HOPPY BEERS
ARE
HAPPY AND HEALTHY BEERS !!!

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Organic Chemistry
Natural Products
Medicinal Plants
HOPS

Bibbiano, 9 September 2012
HOP IS KNOWN SINCE ANCIENT TIMES TO BE
A VERY IMPORTANT MEDICINAL PLANT

Bibbiano, 9 September 2012
HOP IS THE "FLAVORING AGENT" IN BEER

HOP IS AN EXTREMELY POTENT MEDICINAL PLANT
‘Secret’ mixture of herbs that the medieval brewers had to buy from the ‘gruutheer’

LODEWIJK VAN GRUUTHUSE

The Gruuthuse noblemen from Bruges received in 1200 the so-called ‘gruutrecht’ from the count of Flanders, Boudewijn IX. Thus, the Gruuthuses possessed the monopoly on the sale of gruut to the brewers.

Ingredients were sometimes very stimulating and even toxic such as ABSINTH!
USE OF HOP FOR BEER BREWING

- Few references before the year 1,000
- Slow introduction from the 14th century on
- Increasing popularity in the 15th and 16th centuries

FINAL BREAKTHROUGH OF HOP AS AN ESSENTIAL INGREDIENT IN BEER BY THE FAMOUS ‘REINHEITSGEBOT’

‘REINHEITSGEBOT’ – ‘LAW OF BEER PURITY’ (1516)

BEER MAY ONLY BE BREWED USING BARLEY, HOP AND PURE WATER. LATER (> 1800), YEAST WAS ADDED.

WILHELM IV DUKE OF BAVARIA
HOP

- Natural preservative
  - Bacteriostatic properties
    - Bitter taste formed only by prolonged heating
- Calming and sedative activity

Beer was in medieval times the only safe drink!

Water was often infected by deadly epidemia such as typhus, cholera, pest, etc...

Beer consumption was more than 300 liters per head and per year - inclusive women and children!!
Pieter Bruegel the Elder
(about 1525-69)
<table>
<thead>
<tr>
<th>Kingdom:</th>
<th>Plantae</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Angiosperms</td>
</tr>
<tr>
<td>Order:</td>
<td>Rosids</td>
</tr>
<tr>
<td>Family:</td>
<td>Rosales</td>
</tr>
<tr>
<td>Genus:</td>
<td>Cannabaceae</td>
</tr>
<tr>
<td></td>
<td><strong>Humulus L.</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Humulus lupulus</strong> L.</td>
</tr>
<tr>
<td><strong>Humulus japonicus</strong> Siebold &amp; Zucc.</td>
</tr>
<tr>
<td><strong>Humulus yunnanensis</strong> Hu</td>
</tr>
</tbody>
</table>
HOP (Humulus lupulus L.)

Only in the female hop plant, the inflorescences develop into new plant structures called hop cones.
## HOP GROWING IN THE WORLD - 2011
### (AREAS IN HECTARES)

### NORTHERN HEMISPHERE (harvest in AUGUST - SEPTEMBER)

<table>
<thead>
<tr>
<th>Country</th>
<th>Area</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germany</td>
<td>17,124</td>
<td>(37.4%)</td>
</tr>
<tr>
<td>United States</td>
<td>12,250</td>
<td>(26.7%)</td>
</tr>
<tr>
<td>Czech Republic</td>
<td>4,368</td>
<td>(9.5%)</td>
</tr>
<tr>
<td>People's Republic of China</td>
<td>3,531</td>
<td>(7.7%)</td>
</tr>
<tr>
<td>SLOVENIA</td>
<td>1,250</td>
<td></td>
</tr>
<tr>
<td>POLAND</td>
<td>1,200</td>
<td></td>
</tr>
<tr>
<td>United Kingdom</td>
<td>1,050</td>
<td></td>
</tr>
<tr>
<td>UKRAINE</td>
<td>640</td>
<td></td>
</tr>
<tr>
<td>SPAIN</td>
<td>510</td>
<td></td>
</tr>
<tr>
<td>BELGIUM</td>
<td>189</td>
<td>(0.4%)</td>
</tr>
</tbody>
</table>

