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REVIEWS

Pesticide Residues in Grapes, Wine, and Their Processing Products

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In this review the results obtained in the 1990s from research on the behavior of pesticide residues on grapes, from treatment to harvest, and their fate in drying, wine-making, and alcoholic beverage processing are reported. The fungicide residues on grapes (cyproconazole, hexaconazole, kresoxim-methyl, myclobutanil, penconazole, tetraconazole, and triadimenol), the application rates of which were of a few tens of grams per hectare, were very low after treatment and were not detectable at harvest. Pyrimethanil residues were constant up to harvest, whereas fluazinam, cyprodinil, mepanipyrim, azoxystrobin, and fludioxonil showed different disappearance rates ($t_{1/2} = 4.3$, 12, 12.8, 15.2, and 24 days, respectively). The decay rate of the organophosphorus insecticides was very fast with $t_{1/2}$ ranging between 0.97 and 3.84 days. The drying process determined a fruit concentration of 4 times. Despite this, the residue levels of benalaxyl, phosalone, metalaxyl, and procymidone on sun-dried grapes equalled those on the fresh grape, whereas they were higher for iprodione (1.6 times) and lower for vinclozolin and dimethoate (one-third and one-fifth, respectively). In the oven-drying process, benalaxyl, metalaxyl, and vinclozolin showed the same residue value in the fresh and dried fruit, whereas iprodione and procymidone resides were lower in raisins than in the fresh fruit. The wine-making process begins with the pressing of grapes. From this moment onward, because the pesticide on the grape surface comes into contact with the must, it is in a biphasic system, made up of a liquid phase (the must) and a solid phase (cake and lees), and will be apportioned between the two phases. The new fungicides have shown no effect on alcoholic or malolactic fermentation. In some cases the presence of pesticides has also stimulated the yeasts, especially *Kloeckera apiculata*, to produce more alcohol. After fermentation, pesticide residues in wine were always smaller than those on the grapes and in the must, except for those pesticides that did not have a preferential partition between liquid and solid phase (azoxystrobin, dimethoate, and pyrimethanil) and were present in wine at the same concentration as on the grapes. In some cases (mepanipyrim, fluazinam, and chlorpyrifos) no detectable residues were found in the wines at the end of fermentation. From a comparison of residues in wine obtained by vinification with and without skins, it can be seen that their values were generally not different. Among the clarifying substances commonly used in wine (bentonite, charcoal, gelatin, polyvinylpolypyrrolidone, potassium caseinate, and colloidal silicon dioxide), charcoal allowed the complete elimination of most pesticides, especially at low levels, whereas the other clarifying substances were ineffective. Wine and its byproducts (cake and lees) are used in the industry to produce alcohol and alcoholic beverages. Fenthion, quinalphos, and vinclozolin pass into the distillate from the lees only if present at very high concentrations, but with a very low transfer percantage (2, 1, and 0.1%, respectively). No residue passed from the cake into the distillate, whereas fenthion and vinclozolin pass from the wine, but only at low transfer percentages (13 and 5%, respectively).

Keywords: *Pesticides; residues; grapes; raisins; wine; alcoholic beverage*

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INTRODUCTION

The main distribution area of vine is in the Mediterranean countries, where about three-fourths of its total world distribution is present. Most of the production of grape is destined to wine-making. Wine, and its byproducts cake and lees, can be distilled to obtain alcohol or alcoholic beverages (brandy, grappa, and cognac). Grapes can be consumed fresh, as raisins, and also as juice. Therefore, the products obtained from vine are grapes and its processed products raisin, grape juice, wine, brandy, grappa, and cognac. To obtain a good-quality grape, the vine must be protected from parasite attacks until it ripens. The principal parasites of vine in the Mediterranean countries are the grape moth (*Lobesia botrana*), downy mildew (*Plasmopora viticola*), powdery mildew (*Uncinula necator*), and gray mold (*Botrytis cinerea*). To control these parasites, insecticides and fungicides have to be used, and at harvest time one can find pesticide residues on grapes, which can pass into the processed products depending on the technological process and the concentration factor of the fruit.

