1,2,3,4-Tetrahydro-β-carboline-3-carboxylic Acid and 1-Methyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylic Acid in Wines

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1,2,3,4-Tetrahydro-β-carboline-3-carboxylic acids were analyzed in 16 table wines, 34 old and new dessert and aperitif wines, 8 sparkling wines, 18 distillates, and 5 grape juices. The concentration found ranged from 0 to 17.8 mg/L for 1-methyl-1,2,3,4-tetrahydro-β-carboline-3-COOH (MTCA) and from 0 to 0.65 mg/L for 1,2,3,4-tetrahydro-β-carboline-3-COOH (THCA). Higher concentration was generally found in fortified wines than in table wines and very low or no concentration at all in distillates and grape juices. No correlation was detected between the two tetrahydro-β-carboline-3-COOHs and the concentration of tryptophan or acetaldehyde in the wines. However, a good correlation in the formation of tetrahydro-β-carboline-3-COOH was found when tryptophan or tryptophan and acetaldehyde were added to a sherry and a white wine, respectively. This may be due to the blocking effects of sulfur dioxide that would be variable from wine to wine. This effect will be reported on later.

INTRODUCTION

1,2,3,4-Tetrahydro-9*H*-pyrido[3,4-*b*]indole (1,2,3,4-tetrahydro-β-carboline) is synthesized as a product of the reaction between an indole amine and aldehydes. The reaction between tryptophan and aldehydes forms tetrahydro-β-carboline-3-carboxylic acids. Tetrahydro-β-carbolines have been reported as possible neurotransmitters or neuromodulators and have been related with alcoholism (Buckholtz, 1980; Beck et al., 1982; Tuomisto et al., 1982; Bosin et al., 1986). Tetrahydro-β-carbolines can also be postulated as possible precursors of β-carboline-3-carboxylate, a benzodiazepine receptor antagonist (Braestrup et al., 1980).

1-Methyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid has been reported as a precursor of mutagenic *N*-nitroso compounds when tested in Ames test using *Salmonella typhimurium* (Wakabayashi et al., 1983, 1984). Valin et al. (1985) studied the mutagenicity of some tetrahydro-β-carbolines after nitrosation reaction. Tetrahydro-β-carbolines can react with nitrite already in foods, in the mouth, or in the stomach, giving rise to mutagenic compounds. Salvi and Choughuley (1990) reported the nitrosation of some food-related tetrahydro-β-carboline-3-carboxylic acids.

Endogenous formation of tetrahydro-β-carbolines after ingestion of alcohol, along with diets containing tryptophan, has been pointed out (Valin et al., 1985). Tetrahydro-β-carbolines have also been reported in different foodstuffs such as cheese, soy sauce, smoked foods, and also human milk (Adachi et al., 1991; Papavergou and Clifford, 1992) and in alcoholic fermentation products such as sake, beer, wine, and distillates (Beck and Holmstedt, 1981; Beck et al., 1983; Bosin et al., 1986; Adachi et al., 1991). The ingestion of those products can increase the level of these compounds in the human diet. Therefore, more research concerning the composition of tetrahydro-β-carbolines in foods and beverages, along with the determination of the factors influencing their formation during processing, is still needed.

This paper reports the concentration of several tetrahydro-β-carboline-3-carboxylic acids in table and dessert wines as well as distillates and discusses chemical and technological factors influencing the composition of these compounds in beverages.

