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Full Length Research Paper

Prevalence of ethyl carbamate in spirits from different sources

Iwouno J.O and Igwe Victory

Department of Food Science and Technology, Federal University of Technology, P.M.B., 1526, Owerri, Imo State, Nigeria

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The amounts of ethyl carbonate (urethane) in some selected sources of ethyl alcohol distilled in Nigeria were evaluated. Three different sources of ethyl alcohol were purchased from major distributors in Aba. The ethyl alcohol samples were analyzed for glycosidic cyanide content and values obtained converted to urethane equivalent using linear regression equation as. Results obtained showed that all the ethyl alcohol samples evaluated contained glycosidic cyanide but at levels regarded as safe in human foods with values 16.59, 19.18, 20.53, 23.23, 33.755, 36.84 respectively for P1, P2, C1, C2, S1, S2. The corresponding urethane content ranged between 1.1–1.71 mg/120ml respectively coded as above are also regarded as safe.

Keywords: Urethane, distilled, ethyl alcohol, glycosidic cyanide.

INTRODUCTION

Ethyl carbonate or urethane (CAS) 51 – 79 – 6) is an ethyl ester of carbonic acid. It can be found in fermented food and beverages like spirits, wine, beer, bread, soy sauce and yoghurt; thus a byproduct of fermentation which occurs in fermented beverages (Conacher and Page, 1986; Dennis *et. al.*, 1989; Battaglia et al., 1992; Sen et al., 1993; Benson and Beland, 1997; Kim *et. al.*, 2000). The chemistry of action of ethyl carbamate is illustrated in figure 1.

Urethane is a white crystalline or granular powder and soluble in water (Anon, 1974a). One of the sources of urethane is by hydrolyzing ethanol to carbomyl phosphate and further to phosphoric acid and then urethane (Ough, 1976). According to Finar, (1951). It is anester of carbamic acid, and that urea in ethanol at elevated temperature produces urethane. It was reported that cyanides are precursors of ethyl carbamate (Aylott et al., 1987; Mackenzie *et. al.*, 1990; McGill and Morley, 1990). There are a number of precursors in food and beverages that can form ethyl carbamate including hydrocyanic acid, urea, citrulline, cyanogenic glucosides and other N-carbomyl compounds.

*Corresponding Author E-mail: detwinslatwins@yahoo.com

Cyanic acid reacts with ethanol to form ethyl carbamate (Harry *et. al.*., 1989; Mackenize *et. al.*, 1990; McGill and Morley, 1990) reported on the cyanide content and the corresponding ethyl carbamate content in an alcoholic beverage (5% V/V) as shown.

Cyanide (mg/100mg): 0.50, 3.75, 4.50, 13.30 and ethyl carbamate (mg/100g): 1:00, 7.50, 1.25, 1.75, and 2.25 respectively.

Therefore the aim of this present work was to determine the prevalence of ethyl carbamate in ethyl alcohol from different material origin of production. It will provide the impetus and frame work for more researchers in this area.

MATERIALS AND METHODS

The three spirit samples from different materials of production; Cassava, Sugarcane and Palm wine represented as C, S, P were purchased from major distributors in Aba, Abia state, Nigeria. All equipments used were obtained from the department of Food Science and Technology and Industrial Chemistry of the Federal University of Technology Owerri, Imo State. Other materials and reagents were of analytical grade and supplied by the same departments.

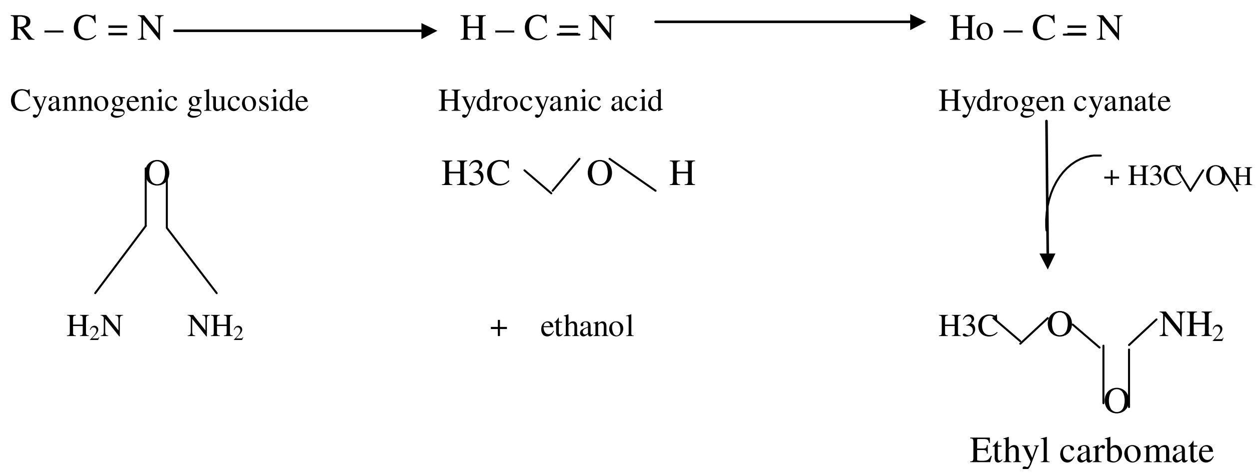

Figure 1. The formation of ethyl carbamate from ethanol and hydrogen cyanate (top) or from ethanol and urea (bottom).