Most studies on pesticide residues deal with the transformation from vine to wine, whereas only a few studies have been dedicated to fruit juice, raisins, or alcoholic beverages. The first review on wine was by Lemperle in 1975, followed by Cabras et al. in 1987, Zironi et al. in 1991, and Farris et al. in 1992. These reviews deal with the state of the art of the fungicides used at the time (i.e., EBCD, acylalanines, phthalimides, dichlofluanid, cymoxanil, bezimidazoles, thiophanates, and dicarboximides). The results reported showed a complete knowledge of their fate during vinification and of the influence of each technological process on the residue amount.

Prolonged and repeated uses of these fungicides caused resistance, thus reducing their efficacy. It was thus necessary to provide new molecules that acted with different mechanisms. In the 1990s a number of new fungicides (Figure 1) belonging to new chemical classes were marketed (strobilurines, anilinopyrimidines, dinitroanilines, phenylpyrroles) that showed a good activity. In this review we show the data obtained during the wine-making process from research studies on these new molecules. Moreover, we report studies on pesticides (insecticides and triazoles) in wine and other grape and wine products that have not been reported in earlier reviews.

Residues on Grapes. Residue data on grapes reported in Tables 1−3 were obtained in field trials with commercial formulations applied at the doses recommended by the manufacturers.

(a) Fungicides. A few fungicides (kresoxim-methyl, penconazole, and tetraconazole) were applied at doses of a few tens of grams per hectare. Their residues on the grapes after treatment were therefore very low and not determinable at harvest (Table 1). Among the anilinopyrimidines, cyprodinil and mepanipyrim showed the same decay rate ($t_{1/2}$ = 12 days), whereas pyrimethanil was constant up to harvest. Fluazinam disappeared very quickly ($t_{1/2}$ = 4.3 days) and azoxystrobin more slowly ($t_{1/2}$ = 15.2 days), whereas fludioxonil showed the lowest decay rate ($t_{1/2}$ = 24 days). Pesticides belonging to the same chemical family differ in the doses used during treatment and often also in their residue

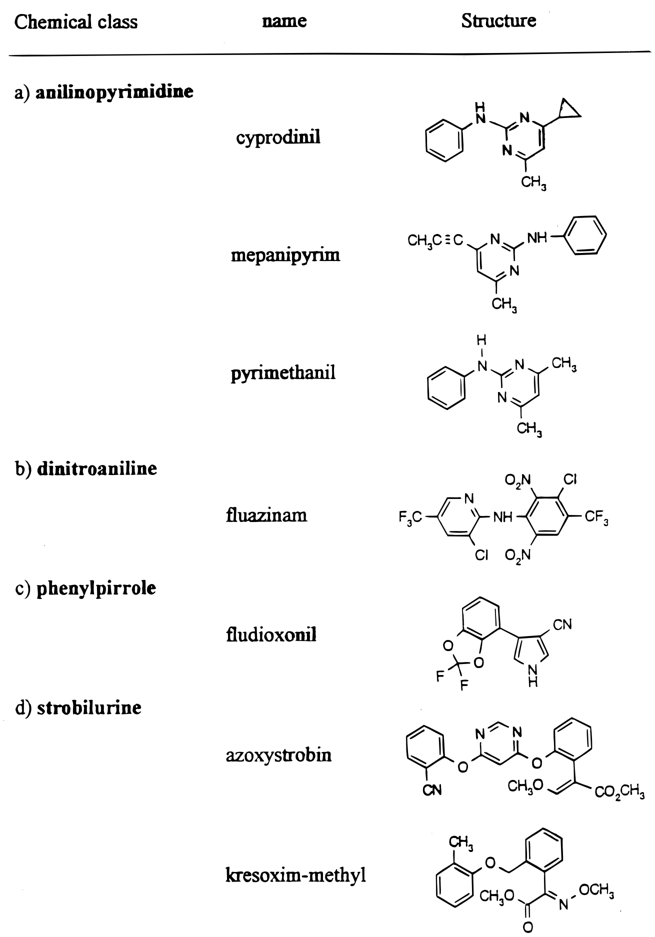

Figure 1. New fungicides discussed in this review.

decay rate. Flori and Brunelli (1995) carried out many field trials for the control of powdery mildew by several ergosterol biosynthesis inhibitors (EBI) (cyproconazole, hexaconazole, myclobutanil, penconazole, and triadimenol). The residues on the grapes at harvest were not determinable in most cases or at very low levels (0.02 mg/kg).