MATERIALS AND METHODS

Tetrahydro-β-carboline-3-carboxylic Acid Used as Reference. 1-Methyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid (MTCA) and L-tryptophan were purchased from Sigma. Acetaldehyde was purchased from Fisher, formaldehyde from Baker Chemicals, propionaldehyde from Kodak, and isovaleraldehyde from Aldrich. The diastereoisomeric mixture of (−)-(1*S*,3*S*)-methyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid (*S*,*S*-MTCA) and (−)-(1*R*,3*S*)-methyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid (*R*,*S*-MTCA) was obtained by acidic catalyzed reaction from tryptophan and acetaldehyde (Jacobs and Craig, 1936; Brossi et al., 1973). 1,2,3,4-Tetrahydro-β-carboline-3-carboxylic acid (THCA) was synthesized in the same manner from L-tryptophan and formaldehyde. 1-Ethyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid was obtained as before from L-tryptophan and propionaldehyde and 1-isobutyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid (IBTCA) from L-tryptophan and isovaleraldehyde. Confirmation of structures was carried out by ^{1}H NMR and ^{13}C NMR.

Samples Analyzed for Tetrahydro-β-carboline-3-COOH. Samples of table wines, fortified wines, including very old and new U.S. and Spanish sherries, ports, vermouths, marsalas, cream sherries, and sparkling wines, grape juices and distillates were collected from different sources and from the Department of Viticulture and Enology, University of California, Davis. Samples were stored in a cold room (0 °C) until analysis for tetrahydro-β-carbolines.

Isolation of Tetrahydro-β-carbolines. An aliquot of 5 mL (up to 20 mL) of sample was spiked with 1 mL of the internal standard 1-ethyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid solution (ETCA) (10 μg/mL). Semicarbazide was added at 1 mg/mL to avoid any formation of artifacts as previously was indicated (Bosin et al., 1986). The sample was acidified to pH 2–2.5 with some drops of 1 N hydrochloric acid and loaded onto benzenesulfonic acid-derivatized silica SCX cartridges (Bond Elut, 3-mL size, Varian, Harbor City, CA) following the procedure reported by Adachi et al. (1991). The columns were previously conditioned with 6 mL of methanol and 6 mL of 0.1 N HCl. After samples were loaded, the columns were washed with 6 mL of 0.1 N HCl, 2 mL of methanol, and 6 mL of HPLC water and rinsed by 2 mL of 0.4 M phosphate buffer, pH 9.1. Tetrahydro-β-carboline-3-carboxylic acids were eluted with 4 mL of a mixture (1:1) of methanol and 0.4 M phosphate buffer, pH 9.1. The eluates

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were collected and filtered through 0.45-μm nylon membrane syringe filters for HPLC analysis.

Thin-Layer Chromatography. Thin-layer chromatography (TLC) was carried out in silica gel plates with some of the samples of tetrahydro-β-carbolines obtained. Twenty percent of methanol in 50 mM buffer ammonium phosphate monobasic, adjusted to pH 3 with phosphoric acid, was used as chromatographic eluent.

High-Performance Liquid Chromatography. A Hewlett-Packard (Santa Clara, CA) 1090 HPLC apparatus with diode array detector and a fluorescent detector was used for analysis of tetrahydro-β-carboline-3-carboxylic acids. A Hewlett-Packard 9000 Chem-Station was used for data processing. An ODS Hypersil narrow-bore column (200 × 2.1 mm, 5-μm particle size, Hewlett-Packard) was used for the separation of the tetrahydro-β-carbolines. Column oven temperature was kept at 40 °C for all separations. Fluorescence detection was carried out at 270 nm for excitation and at 343 nm for emission. The photomultiplier gain was set at 13. The mobile phase was filtered through 0.45-μm membrane filters (Millipore, Bedford, MA) and degassed with helium. Solvent A was 50 mM ammonium phosphate monobasic, pH adjusted to 3.0 with 85% phosphoric acid. Solvent B was 20% A in acetonitrile. Ammonium phosphate, phosphoric acid, and acetonitrile were of HPLC grade purchased from Fischer Scientific (Fair Lawn, NJ). The water was of HPLC grade, purified by a Milli-Q water system (Millipore). The separation gradient was 100-40% of A from 0 to 10 min and then 40-0% A from 10 to 12 min. Tetrahydro-β-carbolines eluted within 10 min. The column was then washed with 100% solvent B for 5 min and equilibrated with solvent A before the next sample was injected. The flow rate was 0.45 mL/min, and injection volume was 5 μL.