### SOUTHERN HEMISPHERE (harvest in FEBRUARY - MARCH)

<table>
<thead>
<tr>
<th>Country</th>
<th>Area</th>
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</thead>
<tbody>
<tr>
<td>South Africa</td>
<td>492</td>
</tr>
<tr>
<td>Australia</td>
<td>455</td>
</tr>
<tr>
<td>New Zealand</td>
<td>385</td>
</tr>
<tr>
<td>Argentina</td>
<td>129</td>
</tr>
</tbody>
</table>

**HOP AREA IN THE WORLD:** 45,810 ha (- 3,259 ha with respect to 2010)

**HOP PRODUCTION IN THE WORLD:** 100,604 ton (tons)
VEGETATIVE REPRODUCTION

HOP SHOOTS

CULINARY DELICACY

Only few weeks from February until April
Hop is the fastest growing climbing (clockwise) plant in nature
10 cm growth average per day – 6-8 m height in 7/8 weeks

Hop is very susceptible to various diseases, pests, moulds, aphids …

Hop is dioecious: separate male and female plants

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Male inflorescence
“Hop flowers”
“Hop cones”

Female inflorescence

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MALE HOPS

- Not used in practice
- Fertilization of female hops occurs when in each other’s proximity
- Fertilized female hop contains a seed in each bracteole of a hop cone

Seeds are composed of fats and oils: deleterious to beer foam

IT IS WORLDWIDE FORBIDDEN TO GROW MALE HOPS WITHIN A CERTAIN DISTANCE FROM FEMALE HOPS

BEER IS BREWED WORLDWIDE USING EXCLUSIVELY FEMALE HOPS EXCEPT IN UK
Lupulin glands

FEMALE HOPS
Hops are an example of plants that are characterized by the presence of **glandular trichomes or plant hairs or “lupulin” glands**: specialized epidermis cells containing volatile oils and other secretions.

**SECRETIONS COMPRIS A COMPLEX OF CHEMICALS CALLED SECONDARY PLANT METABOLITES**

*** NOT ESSENTIAL TO THE LIFE OF THE PLANT

*** NECESSARY FOR SURVIVAL OF THE PLANT

- Hops are very sensitive to various life-threatening factors in the environment – from biological origin to climatological conditions.
- Massive quantities of secondary metabolites (up to 40% of the dry weight of a hop cone!!!) are produced and accumulated in the lupulin glands.
## Average Chemical Composition of a Dry Hop Cone

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Percentage (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha-Acids/Humulones</td>
<td>2-23</td>
</tr>
<tr>
<td>Beta-Acids/Lupulones</td>
<td>2-12</td>
</tr>
<tr>
<td>Essential oil</td>
<td>0.5-4.4 (v/w)</td>
</tr>
<tr>
<td>Polyphenolics</td>
<td>3-7</td>
</tr>
<tr>
<td>Water</td>
<td>8-12</td>
</tr>
<tr>
<td>Cellulose-lignin</td>
<td>40-50</td>
</tr>
<tr>
<td>Ash/Salts</td>
<td>10</td>
</tr>
<tr>
<td>Proteins</td>
<td>15</td>
</tr>
<tr>
<td>Pectins</td>
<td>2</td>
</tr>
<tr>
<td>Monosaccharides</td>
<td>2</td>
</tr>
<tr>
<td>Oils and fatty acids</td>
<td>1-5</td>
</tr>
<tr>
<td>Amino acids</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**SECONDARY HOP METABOLITES**

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MAIN CLASSES OF HOP SECONDARY METABOLITES

- ALPHA ACIDS & BETA-ACIDS (4-35%)
- ESSENTIAL OIL (0.5-4.4%)
- POLYPHENOLICS (3-7%)

TASTE

FLAVOR

HEALTH

Bibbiano, 9 September 2012
MAIN CLASSES OF HOP SECONDARY METABOLITES

**ALPHA-ACIDS & BETA-ACIDS**
- RELATIVELY SIMPLE COMPOSITION
- PRECURSORS OF BITTERNESS AND OTHER BEER FEATURES
- BIOLOGICALLY ACTIVE

**ESSENTIAL OIL**
- VERY COMPLEX COMPOSITION
- DETERMINE BEER FLAVOR AND HOPPY AROMA
- BIOLOGICALLY ACTIVE

**POLYPHENOLICS**
- VERY COMPLEX COMPOSITION
- DETERMINE MOUTHFEEL AND OXIDATIVE STABILITY OF BEER
- POTENT BIOACTIVITIES