(b) Insecticides. The reported insecticides belong to the organophosphorus family and are among the more commonly used pesticides in controlling the grape moth. Their decay rates are very fast, with a $t_{1/2}$ ranging between 0.97 and 3.84 days. Therefore, residues at harvest were either very low or not detectable (Table 2). Dimethoate showed an anomalous behavior: it degraded rapidly during the first week, but it was constant in the following two weeks. Also, azinphos-methyl was constant in the two weeks after the treatment.

Residues on Raisins. Two methods are used for the production of raisins: exposure to sunlight and oven-drying. The drying process determined a concentration of the fruit of a factor 4. Therefore, the pesticide residues on grapes at harvest could theoretically increase by the same factor, if no loss occurred during the drying process. The residue levels of benalaxyl, phosalone, metalaxyl, and procymidone in sun-dried grapes were the same as those on the fresh grapes, whereas those of iprodione were higher (1.6 times) and those for vinclozolin and dimethoate lower (one-third and one-fifth, respectively). In the oven-drying process, benalaxyl, metalaxyl, and vinclozolin showed the same residue value in both fresh and dried fruits, whereas iprodione and procymidone resides were lower in raisins

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Table 1. Fungicide Residues (Milligrams per Kilogram ± SD) in Grapes

pesticide	residues at intervals (days) after last application					$t_{1/2}$ (days)	refs
	0−1	6−7	14	21	28		
azoxystrobin	0.50 ± 0.09	0.31 ± 0.11	0.23 ± 0.03	0.19 ± 0.06		15.2	Cabras et al., 1998b
cyprodinil	5.54 ± 0.28	2.27 ± 0.48	1.69 ± 0.73	1.08 ± 0.24	1.03 ± 0.24	12	Cabras et al., 1997c
fluazinam	1.21 ± 0.30	0.51 ± 0.05	0.15 ± 0.03	0.04 ± 0.01		4.3	Cabras et al., 1998b
fludioxonil	1.86 ± 0.09	1.59 ± 0.26	1.46 ± 0.19	1.20 ± 0.22	0.78 ± 0.13	24	Cabras et al., 1997c
kresoxim-methyl	0.15 ± 0.03	0.08 ± 0.01	<0.01	<0.01			Cabras et al., 1997c
mepanipyrim	1.00 ± 0.30	0.55 ± 0.19	0.34 ± 0.10	0.14 ± 0.02		12.8	Cabras et al., 1998b
penconazole	0.08	0.07	0.05	0.02			Liuzzi et al., 1994
pyrimethanil	1.62 ± 0.40	1.31 ± 0.30	1.24 ± 0.11	1.19 ± 0.10	1.11 ± 0.18	57	Cabras et al., 1997c
tebuconazole	4.84 ± 0.49	3.16 ± 0.39	2.69 ± 0.57	0.68 ± 0.25	0.42 ± 0.06	4.84	Cabras et al., 1997c
tetraconazole	0.14 ± 0.02	0.06 ± 0.01	0.03 ± 0.01	<0.01		6.3	Cabras et al., 1998b

