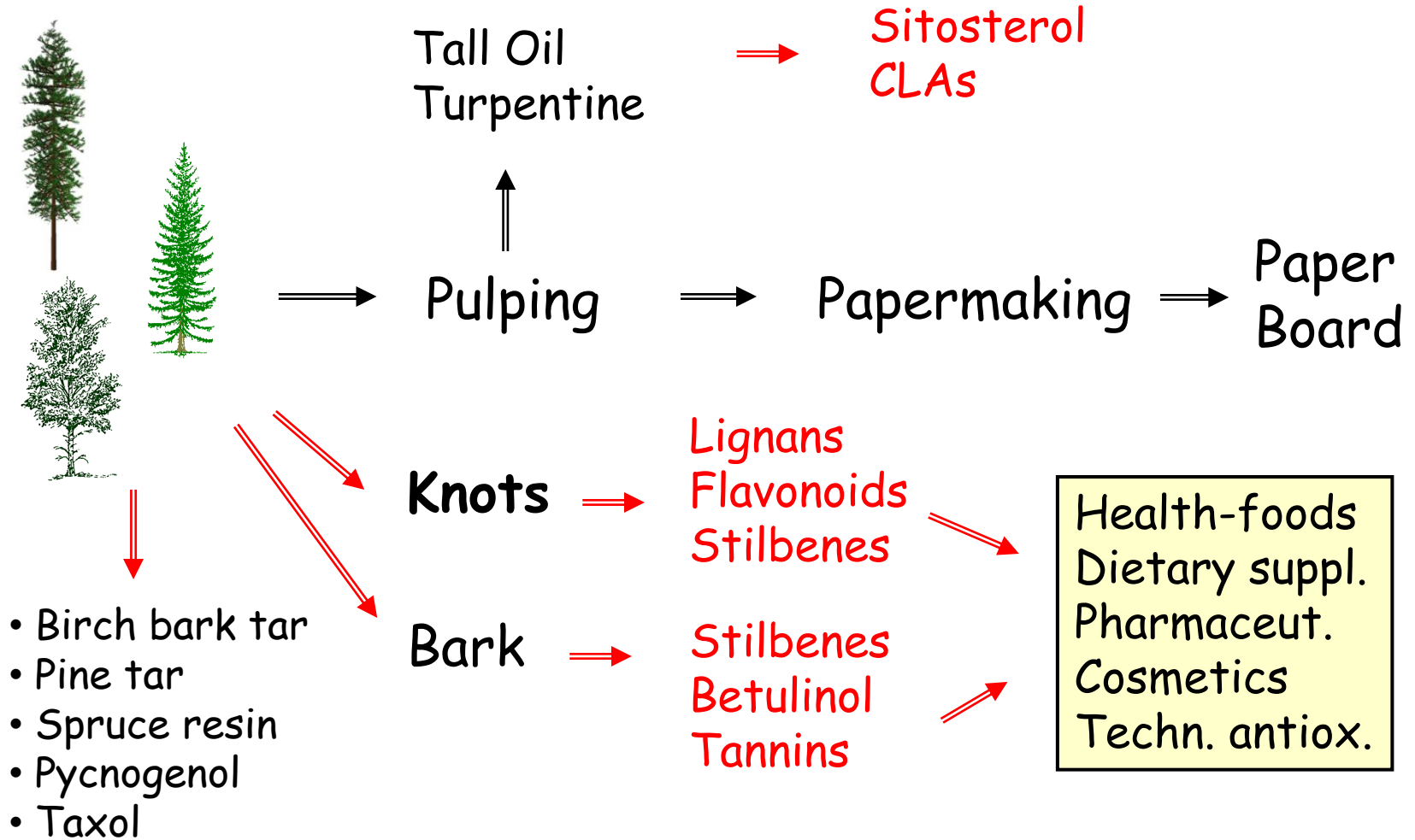


Utilization of betulinol

- Ingredient in cosmetics
- Paper filler or pigment
- Raw material for betulinic acid and other derivatives