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CONTRIBUTIONS OF HOPS TO BEER

- Natural preservative
- Bitter taste
- Hoppy flavor
- Foam stability
- Aid in precipitation of proteins during wort boiling
- EXCLUSIVE HEALTH-BENEFICIAL PROPERTIES

- Light-induced decomposition: ‘Skunky flavor’
- Heat-induced decomposition: Oxidative off-flavors
Mechanism for Formation of the Lightstruck Flavor in Beer Revealed by Time-Resolved Electron Paramagnetic Resonance


Abstract

Time-resolved electron paramagnetic resonance (TREPR) data obtained during the photodegradation of iso-α-a-acids (isohumulones), the principal bittering agents from hops in beer, are presented and discussed. From the data, the photophysics leading to free-radical production as the primary step in the photodecomposition of iso-α-acids toward the development of “lightstruck” beer is explained. During laser-flash photolysis of iso-α-acids at 308 nm in undiluted lightstruck beer (3.5% v/v), TREPR spectra exhibit net spin-signals that are strongly upfield perturbed by the triplet mechanism of chemically induced electron spin polarization. The TREPR data show that although the first step, an excited-state triplet, is the primary light-absorbing chromophore, transient intermediary triple energy transfer process leads to Norlim type 1 compounds at a second site, an isohumulone triplet. The energy transfer mechanism is supported by additional TREPR experiments with chemically modified hop components. Structural parameters (hyperfine coupling constants, g-factors, fine widths) for the observed free radicals, obtained from computer simulations, are presented and discussed.

Introduction

Beer is a complex mixture consisting mainly of water and ethanol, with a fraction of about 0.5% voltech that contains over 200 different substances. These constituents are derived from various raw materials, principally barley malt, wheat, hops, and yeast. In an early stage of the brewing process, a solution of carbohydrates, called wort, is produced by enzymatic degradation of starch provided by barley malt and, in some cases, corn grains or rice. The boiling of the wort, with hops added at boiling again, produces a liquid called hopped wort in which fermentation takes place after addition of yeast. The components shown in Scheme 1, which are contained in the powdery lactic glands of female hop cones, are called iso-α-acids, and are generally present as a mixture of homologous (1α), isohumulone (1α), and adhumu-}

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2018 Leuven (Belgium)

[4] FULL ELUCIDATION OF BEER LIGHTSTRIK FLAVOR

FULL PAPER


FULL ELUCIDATION OF BEER LIGHTSTRIK FLAVOR


Mechanism for Formation of the Lightstruck Flavor in Beer Revealed by Time-Resolved Electron Paramagnetic Resonance


Abstract

Time-resolved electron paramagnetic resonance (TREPR) data obtained during the photodegradation of iso-α-a-acids (isohumulones), the principal bittering agents from hops in beer, are presented and discussed. From the data, the photophysics leading to free-radical production as the primary step in the photodecomposition of iso-α-acids toward the development of “lightstruck” beer is explained. During laser-flash photolysis of iso-α-acids at 308 nm in undiluted lightstruck beer (3.5% v/v), TREPR spectra exhibit net spin-signals that are strongly upfield perturbed by the triplet mechanism of chemically induced electron spin polarization. The TREPR data show that although the first step, an excited-state triplet, is the primary light-absorbing chromophore, transient intermediary triple energy transfer process leads to Norlim type 1 compounds at a second site, an isohumulone triplet. The energy transfer mechanism is supported by additional TREPR experiments with chemically modified hop components. Structural parameters (hyperfine coupling constants, g-factors, fine widths) for the observed free radicals, obtained from computer simulations, are presented and discussed.

