DETERMINATION OF FREE HYDROCYANIC ACID IN FRUIT BRANDIES PRODUCED UNDER INDUSTRIAL AND HOMEMADE CONDITIONS

Aleksandar Piperevski[1,2], *Violeta Dimovska[2], Atanas Runchev[1], Dejan Milanov[1]*
Aleksandar Runchev[3], Gjorgi Kukutanov[4]

[1]Imako Vino Winery, Mihajlo Apostolski 34/5 2000 Stip, North Macedonia
[2]Faculty of Agriculture, Goce Delčev University, Krste Misirkov 10A, 2000 Štip, North Macedonia
[3]Podrum Palić, Josipa Kolumba 33, 24413 Palić, Serbia
[4]Kukutanov Winery, Bela Crkva bb, 2420 Radovis, North Macedonia

ABSTRACT

Fruit brandy is a traditional alcoholic drink in the Republic of N. Macedonia, but also in other Balkan countries. The presence of free hydrocyanic acid in fruit brandies is a significant due to its toxicological effects on human health. HCN is a natural byproduct of fermentation and distillation processes, especially in fruit brandies produced from stone fruits (apples, cherries, plums) that contain cyanogenic glycosides. The determination of free hydrocyanic acid levels in fruit brandies is crucial for ensuring consumer safety and compliance with regulatory standards. In this study, the content of free hydrocyanic acid was determined in 10 homemade samples of fruit brandies and 10 samples of fruit brandies produced in industrial conditions (rectification column) in order to determine safety for consumption. The free HCN content was determined spectrophotometrically using a pyridine-pyrazolon reagent. From the obtained results it can be observed that the content of free hydrocyanic acid depends on the type of fruit (stone fruit or seed fruit), the type of fermentation, the contact time between the seed and the pulp during the fermentation as well as the distillation process (Balcerek & Szopa, 2012).

INTRODUCTION

Hydrocyanic acid (HCN), commonly known as hydrogen cyanide, is a highly toxic compound that can be found in various fruit products, especially fruit brandies. These brandies are made by distilling fermented fruits, such as apples, pears, plums, or cherries, which may naturally contain traces of cyanogenic compounds, primarily in the seeds. Hydrocyanic acid is formed in brandy during alcoholic fermentation as a result of enzymatic hydrolysis of cyanogenic glycosides present in the seeds of the fruit from which the brandy is produced. During the fermentation and distillation processes, as a result of enzymatic hydrolysis of cyanogenic glycosides, the formation of sugar and cyanohydrin occurs. Cyanohydrins can decompose spontaneously or in the process of enzymatic reactions during fermentation, catalyzed by hydroxynitrile lyase, resulting in the formation of a ketone or aldehyde and free HCN **Figure 1**. The determination of free hydrocyanic acid in fruit brandies is critical for assessing their safety for consumption.

