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Contamination of Alcoholic Products by Trace Quantities of Ethyl Carbamate (Urethane)

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Ethyl carbamate (carbamic acid-ethyl ester), or urethane as it is more commonly known, has previously been identified at low microgram quantities (ug/kg:ppb) in wines (Walker et al. 1974; Joe et al. 1976) and other fermented products such as beer, ale, sake, olives, soy sauce and yogurt. Although low levels of ethyl carbamate are known to occur naturally as a result of the fermentation process, elevated levels of ethyl carbamate have also been observed when the antimicrobial agent diethyl pyrocarbonate is used or where urea is used as a nitrogen source (Lofroth 1971; Ough 1976 a,b). More recently, ethyl carbamate has been identified in various fermented beverages and distilled products commercially available, (Cairns et al. 1987; Clegg et. al. 1987). Urethane is recognized as a carcinogen (Nettleship et al. 1943; Mirvish 1968) and several Federal regulatory agencies have examined the possibility of limiting levels present in alcoholic beverages (Conacher 1987; Food Chemical News 1986). More specifically, the Canadian Department of Health and Welfare established guidelines limiting amounts of ethyl carbamate in alcoholic beverages. The levels are as follows: wines, 30 ug/L, fortified wines (sherries and ports, 100 ug/L; distilled spirits, 150 ug/L; fruit brandies and liqueurs, 400 ug/L (Conacher 1987).

The following report summarizes concentrations of ethyl carbamate found in a variety of commercial products and examines the potential sources or contributing factors associated with formation of elevated levels of ethyl carbamate in these products.

MATERIALS AND METHODS

The various samples used for analysis in this study were products commercially available at Liquor Control Board of Ontario (LCBO) stores and represented both local and imported products.

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The majority of samples were sent to our laboratory for the analysis of ethyl carbamate under the regulatory program established by Health and Welfare Canada. Since these samples were being tested soon after the problem was identified, ie. when products required certificates of analysis, the data base is probably biased towards more positive (higher) results and does not necessarily reflect levels of ethyl carbamate currently found in alcoholic beverages.

The analytical procedure used was identical to that previously reported (Clegg and Frank 1987) with the final determinations and quantitation being made by capillary gas chromatography-mass spectrometry (GC/MS).

RESULTS AND DISCUSSION

The concentrations of ethyl carbamate found in 861 samples representing the various categories of alcoholic beverages are given in Tables 1 and 2. A number of other miscellaneous products were analyzed and are reported in Table 3.
According to the data presented in Table 1, 15% of white wines tested were above the permitted level of 30 ug/L whereas only 5.9% of red wines tested were greater than the guideline value. In the majority of samples it was also noted that these wines were fermented with urea as a nitrogen source with two of these wines having concentrations of ethyl carbamate of 770 and 1800 ug/L.

A number of sparkling wines and champagnes were analyzed and no residues of ethyl carbamate were detected greater than 10 ug/L. Two wine coolers as well as four grape concentrates (2 red and 2 white) were analyzed and no residues of ethyl carbamate were detected.

The results of the analyses of a number of sherries and ports are also given in Table 1. In contrast to the wines, a greater number of sherries and ports were above the established guideline of 100 ug/L. A total of 34% of the sherries and 37% of the ports were identified as containing elevated levels of ethyl carbamate. One port showed a concentration of 830 ug/L (ethyl carbamate) after barrel aging. In comparison, a similar port which had been aged in stainless steel showed a residue of only 170 ug/L. These results and other preliminary findings (Clegg 1986) indicate a potential for elevated levels of ethyl carbamate following heat treatments and/or barrel aging. Also in Table 2 a total of seven vermouths were analyzed and 57% (4) were found to contain levels of ethyl carbamate greater than 100 ug/L.

In-house experiments showed that when wines were heat-treated under reflux conditions, elevated levels of ethyl carbamate were observed. For example, a white wine with an initial concentration of 400 ug/L ethyl carbamate was heated for an extended period of time and the level of ethyl carbamate increased to 28000 ug/L after 20 hours. This may indicate that precursors are present in the wine and through a heat process elevated levels are formed.

This chemical formation of ethyl carbamate is concomitant to levels of ethyl carbamate formed following fermentation or microbial processes.