Table 2. Insecticide Residues (Milligrams per Kilogram ± SD) in Grapes

pesticide	residues at intervals (days) after last application					$t_{1/2}$ (days)	refs
	0	1−2	5−7	14	21		
azinphos-methyl			0.71 ± 0.21	0.63 ± 0.37	0.72 ± 0.45		Goodwin and Ahmad, 1998
chlorpyrifos-methyl	0.16 ± 0.07	0.06 ± 0.02	0.01 ± 0.00			1.28	Cabras et al., 1995b
chlorpyrifos-methyl		0.16	0.08	0.04			Liuzzi et al., 1994
dimethoate	1.13 ± 0.36		0.21 ± 0.08	0.26 ± 0.06	0.28 ± 0.07		Cabras et al., 1994a
fenitrothion	2.40	0.23	0.07	0.03	0.02	3.84	Cascolla et al., 1988
fenthion	0.28 ± 0.07	0.18 ± 0.07	0.06 ± 0.02			3.27	Cabras et al, 1995b
malathion	2.90	0.73	0.03			1.05	Cascolla et al., 1988
methidathion	0.56 ± 0.13	0.25 ± 0.07	0.04 ± 0.01			1.46	Cabras et al., 1995b
parathion-methyl	0.37 ± 0.04	0.07 ± 0.03	0.01 ± 0.00			0.97	Cabras et al., 1995b
parathion-methyl	0.64	0.08	0.02			1.20	Cascolla et al., 1988
quinalphos	0.39 ± 0.04	0.18 ± 0.02	0.05 ± 0.02			1.73	Cabras et al., 1995b

Table 3. Pesticide Residues (Milligrams per Kilogram ± SD) in Fruits during the Drying Process

pesticide	fresh fruit	fruit dried by sunlight	fruit dried by oven
benalaxyl	0.05 ± 0.02	0.04 ± 0.02	0.07 ± 0.03
dimethoate	1.02 ± 0.09	0.19 ± 0.06	0.28 ± 0.08
iprodione	1.74 ± 0.30	2.79 ± 0.67	0.81 ± 0.24
metalaxyl	0.13 ± 0.02	0.10 ± 0.03	0.09 ± 0.02
phosalone	0.97 ± 0.25	0.69 ± 0.24	2.73 ± 0.72
procymidone	2.63 ± 0.53	2.42 ± 0.55	1.58 ± 0.30
vinclozolin	0.30 ± 0.06	0.08 ± 0.03	0.19 ± 0.03

than in fresh fruits (Table 3). This was due to the washing procedure that was carried out on the grape before they were placed in the oven. Dimethoate showed a decrease similar to that obtained by sunlight. Phosalone underwent a smaller degradation in the oven than when dried in the sun, perhaps because it is more sensitive to the solar radiation. Experiments carried out with a model system showed that the decrease in dimethoate was attributable to the action of heat, whereas the decrease in benalaxyl, phosalone, and procymidone was due to codistillation and the decrease in iprodione, metalaxyl, and vinclozolin to the combined action of heat and codistillation (Cabras et al., 1998a).

Pesticide Residues and Fermentative Microflora. In the productive cycle of wine, two fermentative processes occur: alcoholic fermentation and malolactic fermentation. The former occurs by the action of yeasts, the latter by lactic bacteria. The activity of these microorganisms can be affected by the presence of pesticide residues. The first fungicides used to control downy mildew (folpet and captan) showed remarkable antiseptic activity on the yeasts (Cabras et al., 1987 and references cited therein). The other two fungicides, captafol and dichlofluanid, which were later introduced on the market, showed an analogous behavior. Fermentation delays have also been observed in the presence of thiophanate-methyl and fenarimol (Zironi et al., 1991 and references cited therein). Today new pesticides can be traded only after their inactivity on fermentative microflora has been shown. In some cases the presence of pesticides can also stimulate the yeasts, particularly

Table 4. Effect of Yeasts Producing H_2S and SO_2 on Pesticide Residues

pesticide	sample	residues (mg/kg ± SD)	
		0 days	7 days
chlorpyrifos-methyl	control	0.90 ± 0.05	0.65 ± 0.06
	liquid	0.59 ± 0.04	0.17 ± 0.01
	yeasts	0.17 ± 0.01	0.11 ± 0.01
fenitrothion	control	0.88 ± 0.04	0.81 ± 0.01
	liquid	0.81 ± 0.03	0.25 ± 0.01
	yeasts	0.10 ± 0.02	0.10 ± 0.03
parathion	control	1.07 ± 0.03	1.02 ± 0.03
	liquid	0.85 ± 0.05	0.41 ± 0.01
	yeasts	0.13 ± 0.04	0.09 ± 0.02
quinalphos	control	0.95 ± 0.01	0.87 ± 0.03
	liquid	0.78 ± 0.02	0.36 ± 0.02
	yeasts	0.10 ± 0.01	0.07 ± 0.01