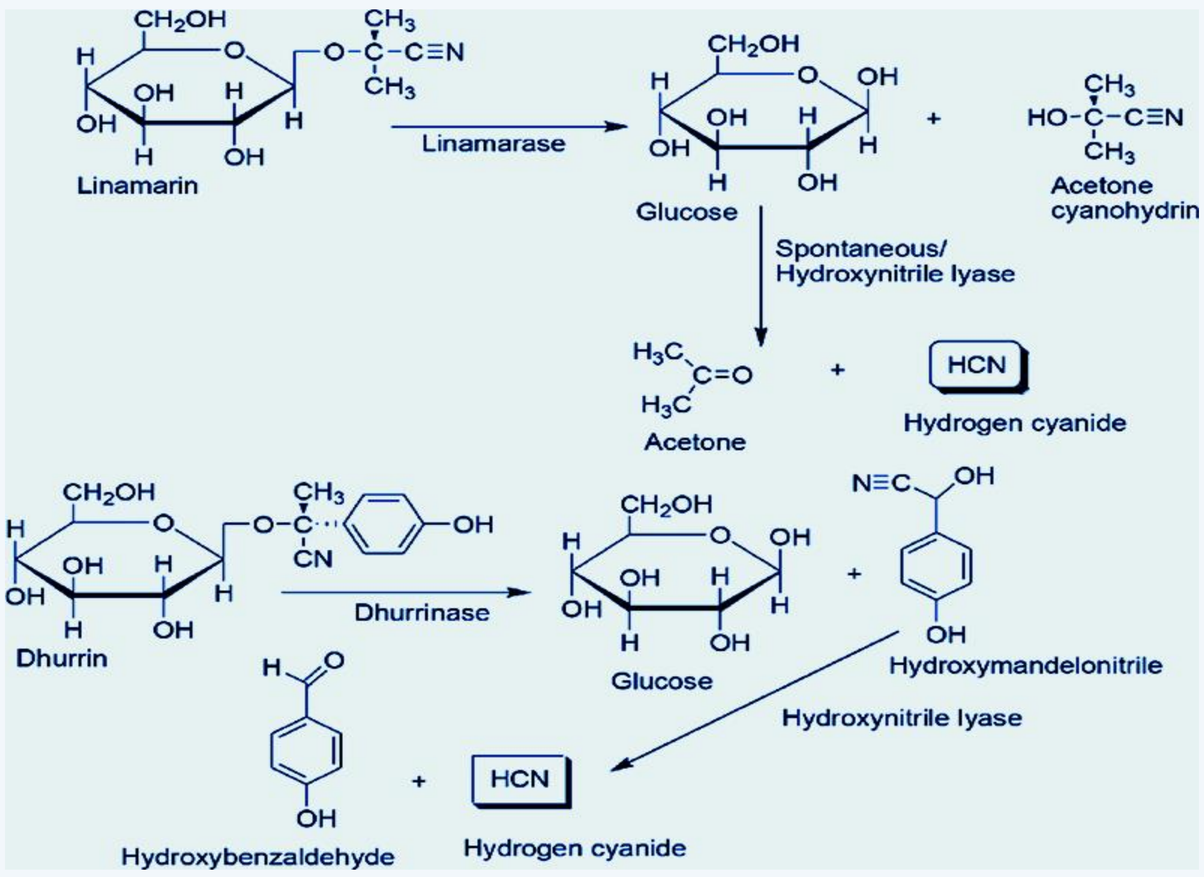

Figure 1. *Reactions of formation of free hydrocyanic acid during the fermentation process*

MATERIALS AND METHODS

5 samples of brandy produced from blue plums,
5 samples of brandy produced from yellow plums
Homemade conditions, collected by private producers
Traditional distillation was applied

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, colored pink 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 **Figure 2**.

Figure 2. *Fruit brandy samples and pyridine-pyrazolon complex formation*

RESULTS AND DISCUSSION

Sample-Plum (Blue)	Region	Free HCN (µg/L)	Sample-Plum (Yellow)	Region	Free HCN (µg/L)
P-1	Berovo	8,787	P-1	Kocani	0,177
P-2	Ratevo	7,882	P-2	Stip	0,114
P-3	Smojmirovo	9,372	P-3	Smojmirovo	0,132
P-4	Rusinovo	7,884	P-4	Rusinovo	0,157
P-5	Kavadarci	2,465	P-5	Kavadarci	0,141

Table 1. *Content of free HCN in homemade produced fruit brandy samples*

Sample-Plum (Blue)	Free HCN (µg/L)	Sample-Plum (Yellow)	Free HCN (µg/L)
P-1	0,022	P-1	0,012
P-2	0,019	P-2	0,019
P-3	0,033	P-3	0,013
P-4	0,025	P-4	0,017
P-5	0,015	P-5	0,020

Table 2. *Content of free HCN in industrially produced fruit brandy samples*

From the obtained results, it can be concluded that in industrially produced fruit brandies the content of free HCN (ranging from 0,012 µg/L to 0,033 µg/L) is lower compared to the content of free HCN in brandies produced under homemade conditions (ranging from 0,114 µg/L to 9,372 µg/L). Fruit brandies produced in industrial conditions have more controlled processes, such as fermentation distillation, and removal of toxic compounds. Industrial equipment uses more precise temperature controls and better separation methods It was also observed that all brandies contained free HCN below the maximum allowed limit (< 70 µg/L) and were safe for consumption.

MATERIALS AND METHODS

5 samples of brandy produced from blue plums
5 samples of brandy produced from yellow plums
Under industrial conditions (rectification column)
and controlled distillation conditions.

CONCLUSION

A fast, inexpensive, and easily applicable spectrophotometric method has been established for the determination and control of the content of free HCN in fruit brandies. This research highlight the importance of proper monitoring and control in the distillation process to ensure the safety and quality of fruit brandies, especially in homemade production, where the risk of higher cyanide levels may be more significant. Regular testing for HCN content is essential to meet safety standards and avoid potential health risks associated with cyanide toxicity in alcoholic beverages.

REFERENCES

Balcerek M., Szopa J. (2012). Ethanol biosynthesis and hydrocyanic acid liberation during fruit mashes fermentation, *Czech J. Food Sci*, **30**, 144–152.