Calibration Curves for Quantification of Tetrahydro-β-carbolines. Standard solutions of tetrahydro-β-carboline-3-carboxylic acids with 0.2, 0.5, 1.0, 2.0, and 4.0 mg/L were prepared in 12% ethanol/water. To a 5 mL of each standard was added 1 mL of internal standard spiking solution (10 μg/mL of 1-ethyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid). For these calibration curves, the isolation procedure of Adachi et al. (1991) was followed. The calibration curves obtained from these by HPLC were linear in the interval of concentration considered (r higher than 0.99).

Analysis of Tryptophan and Acetaldehyde. Tryptophan was analyzed by direct injection of the wine following the same chromatographic procedure reported for tetrahydro-β-carboline-3-COOHs.

Acetaldehyde was analyzed by direct injection of wine in a glass column packed with 80/120 Carbopack B Aw/5% Carbowax 20 M, 183 cm × 2 mm i.d. (Supelco). The chromatographic conditions were 105 °C isothermal temperature in the oven and 150 °C for injector and detector temperatures. The gas chromatograph was a Hewlett-Packard 5710A with flame ionization detector. A Hewlett-Packard 3396A integrator recorded the values.

RESULTS AND DISCUSSION

Figure 1A shows the chromatogram of a synthetic sample of standards tetrahydro-β-carboline-3-COOH, THCA, MTCA, ETCA, and IBTCA as well as tryptophan. The two diastereoisomers of MTCA, (1*S*,3*S*)-MTCA and (1*R*,3*S*)-MTCA, are also shown in the chromatogram. The diastereoisomer ratio for 1-methyl-1,2,3,4-tetrahydro-β-carboline-3-COOHs synthesized in the laboratory was 8.6. 1-Ethyl-1,2,3,4-tetrahydro-β-carboline-3-COOH (ETCA) appears also as a mixture of diastereoisomers with a ratio of 12.8, but the diastereoisomer ETCA used as internal standard was the peak in the highest concentration. Parts B, C, and D of Figure 1 show the chromatograms of a wine, sherry, and cream sherry, respectively. The method used for the isolation of tetrahydro-β-carboline-3-COOHs, first reported by Adachi et al. (1991), provides a clean chromatogram of these compounds without any interferences of other fluorescent compounds in the wine samples.

The importance of avoiding artifact production during the isolation and analysis of these compounds has been noted (Bosin et al., 1982, 1986). The isolation method used showed absence of artifacts when standards of tryptophan (40 mg/L) and acetaldehyde (160 mg/L) in ethanol 12% and pH 3.5 were passed promptly through the column. Recoveries of the tetrahydro-β-caroline-3-carboxylic acids were in excess of 95% and in agreement with previous results (Adachi et al., 1991). Identification of tetrahydro-β-carboline-3-COOH compounds in wine was reported previously by coupling HPLC to MS (Adachi et al., 1991) or by MS after the HPLC peaks were collected