Kloeckera apiculata, to produce more alcohol (Cabras et al., 1999). If pesticides can affect the activity of yeasts, the yeasts can reduce the residue content. Yeasts have shown the ability to degrade some pesticides belonging to the pyrethroid class (Fatichenti et al., 1983, 1984). Yeasts producing H_2S and SO_2 can degrade some insecticides (chlorpyrifos-methyl, fenitrothion, parathion, quinalphos; Table 4) belonging to the class of the thiophosphates (Cabras et al., 1995a−c). Moreover, yeasts adsorb some pesticides, thus contributing to their removal from the wine at the end of fermentation (Cabras et al., 1988; Farris et al., 1989).

The effect of pesticides on malolactic fermentation is less studied. Radler and Schoning (1974) found that mancozeb and methylmetiram inhibit the activity of lactic bacteria. Except in this case, neither old pesticides (Sapis-Domercq, 1980; Haag et al., 1988; Cabras et al., 1994a,b) nor new ones (Cabras et al., 1999) have shown relevant negative effects on malolactic fermentation. Lactic bacteria do not degrade the main fungicides used in viticulture.

Effects of Wine-Making on Residues. The wine-making process begins with the pressing of the grapes. From this moment onward, the pesticide on the grape surface comes into contact with the must, which is an acid solution (pH 2.7−3.7). The pesticide is therefore in

Table 5. Fungicide Residues (Milligrams per Kilogram ± SD) in Wine

pesticide	grape	must	clarified must	wine without maceration	wine with maceration	refs
azoxystrobin	0.19 ± 0.06	0.13	0.13	0.13	0.09	Cabras et al., 1998b
cyprodinil	1.03 ± 0.24	0.36	<0.02	0.18	0.21	Cabras et al., 1997c
fenarimol	0.83 ± 0.19[a]	0.31 ± 0.03			0.14 ± 0.03	Navarro et al., 1999
fluazinam	1.21± 0.30[a]	0.30	0.08	<0.01	<0.01	Cabras et al., 1998b
fludioxonil	0.78 ± 0.13	0.39	<0.05	0.23	<0.05	Cabras et al., 1997c
kresoxim-methyl	0.15 ± 0.05[a]	0.13	0.05	0.18	0.09	Cabras et al., 1998b
mepanipyrim	0.31 ± 0.06	0.16	0.07	<0.01	<0.01	Cabras et al., 1998b
myclobutanil	0.27	<0.01			<0.01	Flori et al., 1995
penconazole	0.58 ± 0.06[a]	0.18 ± 0.02			0.09 ± 0.09	Navarro et al., 1999
penconazole	0.02	0.01			<0.002	Flori et al., 1992a
penconazole	0.9[b]			0.47		Navarro et al., 1997
propiconazole	0.44[b]	0.28			0.13	Flori et al., 1992b
pyrimethanil	1.11 ± 0.18	1.03	0.94	1.02	1.01	Cabras et al., 1997c
tebuconazole	0.42 ± 0.06	0.20	<0.05	0.16	0.22	Cabras et al., 1998b
tetraconazole	0.14 ± 0.02[a]	<0.01	<0.01	<0.01	<0.01	Cabras et al., 1997c

[a] Grapes were harvested 0−2 days after treatment. [b] Grapes were fortified with pesticide.