To examine the potential for ethyl carbamate formation, various other factors were examined. Copper as a trace contaminant or available as a result of copper distillation kettles has been thought to contribute to elevated levels of ethyl carbamate by potentially acting as a catalyst. Pesticides have also been implicated, i.e. the presence of the parent pesticide and/or their

Table 1. Distribution of ethyl carbamate concentrations observed in wines and fortified wines

	Concentrations (ug/L)					
WINES[1]	<10	10-30	31-100	>100	Total	%Positive[3]
White wines	151	15	16	14	196	15
Red wines	44	4	3	0	51	5.9
Sparkling wines	14	0	0	0	14	0
Wine coolers	2	0	0	0	2	0
Grape Concentrates (white & red)	4	0	0	0	4	0
				Total	267	

FORTIFIED WINES	<10	11-50	51-100	101-200	>200	Total	% Positive[3]
Sherries	50	52	68	48	38	256	34
Ports	15	7	14	8	13	57	37
Vermouths	0	1	2	4	0	7	57
				Total		320	

1 - Guideline level of 30 ug/L (ppb)
2 - Guideline level of 100 ug/L (ppb)
3 - Percentage of samples greater than guideline levels

corresponding degradation or decomposition products may contribute to levels of ethyl carbamate. Therefore several samples were analyzed that addressed these conditions i.e. they were fortified with copper, urea, and the pesticides captan, EBDC's and carbaryl. Under the same experimental conditions indicated above, the addition of copper and pesticides such as captan, EBDC's and carbaryl did not result in elevated levels of ethyl carbamate. On the other hand, the addition of urea was found to increase concentrations under these conditions. This is in agreement with earlier works (Ough 1972a).

The results of the analyses of various distilled products are given in Table 2. It is interesting to note that while detectable levels of ethyl carbamate were observed in all types of distilled products (except vodkas and gins), levels above the guideline of

Table 2. Ethyl carbamate levels in distilled products and fruit brandies and liqueurs

	Level (ug/L)				
DISTILLED PRODUCTS[1]	<50	51-150	>150	Total	% Positive[3]
Canadian whiskey	14	4	0	18	0
Rum	15	5	0	20	0
Vodka	5	0	0	5	0
Gin	4	0	0	4	0
Scotch whiskey	6	1	0	7	0
Bourbon whiskey	3	7	9	19	47
			Total	73	

	<50	51-200	201-400	>400	Total	%Positive[3]
FRUIT BRANDIES & LIQUEURS[2]	49	17	34	23	123	19

1 - Guideline level of 150 ug/L (ppb)
2 - Guideline level of 400 ug/L (ppb)
3 - Percentage of samples greater than guideline level.

Table 3. Distribution of ethyl carbamate concentrations in 72 miscellaneous alcoholic products

	Concentrations (ug/L)					
	<10	11-50	51-100	101-150	>150	Total
Blending agents[1]	4	21	4	1	14	44
Alcohols[2]	11	0	0	1	1	13
Mashes[3] (i)	10	0	0	0	0	10
(ii)	6	0	0	0	0	6
(iii)	0	0	0	0	5	5
					Total	78

1 - Blending agents were diluted
2 - Alcohols found positive were synthetic alcohols
3 - Mashes (i) corn mash
(ii) cherry mashes prior to distillation
(iii) cherry mashes after distillation.

150 ug/L were observed only in Bourbon whiskies. It is not understood why these differences occur but the type of mashes used and/or the distillation processes involved in the production of these products may lead to formation of ethyl carbamate. One interesting note with respect to bourbons was that ethyl carbamate was not detected in any mashes that were analyzed prior to distillation (See Table 3). This finding supports a hypothesis that ethyl carbamate may be formed during the distillation process

or through thermal processes.

The results of the analyses of various fruit brandies and liqueurs are also given in Table 2. A total of 19% of those samples analyzed were above the permitted level of 400 ug/L. The interesting trend observed in these analyses was that those products distilled from pitted fruit, i.e. cherries or peach, rather than non-pitted fruit, such as apple or pear were found to contain elevated levels of ethyl carbamate. The association of pitted fruit and the distillation process to ethyl carbamate formation is also indicated in the results shown in Table 3. A total of six cherry mashes were analyzed prior to distillation and no residues of ethyl carbamate were detected. Residues of ethyl carbamate were only observed following distillation.

The results of the analyses of other miscellaneous products for ethyl carbamate are given in Table 3. No tolerances were established for these types of products but it may be assumed that tolerances would be that of the end product. Although 14 blending agents analyzed showed residues greater than 150 ug/L, these products were intended for blending and dilution to various product specifications. The highest level observed was 320 ug/L and even though this would contribute to the levels of ethyl carbamate present in final product, the blending and dilution steps would ensure compliance to the guideline of 150 ug/L for distilled products. Since many products are diluted with alcohol a number of alcohol samples were analyzed and these results are reported in Table 3. Only two alcohols were found to contain residues of 120 and 180 ug/L, respectively. Although the ultimate end use of these alcohols was not identified, it was known that these alcohols were synthetically produced by commercial processes. Several high proof alcohols and high proof molasses spirits were analyzed and levels were found to be less than 10 ug/L. These low levels are most likely attributed to the high degree of purification conferred by such distillations.

Further work is in progress to identify the sources of ethyl carbamate, i.e. potential precursors and specific production conditions that contribute to elevated levels of ethyl carbamate found in various alcoholic beverages.

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