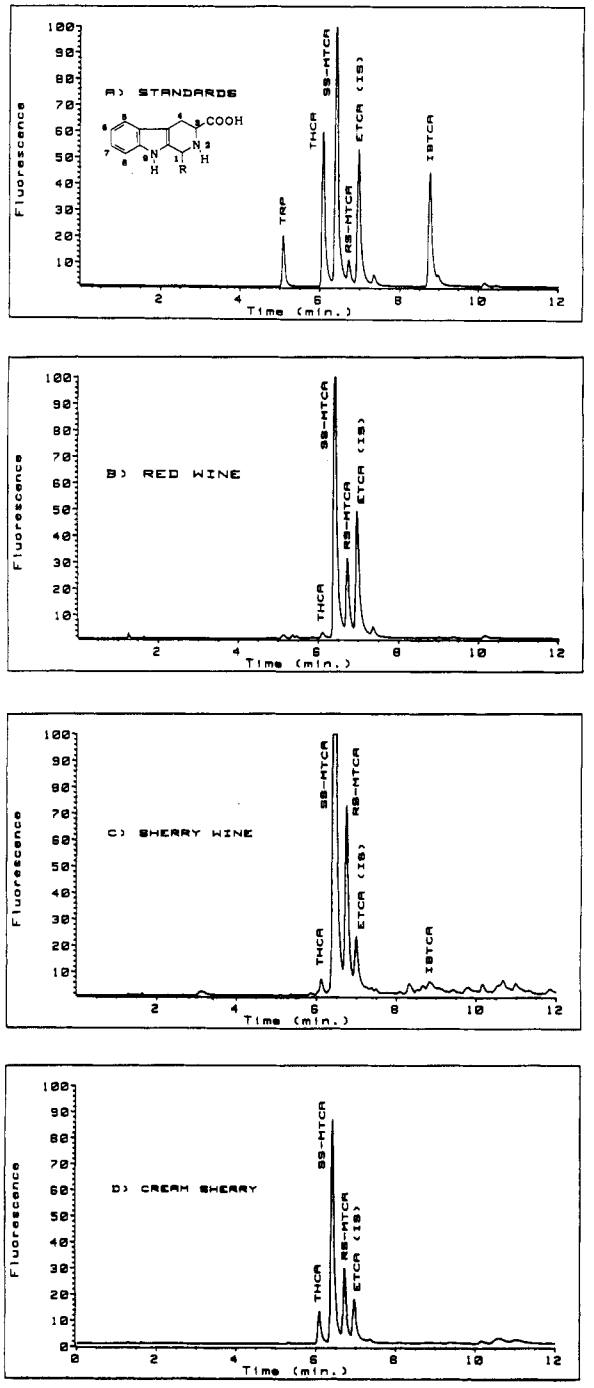

Figure 1. Tetrahydro-β-carboline-3-COOH HPLC chromatograms of a standard mixture (A), red wine (B), sherry wine (C), and cream sherry (D). TRP, tryptophan; THCA, 1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid; SS-MTCA, (1*S*,3*S*)-1-methyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid; RS-MTCA, (1*R*,3*S*)-1-methyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid; ETCA, 1-ethyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid (internal standard); IBTCA, 1-isobutyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid. The diastereoisomers were assigned as in Adachi et al. (1991) and Bosin et al. (1986).

Table I. Concentration of Tetrahydro-β-carboline-3-COOHs in Table and Sparkling Wines and Grape Juices

		tetrahydro-β-carboline-3-COOHs, mg/L							
sample	n^a	THCA	SD[b]	*S,S*-MTCA	SD	*R,S*-MTCA	SD	*S,S*-MTCA/*R,S*,MTCA[a]	SD
table wines									
Sauvignon blanc	3	0.05	0.012	1.16	0.18	0.32	0.05	3.6	0.1
Pinot blanc	3	0.13	0.035	3.79	0.90	1.11	0.35	3.5	0.3
Chardonnay	2	0.02	0.0	1.73	0.26	0.45	0.05	3.8	0.1
Pinot noir	1	0.0		1.42		0.36		3.9	
Ruby Cabernet	2	0.025	0.005	1.81	0.06	0.60	0.04	3.0	0.1
Cabernet sauvignon	4	0.022	0.004	0.43	0.09	0.10	0.02	4.2	0.2
1935 Cabernet sauvignon	1	0.1		1.38		0.38		3.6	
total av $\bar{x}$	16	0.05	0.046	1.65	1.2	0.47	0.37	3.7	0.4
red wine av $\bar{x}$	7	0.034	0.03	0.96	0.63	0.28	0.22	3.7	0.6
white wine av $\bar{x}$	9	0.07	0.05	2.19	1.3	0.61	0.41	3.7	0.2
table wine range	16	0.0–0.18		0.31–4.98		0.10–1.58		2.9–4.6	
sparkling wines									
Chardonnay	4	0.13	0.046	3.63	0.45	1.01	0.11	3.6	0.1
Pinot noir	4	0.16	0.048	2.23	0.48	0.61	0.15	3.7	0.24
total av $\bar{x}$	8	0.15	0.05	2.93	0.84	0.81	0.24	3.6	0.19
sparkling wine range	8	0.08–0.21		1.55–4.39		0.43–1.19		3.4–4.1	
grape juices									
Sauvignon blanc	3	0.0		0.12	0.07	0.023	0.03	6.5	2.8
Chardonnay	1	0.015		0.32		0.06		5.3	
Pinot noir	1	0.0		0.30		0.07		4.5	
total av $\bar{x}$	5	0.005	0.007	0.19	0.11	0.04	0.03	5.7	2.1