Table 6. Insecticide Residues (Milligrams per Kilogram ± SD) in Wine

pesticide	grape	must	clarified must	wine without maceration	wine with maceration	refs
azinphos-methyl	0.63 ± 0.37				0.04	Goodwin and Ahmad, 1998
azinphos-methyl	0.77 ± 0.38				0.52	Goodwin and Ahmad, 1998
chlorpyrifos	0.73 ± 0.21	0.02	0.01	0.03	0.03	Cabras et al., 1994a
chlorpyrifos	1.86 ± 0.30[a]	0.09	<0.01	<0.01	<0.01	Sala et al., 1996
chlorpyrifos	2.00 ± 0.26[a]	0.34 ± 0.02			0.02 ± 0.00	Navarro et al., 1999
chlorpyrifos-methyl	0.16 ± 0.07[a]	0.06	0.02	0.03	0.03	Cabras et al., 1995b
dimethoate	0.28 ± 0.08	0.26	0.23	0.17	0.20	Cabras et al., 1994a
dimethoate		1.2[b]		1.03		Kawar et al., 1979
fenitrothion	1.37 ± 0.13[a]	0.17 ± 0.03	0.10 ± 0.01	0.04 ± 0.01	0.07 ± 0.01	Sala et al., 1996
fenthion	0.06 ± 0.02	0.04	0.04	0.03	0.04	Cabras et al., 1995b
methidathion	0.56 ± 0.13[a]	0.26	0.25	0.21	0.21	Cabras et al., 1995b
parathion-methyl	0.37 ± 0.04	0.13	0.05	0.05	0.05	Cabras et al., 1995b
parathion-methyl	0.28 ± 0.01[a]	0.06 ± 0.01	0.05 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	Sala et al., 1996
quinalphos	0.39 ± 0.04[a]	0.16	0.04	0.07	0.07	Sala et al., 1996

[a] Grapes were harvested 0−2 days after treatment. [b] Samples were fortified with pesticides.

a biphasic system made up of a liquid phase (the must) and a solid phase (cake and lees), and it will be apportioned between the two phases. Data reported in Tables 5 and 6 show that azoxystrobin, dimethoate, and pyrimethanil residues in the must were the same as on grapes. In all other cases, residues in the must were remarkably lower than those on the grapes, and in some case no residues (myclobutanil and tetraconazole) were present in the must. This points out a great affinity of these pesticides for the solid phase. This tendency is confirmed by the fact that must clarification by centrifugation decreases residues, and in the case of some pesticides (cyprodinil, tebuconazole, and chlorpyrifos), it does so up to complete elimination. Some active ingredients, which are unstable in an acid environment, started to degrade after pressing, and at the end of fermentation the active ingredients were no longer present in the wine but only their stable metabolites. The pesticides that had shown this behavior were dichlofluanid (Lemperle, 1975), chlozolinate (Gennari et al., 1992), and folpet (Cabras et al., 1997a; Viviani-Nauer et al., 1997a,b) (Figure 2).

Wine-making can be carried out either with or without skins. In the former case the wine will be made with all of the residues on the grapes; in the latter case the process will include only the residues that have passed in the must. After fermentation, pesticide residue levels in wine were always lower than those on the grapes and in the must, except for those pesticides that did not have a preferential partition between the liquid and solid phases (azoxystrobin, dimethoate, and pyrimethanil) and are present in wine at the same concentration as on the grapes. In some cases (mepanipyrim, fluazinam, and chlorpyrifos) at the end of fermentation no residues were detected in the wines.