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The typically bitter taste is due to the presence of the iso-α-acids in concentrations varying between 15 and 100 ppm (proportionally 1:2 to 1:1). Additionally, these acids contribute to the bacteriostatic properties of beer and they function as antiolastic in the formation of a stable foam head on beer.[5] Photolysis of the iso-α-acids is their pronounced light sensitivity. Exposure of beer to light causes the development of an offensive taste and a “shirty” odor termed the “lightstruck flavor.” This phenomenon has been reported in the literature as early as 1909,[6] but until now the detailed mechanism has not been unraveled. As the lightstruck flavor is not observed in unfiltered beers, hop-derived compounds play a prominent role in this process. As will be demonstrated in detail below, there is convincing evidence that photolysis of the iso-α-acids is a particular important, and, therefore, we have undertaken a study of their photolysis. In this paper, we present time-resolved electron paramagnetic resonance (TREPR) data that give significant details about the primary mechanism of this photochemical reaction. While steady-state EPR methods have been used to study oxidative
APPLICATIONS OF HOPS FOR BEER QUALITIES

- **EARLY HOPPING**
  - BITTERNESS
- **LATE HOPPING**
  - FLAVOR & AROMA
- **DRY HOPPING**
  - FLAVOR & AROMA
**HPLC-Analysis of the hop variety Golding (cleaned-up extract)**

- **Bitter acids**
  - **α-Acids (3 #)**
  - **β-Acids**

- **Prenylflavonoids**
  - **XANTHOHUMOL**
  - **DESMETHYLXANTHOHUMOL (DMX)**

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PIVOTAL REACTION IN BEER BREWING: ISOMERIZATION of HUMULONES or ALPHA-ACIDS (present in hop) to ISOHUMULONES or ISO-ALPHA-ACIDS (present in beer)

HUMULONES
R = CH₂(CH₃)₂: n-humulone
R = CH(CH₃)₂: cohumulone
R = CH(CH₃)CH₂CH₃: adhumulone

ISOHUMULONES
R = CH₂(CH₃)₂: iso-n-humulone
R = CH(CH₃)₂: isocohumulone
R = CH(CH₃)CH₂CH₃: isoadhumulone

Wort boiling with hops (average: 1.5 h): brewing practice
* conversion yields between 20% and 40%
* ratio cis/trans around 7/3

In alkaline media: hop processing companies
* conversion yields > 90%
* ratio cis/trans around 9/1

DISCOVERY OF ISOHUMULONES AT GENT UNIVERSITY
The bitterness of a beer is expressed as an EBU-value (‘European Bitter Units’), which corresponds more-or-less with the content of milligrams of isohumulones (iso-alpha-acids) per liter or ppm (parts-per-million). EBU-values vary from ca. 5 ppm to ca. 100 (?) ppm.

Threshold value for the bitterness of the isohumulones: ca. 4.5 milligrams per liter or ppm (comparable to quinine).
Absolute structures of hop-derived bitter acids revealed

THE
“DE KEUKELEIRE”-HOP STRUCTURES ARE USED IN ALL SCIENTIFIC PUBLICATIONS ON HOPS

STILL TODAY!!!
START OF HOP RESEARCH AT GENT UNIVERSITY

1947: Why is Saaz (Czech Republic) the finest hop in the world?

2012: Not clear yet why!
HOP “TERROIR”

- Precipitation: only 450 millimetres per year due to protection from north-western winds by surrounding mountains - ca. 260 millimetres during the period of hop growth

- Temperatures: average yearly temperatures: 8-9 °C and 14-16 °C during the period of hop growth

- Soil composition: Permian red (Perm period: 250-300 million years ago) in combination with sandy marl soil
  - Elevation: from 200 to 500 metres above sea level
  - Geography: wide open valleys with constant mild winds

“ZATECKY CHMEL” = SAAZ HOP

COMBINATION OF FACTORS UNIQUE IN THE WORLD !!!
HOP DISCOVERIES AT GENT UNIVERSITY

ISOHUMULONES (ISO-ALPHA-ACIDS)

HUMULONES (ALPHA-ACIDS), ISOHUMULONES (ISO-ALPHA-ACIDS): FULL STRUCTURES AND ABSOLUTE CONFIGURATIONS

TETRAHYDRO-ISOHUMULONES (TETRAHYDRO-ISO-ALPHA-ACIDS)

XANTHOHUMOL

8-PRENYLNARINGENIN or HOPEIN:
THE PHYTOESTROGEN IN HOPS

********************************************
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• Ca. 120 hop varieties (cultivars) are available

• All hop varieties are in fact the same plant species: *Humulus lupulus* L.