[a] Number of samples analyzed. [b] Standard deviation. [c] Ratio of diastereoisomers.

Table II. Concentration of Tetrahydro-β-carboline-3-COOHs in Fortified Wines and Distillates

		tetrahydro-β-carboline-3-COOHs, mg/L							
sample	n^a	THCA	SD[b]	*S,S*-MTCA	SD	*R,S*-MTCA	SD	*S,S*-MTCA/*R,S*-MTCA[c]	SD
fortified wines									
old Spanish flor sherry	8	0.15	0.075	4.36	2.14	1.29	0.72	3.6	0.4
old U.S. sherry	2	0.14	0.015	3.32	0.02	1.07	0.09	3.1	0.3
new Spanish flor sherry	3	0.14	0.08	6.06	1.70	1.84	0.58	3.3	0.1
new U.S. sherry	5	0.16	0.11	1.22	0.62	0.31	0.17	4.2	0.8
new U.S. flor sherry	1	0.09		2.44		0.67		3.6	
cream sherry	4	0.48	0.05	4.85	0.98	1.44	0.26	3.3	0.2
old port	3	0.05	0.02	3.13	0.72	1.0	0.24	3.1	0.2
new port	4	0.05	0.04	6.71	4.3	1.98	1.26	3.4	0.1
vermouth	2	0.35	0.3	2.07	0.96	0.65	0.38	3.51	0.6
marsala	2	0.26	0.17	5.88	1.0	1.64	0.13	3.5	0.3
sherry av $\bar{x}$	19	0.15	0.08	3.59	2.29	1.06	0.75	3.7	0.6
port av $\bar{x}$	7	0.05	0.03	5.18	3.73	1.56	1.08	3.3	0.2
total av $\bar{x}$	34	0.19	0.17	4.1	2.65	1.19	0.82	3.5	0.6
fortified wine range	34	0.0–0.65		0.47–13.7		0.08–4.02		2.8–5.8	
distillates									
old brandy from sherry	3	0.036	0.016	0.78	0.17	0.21	0.05	3.8	0.2
brandy	4	0.0		0.07		0.0		0.0	
whisky	5	0.0		0.0		0.0		0.0	
cognac	3	0.0		0.0		0.0		0.0	
gin	1	0.0		0.0		0.0		0.0	
tequila	1	0.0		0.0		0.0		0.0	
rum	1	0.0		0.0		0.0		0.0	

[a] Number of samples analyzed. [b] Standard deviation. [c] Ratio of diastereoisomers.

(Bosin et al., 1986). Thus, in this paper, identification was assigned by retention times and by coelution with standards after following the same isolation procedure of Adachi et al. (1991). Thin-layer chromatography was also carried out and confirmed the presence of these carbolines.