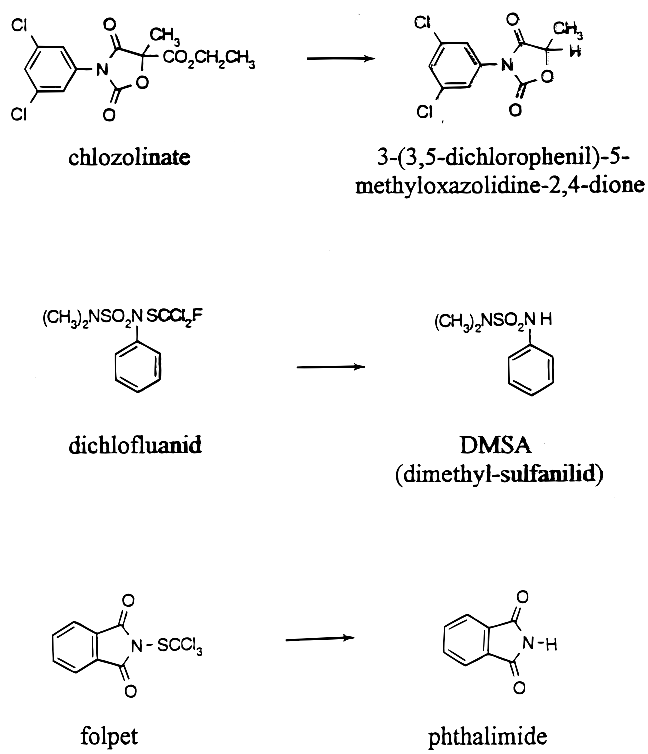

Figure 2. Fungicides and their main degradation products during wine-making.

If we compare the residues in wine obtained with the two techniques (Tables 5 and 6), we can see substantially similar values. Fludioxonil is an exception and showed no residues in the wine obtained with skins, whereas in the wine obtained without skins, the residues were half those found in the initial must.

Wine Clarification. The clarifying substances commonly used in the wine are bentonite, charcoal, gelatin, polyvinylpolypyrrolidone, potassium caseinate, and colloidal silicon dioxide.

Charcoal, especially when the residues are low, allowed the complete elimination of most pesticides. The effectiveness of charcoal generally decreased as the pesticide water solubility increased; therefore, pesticides highly soluble in water, such as dichlorvos and dimethoate, showed no sensible decrease. The other clarifying substances showed no or limited ability to decrease pesticide residues (Cabras et al., 1995c, 1997a,c, 1998b).

Alcoholic Beverages. As seen, in wine-making most pesticides were remarkably adsorbed on the cake and lees and only low percentages passed in the wine. Few active ingredients (dimethoate and pyrimethanil) passed completely from the grapes to the wine. Wine, cake, and lees are used in the industry to produce alcohol and alcoholic beverages. One liter of brandy (45° alcoholic content) is obtained from 4.5 l of wine at 10% alcohol. One liter of grappa (45% alcoholic content) is obtained from 10 kg of cake at 4.5% alcohol, and 1 L of 95% alcohol is obtained from 21 kg of lees at 4.5% alcohol. On average, 0.65 L of wine, 0.17 kg of cake, and 0.055 kg of lees are obtained from 1 kg of grapes.

If the residues on the grape passed completely into the wine, cake, or lees and from these into the alcoholic drink, a factor of concentration of about 7, 59, and 382 times, respectively, would be obtained. These theoretical factors of concentration point out the toxic potential that wine distillates and their byproducts could have, if the technological process did not contribute remarkably to reduce residues. Despite the potential toxic risk presented by the distilled spirits of wine and its byproducts, this issue was neglected from the pesticide research. The first study on pesticides in the distilled spirits of wine was carried out by Bertrand (1980). Samples of wine fortified with 20 mg/L of phosethyl-Al were submitted to distillation to give a spirit without pesticide residues. In a study (Cabras et al., 1997b) on the distillation of wine, cake, and lees fortified with eight fungicides (benalaxyl, fenarimol, iprodione, metalaxyl, myclobutanil, procymidone, triadimefon, and vinclozolin) and five insecticides (dimethoate, fenthion, methidathion, parathion-methyl, and quinalphos), only fenthion, quinalphos, and vinclozolin were found in the distillates. They passed into the distillate (Tables 7 and 8) from the lees only when their concentration was very high but with very low transfer percentages (2, 1, and 0.1%, respectively). No residue passed from the cake into the distillate, whereas fenthion and vinclozolin passed from the wine, but only at low concentrations (13 and 5%, respectively).

