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DETERMINATION OF FREE HYDROCYANIC ACID IN HOMRMADE PRODUCED FRUIT BRANDIES

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INTRODUCTION

- Fruit brandy is a traditional alcoholic drink in the Republic of N. Macedonia, but also in other Balkan countries.
- Fruit brandys are produced by distillation of fermented fruits (plum, apricot, peach, apple, etc), traditioanally (homemade) or industrially.

INTRODUCTION

Chemical composition of brandy

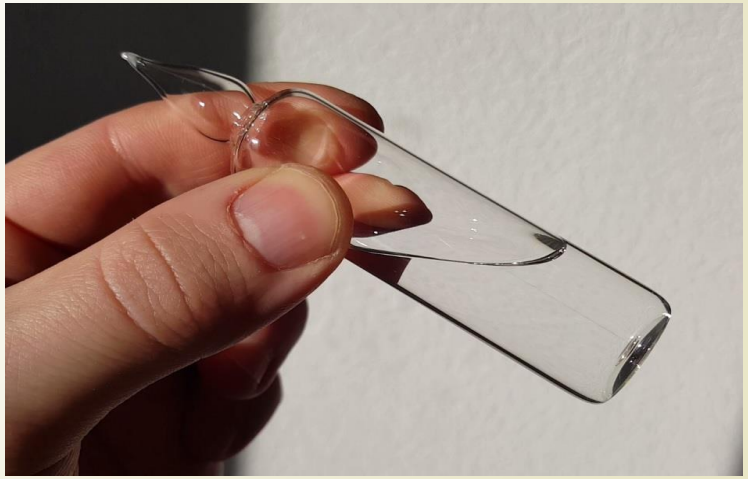
- Water
- Ethyl alcohol - C_2H_5OH (from 40 % to 50 %)
- Methyl alcohol – CH_3OH
- Aldehydes (acetaldehyde, formaldehyde, isobutylaldehyde, acrolein, etc.)
- Higher alcohols (isoamyl alcohol, propanol, hexanol, isobutyl alcohol, etc.)
- Esters (ethyl acetate, aromatic esters)
- Acetic acid and higher fatty acids
- Terpenes (geraniol, linalool, nerol, etc.)

INTRODUCTION

HYDROCYANIC ACID

- Hydrogen cyanide (also known as prussic acid) is a chemical compound with the formula HCN, It is a colorless, extremely poisonous, and flammable liquid.
- Gives bitter taste and almond aromas.
- A large number of stone fruits (apricot, plum) contain hydrocyanic acid
- Almonds have the highest content of hydrocyanic acid