• By CLASSICAL BREEDING, novel and characteristic properties can be obtained for each hop variety or cultivar for example: *Humulus lupulus* L. cv. Nelson Sauvin

**HUMULONES (ALPHA-ACIDS)**
Do not occur elsewhere in the plant kingdom!!!

**EXCLUSIVELY IN HOP!**

**ISOHUMULONES (ISO-ALPHA-ACIDS) are unique!!!**

**EXCLUSIVELY IN BEER!**
**VOLATILES - ESSENTIAL HOP OIL**

**NON-VOLATILES - HOP POLYPHENOLICS**

- Individual components occur also in other plants
- The **QUALITATIVE COMPOSITION (WHAT?)** and the **QUANTITATIVE COMPOSITION (HOW MUCH?)** are different for each hop variety!

**FLAVOR AND AROMA (ESSENTIAL HOP OIL) AND HEALTH (HOP POLYPHENOLICS)** **ARE CHARACTERISTIC** **FOR EACH INDIVIDUAL HOP VARIETY!**
VERY COMPLEX: SEVERAL HUNDREDS OF COMPONENTS


EACH HOP VARIETY HAS A CHARACTERISTIC COMPOSITION

Hop: "secret" of beer!

************************************************

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Mainly terpenoid alcohols (linalool) and ketones (undecan-2-one)

FIG. 2. Total ion chromatogram (A) and selected ion monitoring (SIM) (B) of the sum of ions m/z 41 and m/z 69 of a citrussy hop fraction. (For chromatographic conditions, see Materials and Methods.)
HOP CONES

Pelletizing

HOP PELLETS

Extracting (liquid/supercritical CO₂)

HOP RESIDUE

Hop polyphenolics

Food supplements Phytoproducts

HOP EXTRACT

Hop bitter acids
Hop essential oil

ADVANCED HOP PRODUCTS

HOP FLAVOR PRODUCTS
EXTRACTION OF HOP USING LIQUID OR SUPERCRITICAL CO₂
(temperatures above 32 °C and pressures above 73 atm)
EXTRACTION OF HOP USING LIQUID OR SUPERCRITICAL CO$_2$ (temperatures above 32 °C and pressures above 73 atm)
CO$_2$-HOP EXTRACT

**Separation**

**ESSENTIAL OIL**
- citrussy
- estery
- floral
- herbal
- spicy
- woody

**HOP BITTER ACIDS**

**Liquid-liquid extraction**

**β-ACIDS LUPULONES**

**α-ACIDS HUMULONES**

**Fractionation**

**REDUCED ISO-α-ACIDS**

**REDUCED ISOHUMULONES**

**Alkaline isomerization**

**Reduction**
HOP-O-METER

- Detection of olfactory and sensorial properties of a specific hop variety
- Evaluation by trained panels
Sterling is an American hop variety with resemblances in flavor and aroma to the noble Saaz hop variety. Sterling has a ‘spicy‘ aroma, but not overwhelming, next to a number of other aromatic notes (Hop-o-Meter) with an alpha-content between 6% and 9%.
Amarillo is a relatively new American hop variety which may be considered a "super-Cascade" with an alpha-content between 5% and 11%.

The flavor profile is very citrussy (Hop-o-Meter).

This hop has been developed by Virgil Gamache Farms, Yakima Valley, Washington, USA.
HOP-O-METER
Flavor characteristics of American hop varieties for brewing SINGLE-HOP BEERS

CASCADE

GALENA

SIMCOE
CLASSICAL TYPES OF HOP VARIETIES

- **AROMA HOPS:** pleasant flavor, low content of $\alpha$-acids

- **BITTER HOPS:** high content of $\alpha$-acids, less pleasant flavor
  * High-$\alpha$-hops ($< 14 \% \alpha$): Brewer’s Gold, Cluster, Columbus Marynka, Northern Brewer, Premiant, Pride of Ringwood, Target …
  * Super-$\alpha$-hops ($> 14 \% \alpha$): Admiral, Chinook, Crystal, Galena, Herkules, Magnum, Millenium, Nugget, Taurus, Yeoman …

- **DUAL-PURPOSE OR AMBIVALENT HOPS**
  Challenger, Cascade, Cluster, East Kent Golding, First Gold, Northdown, Northern Brewer, Perle, Whitbread Golding …
CZECH REPUBLIC
Agnus, Kazbek, Premiant, Saaz Special, Sladek …