Table 7. Residues (Milligrams per Kilogram ± SD) of Fungicides in the Distilled Spirits of Wine and Its Byproducts

fungicide	sample	concn	distilled
benalaxyl	wine	1.16	nd[a]
		0.15	nd
	lees	30.7	nd
		1.16	nd
		0.15	nd
	cake	7.7	nd
		1.16	nd
		0.15	nd
fenarimol	wine	0.34	nd
		0.04	nd
	lees	6.1	nd
		0.34	nd
		0.04	nd
	cake	1.6	nd
		0.34	nd
		0.04	nd
iprodione	wine	2.44	nd
		0.31	nd
	lees	19.2	nd
		2.44	nd
		0.31	nd
	cake	11.8	nd
		2.44	nd
		0.31	nd
metalaxyl	wine	2.2	nd
		0.27	nd
	lees	41.2	nd
		2.2	nd
		0.27	nd
	cake	10.97	nd
		2.2	nd
myclobutanil	wine	0.48	nd
		0.06	nd
	lees	12.6	nd
		0.48	nd
		0.06	nd
	cake	2.5	nd
		0.48	nd
		0.06	nd
procymidone	wine	1.25	nd
		0.17	nd
	lees	24.3	nd
		1.25	nd
		0.17	nd
	cake	4.86	nd
		1.25	nd
		0.17	nd
triadimefon	wine	1.58	nd
		0.2	nd
	lees	45.3	nd
		1.58	nd
		0.2	nd
	cake	9.06	nd
		1.58	nd
		0.2	nd
vinclozolin	wine	1.6	0.08 ± 0.03
		0.2	nd
	lees	26.1	0.03 ± 0.01
		1.6	nd
		0.2	nd
	cake	6.5	nd
		1.6	nd
		0.2	nd

[a] nd, not detectable.

CONCLUSIONS

The use of pesticides according to good agricultural practice guaranteed no residues or residues lower than maximum residue limits (MRLs) at harvest. If the grapes are dried, despite a fruit concentration factor of 4 times, the residues do not vary or decrease. Only iprodione increased by a factor 1.6 when the process was carried out by exposure to sunlight. After pressing, the pesticides on the grape were apportioned preferably on the solid phase (lees and cake). Only a few pesticides did not show a preferential partition between the solid phase and the liquid phase. In the transformation process from grapes into wine, no variation was observed in these pesticide residues, whereas a significant reduction or complete disappearance was shown with

Table 8. Residues (Milligrams per Kilogram ± SD) of Insecticides in the Distilled Spirits of Wine and Its Byproducts

insecticide	sample	concn	distilled
dimethoate	wine	1.03	nd[a]
		0.13	nd
	lees	24.9	nd
		1.03	nd
		0.13	nd
	cake	4.90	nd
		1.03	nd
		0.13	nd
fenthion	wine	0.62	0.08 ± 0.02
		0.08	nd
	lees	10.1	0.19 ± 0.03
		0.62	nd
		0.08	nd
	cake	2.50	nd
		0.62	nd
		0.08	nd
methidathion	wine	0.20	nd
		0.03	nd
	lees	4.90	nd
		0.20	nd
		0.03	nd
	cake	1.00	nd
		0.20	nd
		0.03	nd
parathion-methyl	wine	0.25	nd
		0.03	nd
	lees	5.0	nd
		0.25	nd
		0.03	nd
	cake	1.00	nd
		0.25	nd
		0.03	nd
quinalphos	wine	0.25	nd
		0.03	nd
	lees	4.6	0.04 ± 0.01
		0.25	nd
		0.03	nd
	cake	1.00	nd
		0.25	nd
		0.03	nd

[a] nd, not detectable.

all of the other pesticides. No or slight differences in residues were generally observed when the wine-making process was carried out with or without skins. Among the clarifying substances, only charcoal guaranteed total removal of residues for most pesticides, with a few exceptions also in this case. Pesticide residues showed no activity on the fermentative microflora. On the contrary, although in limited cases, pesticide residues decreased by degradation or adsorption on suspended solids and yeasts. During vinification, because pesticides are subjected to a number of steps that significantly reduce the residue levels, wines can be produced with no or very low residues. This statement is confirmed by data obtained in national wine monitoring. If the wine-making technology reduces pesticide residues to low values, distillation reduces them even lower.

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