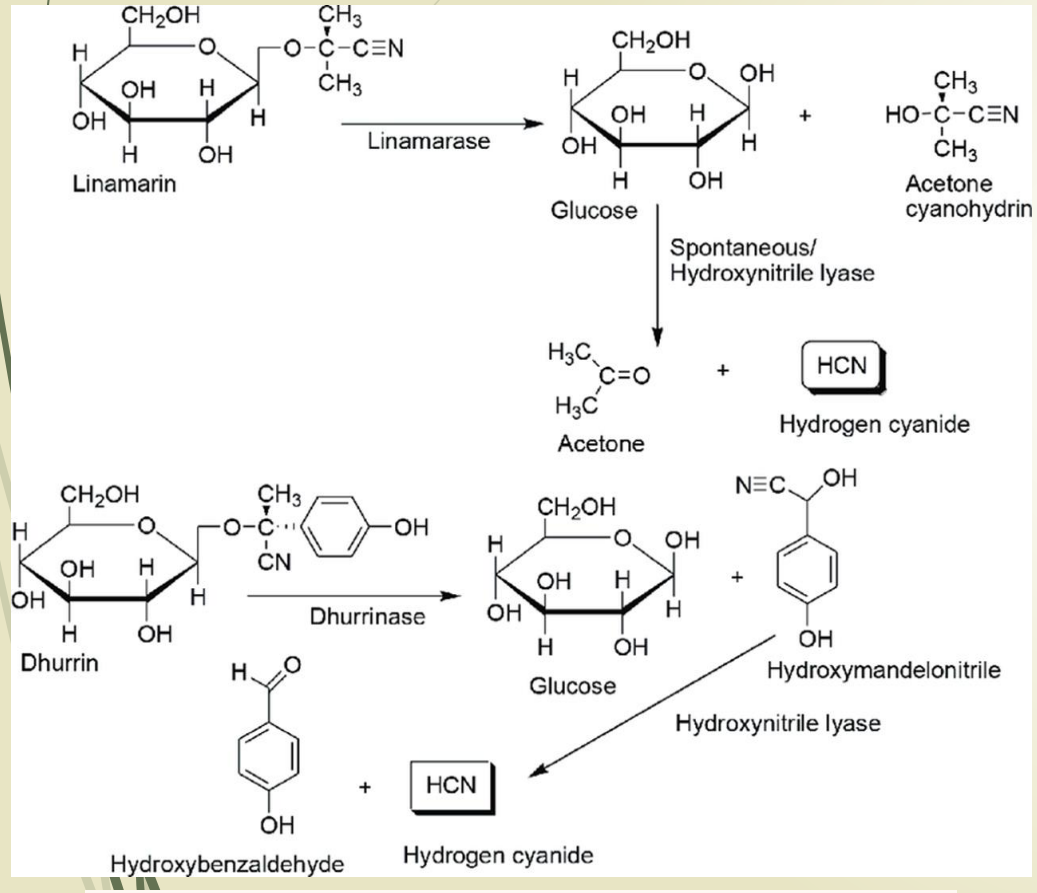
Structural formula of HCN



Pure hydrocyanic acid

INTRODUCTION

The hydrocyanic acid in brandies is produced:



Mechanism of the chemical reaction

- As a result of enzymatic hydrolysis of cyanogenic glycosides.
- During fermentation, the presence of fruit seeds.
- Enzymatic hydrolysis of cyanogenic compounds by β-glucosidases.
- Formation of sugars and cyanohydrin.
- Cyanohydrins can decompose spontaneously or in the process of enzymatic reaction during the fermentation, catalyzed by hydroxynitrile lyase
- Resulting in the formation of a keton or an aldehyd and free HCN.

INTRODUCTION

- The presence of free hydrocyanic acid in brandies is harmful and poisonous to humans.
- The permitted concentration of free hydrocyanic acid in distillates is 70 µg/L. When consuming alcoholic beverages with a higher content of hydrocyanic acid, various symptoms occur, such as:

  (headache, diarrhea, abdominal pain)

- Consuming distilled beverages with high levels of hydrocyanic acid can cause long-term serious liver problems and death.

AIM OF THE RESEARCH

- Determination of free hydrocyanic acid content in fruit brandies.
- Safety for consumption.
- Development of a fast and inexpensive method for the determination of free hydrocyanic acid

EXPERIMENTAL

24 samples of fruit brandies

- 6 brandies from Yellow plum (Prunus Americana).
- 6 brandies from Blue plum ((Prunus domestica).
- 6 brandies from Apricot (Prunus armeniaca).
- 3 brandies from Quince (Cydonia oblonga).
- 3 brandies from Apples (Malus domestica)

EXPERIMENTAL

- All samples were produced traditionally (homemade).
- Classical fermentation
- Classic distillation (copper pot)
- Obtained fruit brandies with an alcohol content of 40%

Classical fermentation of Plums

Classic distillation

Brandies originated from Maleshevia and Tikvesh region

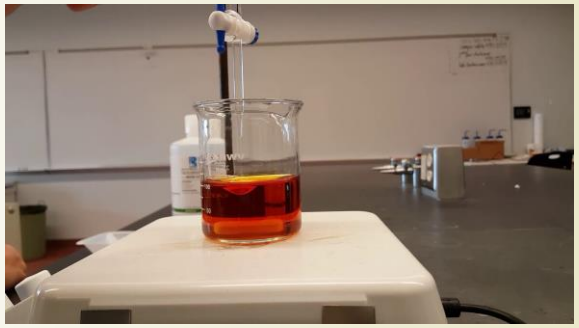
Eastern region and area of Maleshevia

Povardarie region, Tikvesh region

EXPERIMENTAL

- **Determination of the basic parameters of distillates**
- Alcohol content (Distillation)
- Total ester content (Distillation)
- Total aldehyde content (Iodometric)
- Content of total acids (Acidimetric)
- Ethyl acetate content (Spectrophotometric)
- Furfural content (Spectrophotometric)
- Methanol content (Spectrophotometric)
- Total SO_2 content (Iodometric)
- Higher alcohol content (Spectrophotometric)
- Total dry extract (Gravimetric)

