

FLUORIDE IN CALIFORNIA WINES AND RAISINS

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SUMMARY: Fluoride ion-selective electrode analyses of nineteen California wines revealed fluoride concentrations ranging from 0.23 to 2.80 ppm (mean 1.02 ppm, with seven samples above the international limit of 1 ppm). The water-extractable F content of five brands of California raisins varied from 0.83 to 5.20 ppm (mean 2.71 ppm). Elevated F levels in these wines and raisins appear to result from pesticide use of cryolite (Na_3AlF_6) in the vineyards. Potential toxic effects of F in conjunction with aluminum and sulfites in wine are discussed.

Key words: Aluminum; Analysis; California; Cryolite; Fluoride; Raisins; Sulfites; Wines.

INTRODUCTION

In a recent large-scale study, the fluoride (F) content of juices, juice-flavored drinks, and distilled-water-reconstituted frozen concentrates sold in the United States was found to range from 0.02 to 2.80 ppm (mg/L), with white grape juice having the highest mean F concentration of 1.45 ppm.¹ This high F level in white grape juice, which, along with that in other kinds of juices, may be contributing to increased dental fluorosis,¹ evidently results from the use of F-containing pesticides, since grape juice made from only the interior portion of grapes is reported to contain "no detectable amounts of fluoride."²

Because the legally-permitted use of natural cryolite (Na_3AlF_6) in vineyards to control leaf-eating insects is apparently fairly common, especially in the Central Valley of California,³ it would not be surprising to find that "traces of fluoride can sometimes remain in the finished wine products when this pesticide is used."³ By international agreement the F content of wine should not exceed 1 ppm,³ and although F levels in certain European and South American wines have been found to be well below this limit,⁴⁻⁶ the F content of present-day US California wines is not on record, at least in publications included in *Chemical Abstracts*. We therefore undertook such determinations, and we now report F analyses of nineteen California wines along with the amount of water-extractable F in five brands of California raisins.

MATERIALS AND METHODS

With the exception of an earlier package of Rainbow raisins, the various samples of California wines and raisins were purchased during January-April 1997.

Fluoride determinations were performed in duplicate or triplicate by use of an Orion Model 94-09 fluoride ion-selective electrode and a Corning Catalog No. 476350 calomel reference electrode connected to an Orion Model 407A Ion Analyzer. Calibrations were made with 10.0, 1.00, and 0.100 ppm F solutions prepared from reagent-grade sodium fluoride and distilled deionized water.

For each determination, a 5.0-mL portion of the sample solution was mixed with 5.0 mL of TISAB with CDTA (Total Ionic Strength Adjustment Buffer with 1,2-cyclohexylenedinitrotetraacetic acid to liberate F from complexes of poly-

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valent cations). After the electrodes were immersed in the mixture of sample and buffer, constant readings were usually obtained in 5 to 8 min.

Wine samples were analyzed directly without prior treatment. For determination of the water-extractable F in raisins, 20.0-gram samples of each brand were suspended in 100.0 mL of distilled deionized water and stirred vigorously for 10 min in a Waring Vortex 7 blender. To facilitate filtration without introduction of F contamination from Filter Aid or Celite,⁷ the blended mixtures were heated at 90°C for 10 min. They were then partially suction filtered hot through 5.5-cm diameter Whatman No. 1 filter paper that had been freshly washed with 100 mL of hot distilled deionized water.

RESULTS AND DISCUSSION

As seen in Table 1, the F content of these California wines ranged from 0.23 to 2.80 ppm, with 7 of the 19 samples (37%) testing above 1 ppm F. Thus many of these wines appear to be contaminated by what are probably cryolite pesticide residues. If the samples are representative, then at least a third of California wines may have F levels above the international limit of 1 ppm.

TABLE 1. Fluoride content of California wines

Brand name	Vintage *	Type	(Color)	F ppm (mg/L)
Sutter Home	1990	Zinfandel	(red)	0.23
M. G. Vallejo	1994	Cabernet Sauvignon	(red)	0.38
Ernest and Julio Gallo	NS	White Zinfandel	(white)	0.41
Sutter Home	1993	Zinfandel	(red)	0.58
Sutter Home	1995	Cabernet Sauvignon	(red)	0.66
Sutter Home	1995	Chardonnay	(white)	0.68
Sutter Home	1994	Chardonnay Sauvignon Blanc	(white)	0.73
Blossom Hill	NS	White Zinfandel	(white)	0.82
Sutter Home	1995	Soleo	(red)	0.86
Ernest and Julio Gallo	1992	Chardonnay	(pink)	0.90
Vendange	NS	Cabernet Sauvignon	(red)	0.96
Sutter Home	1995	White Zinfandel	(white)	0.98
Vendange	NS	White Zinfandel Autumn Harvest	(white)	1.18
Glen Ellen	1995	Chardonnay	(pink)	1.28
Fairbanks	1995	White Port	(white)	1.35
Livingston Cellars	1996	Burgundy	(red)	1.41
Cook's	NS	Brut Imperial American Champagne	(white)	1.50
Ernest and Julio Gallo	1996	Ruby Cabernet	(red)	1.58
Inglenook	1993	Burgundy Red Table Wine	(red)	2.80
			Mean	1.02
			Median	0.90