UNITED STATES
C-HOPS AND FLAVOR HOPS
Cascade, Centennial, Citra, Columbus …
Chinook, Cluster, Crystal …
Possible substitutes:
Amarillo, Galaxy, Simcoe, Sterling, Warrior …

GERMANY
Polaris, Hallertau Blanc, Mandarina Bavaria, Hüll Melon
POLARIS: up to 23 % alpha and 4.4 % essential oil !!!
# Novel German Hop Varieties

<table>
<thead>
<tr>
<th>Variety name</th>
<th>Aroma characteristic</th>
<th>Alpha acids</th>
<th>Total oil</th>
</tr>
</thead>
</table>
| Polaris (PA)           | intense fruity aroma  
                        |             | 19.0 - 23.0 %                 | 4.1 - 4.4 ml                 |
|                        | fresh minty notes                                    |             | per 100 g leaf hops           |                              |
| Hallertau Blanc (HC)   | flowery-fruity aroma  
                        |             | 9.0 - 12.0 %                  | 1.2 - 1.5 ml                 |
|                        | passion fruit, grapefruit, 
                        |             | per 100 g leaf hops           |                              |
|                        | gooseberry and pineapple                             |             |                              |                              |
| Mandarina Bavaria (MB) | fruity aroma  
                        |             | 7.0 - 10.0 %                  | 1.8 - 2.1 ml                 |
|                        | intense mandarin and citrus note                     |             | per 100 g leaf hops           |                              |
| Hüll melon (HN)        | fruity aroma  
                        |             | 6.9 - 7.5 %                   | 0.5 - 0.8 ml                 |
|                        | strawberry and honeydew melon nuances               |             | per 100 g leaf hops           |                              |
POLYPHENOLICS WITH INTERMEDIARY POLARITY - flavon-3-ols and glycosides (quercetin, kaempferol)

POLAR POLYPHENOLICS - oligomeric tannins - monomeric catechins - phenolic acids

LESS POLAR POLYPHENOLICS ‘TERPENOPHENOLICS’

HOP POLYPHENOLICS (HPLC ANALYSIS)

Hop variety Golding
Is wine healthy for you?
Is beer healthy for you?

BEER IS THE DRINK OF THE ORDINARY PERSON, THE LABORER ....
HEALTH OF WINE AND BEER

WINE

• ALCOHOL (in moderation!)
• GRAPE

BEER

• ALCOHOL (in moderation!)
• Malted Barley, possibly cereals, herbs, fruits …
• Hop (most important!)

Beer contributes to a good health in many more aspects than wine !!!
“Everything is toxic and it is only the dose that makes the poison” (Paracelsus – 1493-1541)

MODERATE BEER CONSUMPTION FITS INTO A HEALTHY LIFESTYLE

“Let food be your medicine” (Hippocrates – 460-377 BC)
HOP POLYPHENOLICS
(HPLC ANALYSIS)

Hop variety Golding

- Full mouthflavor
  - Anti-oxidant

- Anti-oxidant
  - Control of fat metabolism

- Phytoestrogenicity
  - Anti-cancer

- Bitter taste
  - Bacteriostatic
  - Anti-diabetic
  - Anti-inflammatory
THE HEALTH-BENEFICIAL PROPERTIES OF HOPS

PROVEN BY SCIENTIFIC AND BIOMEDICAL STUDIES IN REPUTED RESEARCH INSTITUTES ALL OVER THE WORLD USING CELL CULTURES, VARIOUS TEST ANIMALS AND/OR HUMANS

Sedative and sleep-promoting activity
Potent phyto-estrogenicity and hormonal regulation
Inhibition of cancer at all stages
Strong anti-inflammatory activity
Positive effects on diabetes type 2
Anti-osteoporetic activity
Liver protection
Powerful anti-oxidant features
Anti-bacterial and skin-softening properties
Control on metabolism of fats and cholesterol
Beneficial sexual implications
HOP IS A VERY RICH SOURCE
- “molecular fabric” – of "SPECIAL POLYPHENOLICS"

POLYPHENOLICS

special plant components of mixed biosynthetic origin
(combination of 3 biochemical pathways)
with pronounced biological activities
HOP GENOME
* Not known yet
  * Hemp genome: ca. 35,000 genes
  * Human genome: ca. 23,000 genes
  * Genomes of individual persons differ by only 1%
  * Genome of humans and monkeys differ by only 1%

HOP GENOME
* Will be similar to the hemp genome (Cannabaceae!)
  * Expectation: > 35,000 genes, i.e. 50% more complex than the human genome!!!