Spectrophotometry



Iodimetry

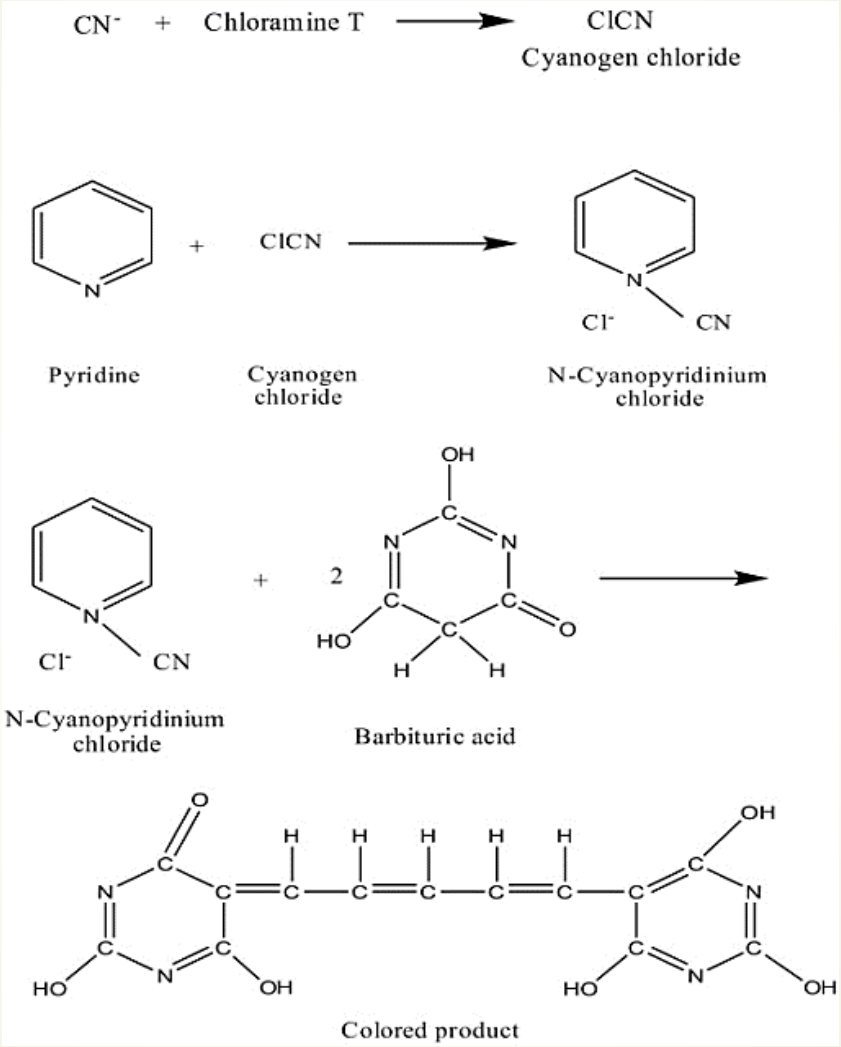
Pycnometery

EXPERIMENTAL

- Spectrophotometric determination of free hydrocyanic acid content
- Free HCN content was determined spectrophotometrically using pyridine-pyrazolon reagents.
- The method involves the conversion of HCN to cyanogen chloride with chloramine T solution.
- As a result of the reaction of this compound with a solution of pyridine and barbituric acid, coloured pinк complex is formed, which was spectrophotometrically measured at a wavelength of 490 nm.
- A series of standard solutions of $K_2[Zn(CN)_4]$ in range from 1 to 20 μg/L free HCN, needed to construct a calibration curve.
- Because the fruit brandy samples were colored dark yellow, before being analyzed they were distilled with water steam, in the presence of H_3PO_4.

EXPERIMENTAL

Fruit Brandy Samples



Colored pyridine-pyrazolon complex

Schematic representation of colored complex formation

RESULTS AND DISCUSSION

- **All samples had expected values for basic parameters**
- Alcohol content (39,4 vol % - 40,55 vol %)
- Total ester content (780 mg/L – 3450 mg/L)
- Total aldehyde content (144,2 mg/L – 305,4 mg/L)
- Content of total acids (0,1657 g/L – 1,2547 g/L)
- Ethyl acetate content (512,5 mg/L – 1860,4 mg/L)
- Furfural content (4,2 mg/L – 90,7 mg/L)
- Methanol content (0,32 vol % - 1,14 vol %)
- Total SO_2 content (6,42 mg/L – 12,5 mg/L)
- Higher alcohol content (1120,5 mg/L – 3780,7 mg/L)
- Total dry extract (1,11 g/L – 4,05 g/L)

RESULTS AND DISCUSSION

Sample-Apricot	Region	Free HCN (µg/L)
P-1	Berovo	8,787
P-2	Ratevo	7,882
P-3	Smojmirovo	9,372
P-4	Rusinovo	7,884
P-5	Kavadarci	2,465
P-6	Negotino	1,102

Sample-Plum (Blue)	Region	Free HCN (µg/L)
P-1	Berovo	0,118
P-2	Stip	0,145
P-3	Smojmirovo	0,214
P-4	Macevo	0,184
P-5	Kavadarci	0,101
P-6	Veles	0,111

Sample-Plum (yellow)	Region	Free HCN (µg/L)
P-1	Kocani	0,177
P-2	Stip	0,114
P-3	Smojmirovo	0,132
P-4	Rusinovo	0,157
P-5	Kavadarci	0,141
P-6	Negotino	0,222

Sample-Quince	Region	Free HCN (µg/L)
P-1	Berovo	0,191
P-2	Stip	0,011
P-3	Kavadarci	0,088

Sample-Apple	Region	Free HCN (µg/L)
P-1	Berovo	0,097
P-2	Stip	0,011
P-3	Kavadarci	0,084

CONCLUSION

- *Determination of the quality of homemade fruit brandies.*
- *Introduction of a cheap and rapid method for the analysis of hydrocyanic acid in brandies.*
- *A method that control laboratories in winerys and distilleries can afford.*

IMAKO

UNILAB

VINARIJA
ZVONKO BOGDAN

THANK YOU FOR YOUR ATTENTION