Concentrations of tetrahydro-β-carboline-3-COOHs in table red and white wines, sparkling wines, and grape juices are included in Table I. All table wines analyzed had (1*S*,3*S*)-MTCA and its diastereoisomer (1*R*,3*S*)-MTCA, as well as THCA, as normal constituents, although in highly variable concentrations. MTCA and THCA concentrations range from 0.31 to 4.98 and from 0.0 to 0.18 mg/L, respectively, in table wines. The average value for the two MTCA isomers in white wines was 2.19 and 0.61 mg/L, whereas it was 0.96 and 0.28 mg/L in the red wines. The wines made from Pinot blanc and Cabernet sauvignon have the highest and lowest concentrations, respectively. Sparkling wines analyzed have higher levels than table wines, with less amounts in wines made from pinot noir than Chardonnay. Compared to wines, grape juices have very low amounts of all tetrahydro-β-carboline-3-COOHs. Increases in the concentration should be expected at fermentation due to the expected increase of aldehydes during yeast growth and fermentation.

Table II shows the concentration of tetrahydro-β-carboline-3-COOHs in fortified wines, including sherry, port, vermouth, and marsala, and in distillates including brandy, whiskey, cognac, rum, tequila, and gin. Higher concentration was generally found in fortified wines than in table wines (4.1 and 1.65 mg/L of *S,S*-MTCA on average, respectively). In all cases flor sherry wines seem to have higher concentrations than other kinds of sherry wines. It is worth mentioning that higher amounts of tetrahydro-β-carboline-3-carboxylic acid (THCA) were found in the cream sherries and vermouth when compared to the rest of the wines. This could be an indication of the higher

Table III. Concentrations of Tryptophan, Acetaldehyde, and Total 1-Methyl-1,2,3,4-tetrahydro-β-carboline (MTCA) Concentration in Some Wines Analyzed

sample	acetaldehyde, mg/L	tryptophan, mg/L	total MTCA, mg/L
sherry	106.4	6.6	2.64
sherry	283.8	0.07	0.98
sherry	253.9	0.81	2.26
sherry	65.4	2.2	1.24
sherry	75.8	1.9	0.55
flor sherry	308.9	0.5	3.11
flor sherry	62.4	0.1	10.2
flor sherry	232.1	0.1	8.72
cream sherry	63.9	1.7	4.59
cream sherry	65.9	1.3	7.4
cream sherry	79.9	1.2	7.55
port	29.3	0.3	8.7
port	26.8	0.1	3.83
port	47.1	0.1	4.5
port	7.7	1.9	17.78
vermouth	23.8	6.9	1.38
table wine	20.0	0.1	2.8
table wine	38.5	2.1	1.87
table wine	69.8	7.9	6.5

presence of formaldehyde in these kinds of wines. The average concentration of *S,S*-MTCA found in port wines was 5.18 mg/L, but a port from the Tinta Madeira grape variety had the highest concentration of MTCA (17.8 mg/L as sum of both isomers). A new tetrahydro-β-carboline-3-COOH, 1-isobutyl tetrahydro-β-carboline (IBTCA), was tentatively identified in sherry wines with less than 0.5 mg/L (results not shown). Sherry wines usually have more isovaleraldehyde than other kinds of wines; therefore, a reaction with tryptophan resulting in tetrahydro-β-carboline could be possible.

Distillates have very low amounts of tetrahydro-β-carboline-3-COOHs, and traces or no concentration at all were detected in most of them. However, brandy from sherry showed slight amounts of THCA and MTCA.

MTCA was the tetrahydro-β-carboline found in the highest concentration in the samples analyzed. This should be the result of the highest concentration of acetaldehyde in alcoholic beverages in comparison with other aldehydes. The concentration ratio between the two diastereoisomers (1*S*,3*S*)-MTCA and (1*R*,3*S*)-MTCA, shown in Tables I and II, was lower than that found after chemical synthesis, generally between 3 and 4 with averages of 3.7, 3.6, 3.5, and 5.7 in table wine, sparkling wine, fortified wine, and grape juice, respectively. Adachi et al. (1991) found a similar ratio for wines, but the value reported here is higher than that reported by Bosin et al. (1986).