Routes to valuable extractives

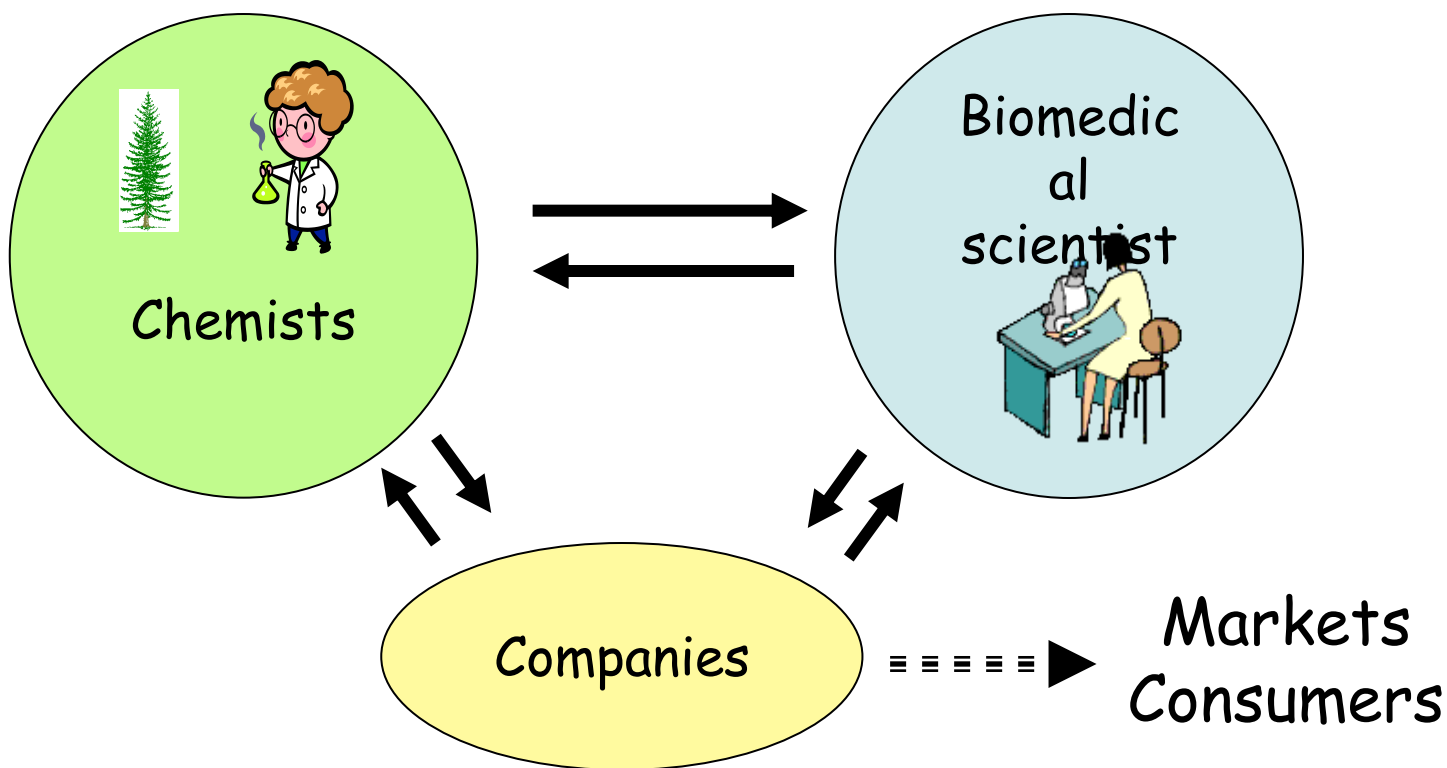


Bioactive extractives from trees

It's a long way

- Identifying the most promising compounds
- Find a rich source
- Efficient extraction and purification techniques
- Biotesting ---- find the best applications
- Regulations / Clearance
- Product concept ---- Marketing

New natural biochemicals ! ?
Transdisciplinary research cooperation
Product and business development



Maybe not large-volume business

But may give profitable margins

And --- may promote human health
in a natural way

Research must go on ---

Still a lot of opportunities
for new forest products

Much of
"Nature's molecular wisdom"
in trees

FuBio Theme 5: Biochemicals for protection of products and health

Separation and analysis of
active components in
raw materials and extracts

WP 1
Hemicelluloses and
Specialty sugars

WP 2
Polyphenols
and Tannins

WP 3
Extractives:
Terpenes & Lipids

Active components for
food and health

Active components for
protection of products

WP 4
Product Roadmaps
Regulations