EACH STEP IN THE FORMATION OF SECONDARY METABOLITES IN THE HOP PLANT REQUIRES CONTROL BY AT LEAST 1 GENE FOR THE PRODUCTION OF A SUITABLE ENZYME

FOR THE FORMATION OF HUMULONES AT LEAST 10 ENZYMES ARE REQUIRED, THUS 10 GENES OR MORE ARE IN CONTROL
Humulones (Alpha-acids)

Polarity of many hop components

NON-POLAR

POLAR

C = carbon
H = hydrogen
O = oxygen
Mixed hydrophilic - hydrophobic (amphiphilic) properties ideally suited for:

- high affinities for biological membranes
- efficient bioavailabilities
- increased interactions with proteins
- potent biological activities
**BEER 2011**

- 1.9 billion hl - + 60 million hl, in particular China
  - China: 490 million hl
  - 4 biggest breweries: > 50 %
  - USA: 1,989 breweries - > 99 % craft breweries
  - Italy: 445 craft breweries!!!

**HOP 2011**

- Lowest alpha and lowest surface area since 1955 (48,500 ha)
  - Highest yields: > 2 tons/ha (100,604 ton) and highest alpha: > 10 % (10,348 tons)
  - Excess alpha: 10,000 tons or > 1 year stock

**POPULARITY OF NOVEL FLAVOR HOPS**

- Characteristic flavors and aromas
  - High alpha
ALL HEALTH-PROTECTING FEATURES OF HOPS ARE PRESENT IN BEERS !!!

BEER: THE ONLY ALCOHOLIC DRINK IN WHICH HOP IS PRESENT
<table>
<thead>
<tr>
<th>Hop cones</th>
<th>± 2 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hop pellets</td>
<td>± 56 %</td>
</tr>
<tr>
<td>Hop extracts</td>
<td>± 42 %</td>
</tr>
</tbody>
</table>

Beers brewed using hop cones or hop pellets contain **ALL components of hop** ↔ **++ HEALTHY**

**CRAFT BEERS**

Beers brewed using hop extracts or high-tech hop products contain **NOT ALL components of hop** ↔ **+ HEALTHY**

**BIG-SCALE LAGER BEERS**
IN SUMMARY

HOP IS AN ESSENTIAL INGREDIENT IN BEER

HOP IS THE CHAMPION IN THE PLANT KINGDOM FOR ITS SUPER-HIGH CONTENT OF SECONDARY METABOLITES

THE HUMULONES AND ISOHUMULONES ARE EXCLUSIVE FOR HOP AND BEER

HOP IS A PLANT WITH PERHAPS THE HIGHEST CONTENT OF SPECIAL POLYPHENOLICS

HOP EXHIBITS A WIDE SPECTRUM OF DIVERSE AND HIGHLY POTENT BIOLOGICAL ACTIVITIES

Bibbiano, 9 September 2012
As each hop variety is unique, a brewer can exploit its characteristic flavor and aroma to produce HAPPY, HEALTHY, HOPPY BEERS!!!
HOP-DERIVED COMPOUNDS IN BEER

USUALLY, LESS THAN 100 MILLIGRAMS PER LITER (ppm)

Isohumulones and derivatives: 5 – 100 (?) ppm
Special polyphenonics: few ppm
Essential oil components: variable

THE SPECIAL HOP POLYPHENOLICS DETERMINE TO A GREAT EXTENT THE HEALTH-BENEFICIAL PROPERTIES OF BEERS

BEER: RICHEST SOURCE OF THE SPECIAL HOP POLYPHENOLICS IN THE DIET

* Hopping regimen
* Choice of hop varieties
* Use of advanced hop products
* Brewing conditions

![Bar graph showing content of 8-PN (ppb) for different beers: A: 21, B: 21, C: 12, D: 11, E: 9, F: 9, G: 8.9, H: 0.](chart.png)