No correlation was found between MTCA concentration and the concentrations of acetaldehyde and tryptophan in wine (Table III). Acetaldehyde was high in some of the sherries, whereas tryptophan concentration was low in most of the wines analyzed. Uptake of the tryptophan by yeast during growth limits the amount available for this reaction. The acetaldehyde may be partially bound by sulfur dioxide and not free to react. These facts suggest that the amounts of the tetrahydro-β-carbolines will be limited in most wines.

To verify if reaction between tryptophan and acetaldehyde gives rise to tetrahydro-β-carboline-3-COOH in wine, tryptophan was added to a sherry wine with 280 mg/L of acetaldehyde. Figure 2 shows a linear increase of the content of the two isomers of MTCA (A) and also in the content of the THCA (B) with the concentration added of tryptophan. Thus, the formation of tetrahydro-β-carboline-3-COOHs correlates with the tryptophan concentration present in this wine. THCA formation, after

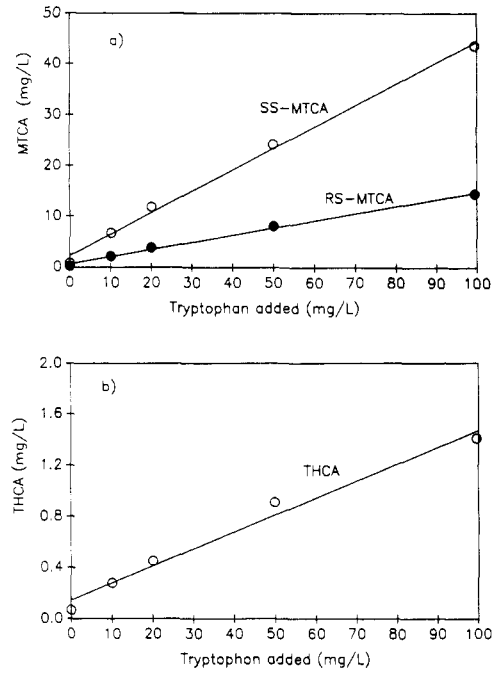

Figure 2. Formation of 1,2,3,4-tetrahydro-β-carboline-3-COOHs after addition of L-tryptophan to a sherry wine with 283 mg/L of acetaldehyde. Wine was kept for 7 days at 25 °C. (A) Formation of MTCA; (B) formation of THCA.

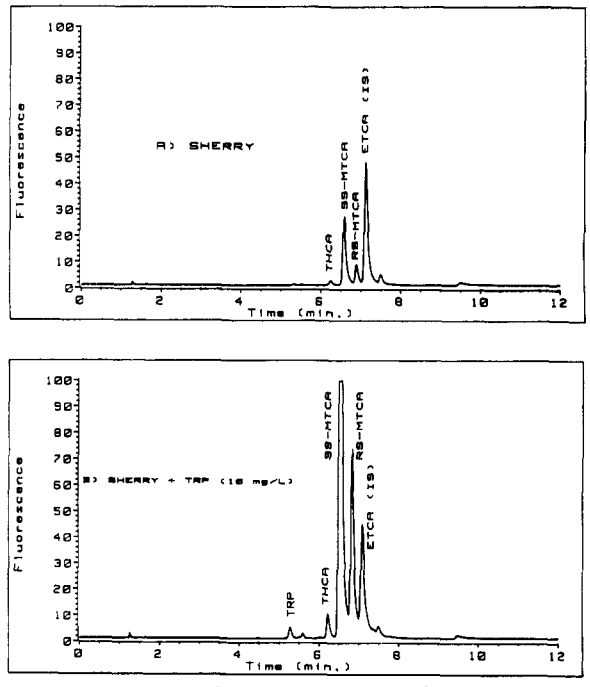

Figure 3. 1,2,3,4-Tetrahydro-β-carboline-3-COOH HPLC chromatograms of a sherry wine control (A) and the same sherry with 10 mg/L of tryptophan added (B). Sherry was analyzed after 7 days at 25 °C. The peaks are as in Figure 1.

addition of tryptophan, indicated that formaldehyde was also present in sherry wine and reacted to give that compound. The formation of the two diastereoisomers of MTCA and THCA, after addition of TRP, provides additional confirmation of the route of formation of these compounds in wine (Figure 3).