NS = not specified

In contrast to these findings, European wines made from relatively uncontaminated grapes have been reported to contain only 0.2 to 0.38 ppm F,^{4,5} Likewise, at least in the past, Argentine wines were found to contain between 0.04 and 0.5 ppm F, with only 16 of 244 samples (6.6%) testing above 0.5 ppm.⁶ On the other hand, in Chile 17 samples of red wines contained 0.084 to 0.94 ppm F (mean 0.44 ppm), whereas 13 samples of white wines generally had higher F levels (like white grape juices, but unlike our California wines), ranging from 0.20 to 1.70 ppm (mean 0.63 ppm).⁸ Moreover, wines from vineyards located near F-polluting ceramic factories in Italy were found to have 0.5 to 9.5 ppm F.⁹

Table 2 records the concentrations of water-extractable F (and therefore less than the total F) in five brands of California raisins. As with the wine samples, the range of concentrations is fairly large, with the F level in Food Club raisins (5.20 ppm) being over six times that in a recently-purchased package of Rainbow raisins (0.83 ppm). That most of this F is on the outside of the raisins was demonstrated by the fact that simply soaking the raisins in distilled water for 1 to 2 hr released 70 to 90% of the amount of F found by the blending procedure. Thus these results, as with grape juices,^{1,2} point to varying levels of vineyard exposure to an F-containing pesticide such as cryolite.

TABLE 2. Water-extractable fluoride content of California raisins

Brand name	F ppm (mg/kg)
Rainbow	0.83
Rainbow (earlier, 1996 purchase)	1.85
Sweet Harvest	2.65
Champion	2.85
Sun-Maid	2.85
Food Club	5.20
Mean	2.71

Although chronic fluoride intoxication would seem unlikely from any but the highest F wines or raisins examined here, in the past habitual heavy users of wines containing 8 to 72 ppm F illegally added to retard fermentation have developed a peculiar type of alcohol-related skeletal fluorosis characterized by severe and painful exostoses and joint deformities.¹⁰ On the other hand, recent studies have shown that rats exposed to as little as 0.5 ppm AlF₃ in their drinking water for 45 to 52 weeks exhibited not only a general decline in body appearance and increased mortality but also significant microvasculature disturbances associated with abnormalities in and loss of neuronal brain cells.¹¹⁻¹³ Since ingested aluminum itself can be neurotoxic^{14,15} and is also able, at elevated levels of intake, to decrease F absorption,¹⁶ it is noteworthy that these and other studies with rats as well as studies with rabbits have shown that toxic cellular uptake of Al in the diet is actually increased by F.^{13,17,18} Consequently, with mean Al levels in US table wine and raisins officially reported to be 0.93 and 3.08 ppm, respectively,¹⁹ possible subtle, long-term synergistic toxic effects from the presence of both F and Al in these products should not be overlooked.

In view of the foregoing evidence of F enhancement of Al absorption and intoxication, the question naturally arises: might F also increase the potential health risks of other toxic substances in wine and raisins? In this light the age-old tradition of adding sulfites as preservatives in wine-making³ bears examination. In the United States sulfites are usually added at the crush stage to bring the SO₂ equivalent level in wine to 30-90 ppm.²⁰ Any such US-market wine bottled after January 1988 must carry a notice that it "contains sulfites,"²¹ and all the wines examined here were so labeled. Allergic-asthmatic reactions to sulfites in the diet are well documented²¹⁻²⁴ and allergic hypersensitivity to low-level F intake is equally well documented.²⁵

Other recent research has shown that chronic intake by rats of sodium metabisulfite (5 mg/day/kg body weight for up to 15 days) leads to significant disruption of lactate dehydrogenase activity and indications of cellular damage to the rat kidney.²⁶ Since kidney cell damage in rats from long-term ingestion of low-level F is on record^{27,28} and has now been confirmed and amplified,¹³ the potential for F to enhance or to combine with sulfite toxicity in wines should also be considered.

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