Table 1. Cyanide and corresponding ethyl carbamate concentration

Measurable cyanide (mg/100g)	**Corresponding ethyl carbamate (mg/120mg)**			
X	Y	XY	X2	Y2
0.5	1.00	0.50	0.25	1.00
3.75	0.75	2.81	7.90	0.56
4.50	1.25	5.63	31.70	1.56
5.50	1.75	9.63	92.74	3.06
13.00	2.25	29.25	855.56	5.06

From (y = a + bx)

Determination of Ethyl Carbamate (Urethane)

Ethyl Carbamate content of chemical sample (ethyl alcohol) were determined first by determining the glycosidic cyanide content of the ethanol as described by FAO (1986) with little modification.

A 20ml of ethyl alcohol sample was transferred into 1 litre distillation flask then 200ml of distilled water and 10ml of orthophospohoric acid added. The flask was stopped, mixed and left for 12 hours (overnight) in an incubator (Gallykamp) at 38^{0}C. The flask was fitted to the distillation apparatus and diluted to the mark using distilled water.

A 100ml of the aliquot was pipetted into a beaker and 2ml of 5% potassium iodide solution and 1ml of 6N ammonia solution added. The mixture was titrated with 0.01N silver nitrate solution until permanent turbidity was observed. It is recommended that a black background should be used for easy recognition of the end point of titration. A Blank test under the same condition as in the sample determination but replacing the distillate with distilled water was carried out.

Calculation

Determination of hydrocyanic acid content

Hydrocyanic acid is amongst one of the precursors of ethyl carbamate thus hydrocyanic acid expressed in milligram of HCN of sample is equal t o

$$\frac{0.54(V_0 – V_1) \times 250 \times 100}{120} = \frac{112.5 (V_0 – V_1)}{m}$$

Where m = Mass of test portion (20)g

V_0 = Volume in ml of 0.01N silver nitrate solution used for the sample determination

V_1 = Volume in ml of 0.01N silver nitrate solution used for the blank test.

The table of result for cyanide and corresponding ethyl carbamate concentration by Aylott *et. al.*, (1990) was used to produce a regression equation as shown (Cass, 1971)

Skipping some mathematical steps; the required values of a and b may be found by solving the following pair of simultaneous equations.

$\Sigma Y = na + b\Sigma X$

$\Sigma XY = a\Sigma X + b\Sigma X^2$

From table 1, n = 5, therefore b = 0.01, and a = 1.346

Table 2. Measurable Cyanide content and the corresponding ethycarbamate (Urethan) content of ethyl alcohol samples.

Ethyl alcohol sample	Measurable cyanide content (mg/120ml)	Ethyl carbamate (mg/120ml)
C_1	20.53	1.55
C_2	23.23	1.57
P_1	16.59	1.51
P_2	19.18	1.53
S_1	33.75	1.68
S_2	36.84	1.71

The required regression equation is Y = a + bX
i.e Y = 1.346 + 0.01X

Therefore, if the value of X (i.e. measurable cyanide) is known, the corresponding value of Y (i.e. ethyl carbamate) can be calculated by substituting the value of X in the regression equation above.

RESULT AND DISCUSSION

Table 2 exhibits the cyanide against corresponding urethane content of the ethyl alcohol samples. All the ethyl alcohol samples tested contained measurable cyanide ranging between 16.59 – 36.84 mg/100ml of the sample and their respective ethyl carbamate content 1.51 – 1.71 mg/120ml of the sample. The glycosidic cyanide of all the samples analyzed were within such concentration of cyanide in food items, the foods or drinks are free from urethane (Aylott et al., 1990).

However beverages (i.e. beers and spirits) should not be stored under adverse conditions such as in the sun as most wholesalers, retailers, distributors do, and certainly storage period should not be prolonged to avoid possible conversion of cyanid to urethane which is possible with subsequent reaction overtime in the presence of heat (Wardlaw and Insel, 1996).

CONCLUSION

Nigeria alcoholic beverages especially the spirits and beers are not completely free from urethane. However, the traces of urethane observed are at safe levels. I advise that more research interest should be paid on this area of research since this work have provided the impetus and frame work.

Since the values for a and b are meant to be determined using the pair of simultaneous equation.

ΣY = na + bΣX

ΣXY = aΣX + bΣ2

Using the first values of the measurable cyanide (mg/120mg) and its corresponding ethyl carbamate (mg/120mg)

If X = 0.5, the Y = 1.00, and also from table 1, is ΣX = 27.25, Vy = 7.00, Σxy = 47.82, ΣX2 = 988.15, Σy2 = 11.24

Substituting Σy = 1.00, n = 5, Σx = 27.25 in equation (1)

7 = 5a + 27.25b

:. 47.82 = 27.25a + 988.15b

Therefore, solving equation (3) and equation (4) simultaneously to obtain the values of a and b.

7 = 5a + 27.25b

47.82 = 27.25a + 988.15b

Multiplying equation (3) by 27.2b and equation (4) by 5

:. 7(27.5) = 5(27.5)a + 27.25(27.5)b

47.82(5) = 27.25(5)a + 988.15(5)b

190.75 = 136.25a + 742.56b

239.10 = 136.25a + 4940.75b

Substracting equation (6) from equation (5) to eliminate "a"

48.35 = 0 + 4198.19b

48.35 = 4198.19b

$$B = \frac{41.35}{4198.19} = 0.01$$

b = 0.01

Therefore substituting b = 0.01 in equation (3) so that "a" will be obtained as follows;

7 = 5a + 27.25(0.01)

7 = 5a + 0.2725

7 – 0.2725 = 5a

$$a = \frac{6.7275}{5} = 1.3455 \approx 1.346$$

a = 1.346

Therefore a = 1.346 and b = 0.01

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