To check the effect of the acetaldehyde, a white wine spiked with 15 mg/L of tryptophan was treated with different amounts of acetaldehyde. As shown in Table IV, a notable increase was obtained in MTCA after 7 days at room temperature. No increase of THCA was produced in this case (Table IV).

Table IV. Concentration of Tetrahydro-β-carboline-3-carboxylic Acids in a White Wine[a] after Addition of Tryptophan and Acetaldehyde

compd added, mg/L		tetrahydro-β-carboline-3-COOHs, mg/L		
Trp	acetaldehyde	THCA	(1S,3S)-MTCA	(1R,3S)-MTCA
			2.13	0.56
15	10		3.92	1.44
15	20		4.54	1.67
15	50		6.21	1.91
15	100		7.77	2.33
15	200		9.13	2.93

[a] The wine was kept for 7 days at 25 °C after addition of tryptophan and acetaldehyde.

The results reported provide the concentration range of tetrahydro-β-carboline-3-COOHs in different kinds of wines and distillates, as well as grape juices. These compounds are found in most of the samples analyzed as a consequence of the reaction between tryptophan and aldehydes. The alcoholic fermentation increases their amount, probably because of the formation of aldehydes. Distillates have very low amounts as tryptophan, and tetrahydro-β-carboline-3-COOHs do not distill readily. In the case of brandy from sherry a final blend with some amounts of sherry could have occurred during the process providing the tetrahydro-β-carboline-3-COOHs.

Dessert and aperitif wines had generally higher concentrations of these tetrahydro-β-carbolines. In this regard, it should be pointed out that these wines suffer a long period of aging, as well as yeast film development in flor sherry or heating process to accelerate maturation for obtaining oxidized character. These wines had generally higher amounts of acetaldehyde than table wines. With these data, no clear correlation could be found between aging of the sherry and the level of tetrahydro-β-carboline-3-COOHs. Reactions appear to be relatively rapid as seen from Table IV and Figure 2.

Tryptophan and acetaldehyde reaction produces MTCA. Molar concentration of tryptophan in wine was usually much lower than acetaldehyde; therefore, it should be expected that the amino acid concentration is of major importance in the formation of tetrahydro-β-carboline-3-COOHs. Regardless of the technology used, Trp content in the grape juice should influence the amount of tetrahydro-β-carboline-3-COOHs in the wine.

CONCLUSIONS

The concentration of tetrahydro-β-carboline-3-COOHs in 81 samples, including wines from different grape varieties as well as grape juices, aperitifs, and dessert wines and distillates ranges from 0 to 18.4 mg/L. These compounds must be considered as normal constituents of alcoholic fermentation products resulting from a reaction of aldehydes and tryptophan. Fortified wines had generally higher concentration than table wines, whereas distillates had very little or no amounts of tetrahydro-β-carboline-3-COOHs. MTCA, as the sum of both diastereoisomers, was the carboline in the highest amount in all samples analyzed. Other foods containing the precursor compounds might well have equal or higher amounts.

Although no correlation was found between the concentration of tryptophan or acetaldehyde and tetrahydro-β-carboline-3-COOH concentration in the wine, this correlation exists as it was demonstrated when either tryptophan or acetaldehyde was added to a wine. Acetaldehyde concentration and mainly tryptophan concentration have a potential role in the formation of those compounds in wine and in alcoholic beverages. The technology used in the wine-making process, such as sulfur dioxide addition, may play a role in reducing the amounts found.

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