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MESUROL (METHIOCARB): Review of 'Status' and of OSU Related Research

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Introduction

Recently there has been publicity concerning the finding of Methiocarb residues in some wines, including wines from Oregon, Washington and New Zealand. This article reviews the current (and potential future?) "status" of the use of Mesurol as a bird repellent on grapes in light of recent Federal legislation and of the research results concerning Mesurol obtained at O.S.U. (and elsewhere). The O.S.U. research was conducted by the Department of Food Science under the direction of the author and with the cooperation of the Department of Agricultural Chemistry, under the direction of Dr. Max Deinzer. This research commenced in 1978 with the objective of obtaining information on the Methiocarb residues on grapes to assist with possible registration. The study was also undertaken to determine whether Methiocarb residues (and metabolites) remained in wine, and if so whether they had any effect on fermentation or sensory properties of wine (refer below).

Current (and future?) status of Mesurol

The use of Mesurol on winegrapes is *not currently permitted in the U.S.* From 1980 to 1984 Mesurol could be applied to grapes under the jurisdiction of Section 18 specific exemptions ("emergency permits") granted by EPA as amended to the Oregon Department of Agriculture, following EPA safe use analysis. The following temporary residue tolerances for Methiocarb and its cholinesterase inhibiting metabolites were approved: 1980 and 1981, 10 ppm for grapes*; 1982, 15 ppm for grapes*; 1983 and 1984, 60 ppm for grapes and 80 ppm for wine. During this period, the same Section 18's were also approved for several other states including Washington, New York, California, Ohio, Maryland and Virginia.

Prior to this period, experimental use permits were issued in 1978 and 1979, with a temporary tolerance of 15 ppm (refer OSU research below).

As a result of recent toxicology tests, in March 1985 the FDA established a new NOEL (no observable effect level) of 5 ppm for Methiocarb (the previous NOEL had been 100 ppm). The manufacturer of Mesurol, Mobay Chemical Corp., voluntarily withdrew from petitioning for registration and *no emergency permit for the use of Mesurol on grapes was issued in 1985.* This means that *no residues of Methiocarb and its metabolites (zero tolerance) are permitted in 1985 wines.*

Any future petitioning for registration for grape use would require a revision of proper use patterns (field application rates) to permit residues of less than 5 ppm in wines. No further toxicology testing has been

requested by FDA, existing tests having demonstrated acute effects (impairment of cholinesterase, neuro muscular functions) but no chronic effects.

Mobay is currently reviewing the situation and considering whether pursuing future registration is worthwhile, in the light of the 5 ppm NOEL and the practical limitations of meeting new tolerances which would be set at no greater than 5 ppm (refer OSU research below).

OSU (and Related) Research

OSU research on Mesurol commenced in 1978 with the issue of the experimental use permits. Grapes were obtained from field application trials conducted by Mobay Corp. and the Department of Fisheries & Wildlife on Oregon and Washington grapes.

Wines were made (OSU pilot plant winery) from Pinot noir and White Riesling grapes which had received application rates of 2 and 4 lb. Mesurol/acre. Wines were subjected to residue analysis for Methiocarb and its metabolites and to taste panel evaluation. In addition the fate of Methiocarb during processing and possible effects on fermentation were investigated. Wines were also made from grapes and grape juice that had been "spiked" with 15 ppm Mesurol which was the temporary tolerance level imposed in 1978 and 1979. The following conclusions were made:

1. A considerable variation in total residues was found on grapes, values ranging from 4 to 58 ppm. Values were often greatly in excess of the tolerance level of 15 ppm.
2. Approximately 50-80% of the total residues originating on the fruit were removed in the pomace; an additional reduction in residues occurred during settling of juice.
3. Total residues ranging from 3-10 ppm were found in finished bottled wines representing 29% (range 26-32%) and 28% (range 13-49%) of the residues originally present on White Riesling and Pinot noir grapes respectively.
4. Residues in clarified wines remained stable during cellar storage for one year.
5. Mesurol had no significant influence on the onset or rate of fermentation (at residue concentrations of up to 60 ppm from field trials and up to 1000 ppm in model studies).
6. Sensory analysis of the above wines indicated no significant differences between the tastes and aroma of wines made from treated and untreated (control) grapes.
7. Similar results to those reported above (conclusions 2-6) were obtained for wines processed in a commercial winery.

A more detailed presentation and interpretation of these results was recently published (1)** and will be complemented by a second paper which has been submitted for publication (2). In addition, there has already been a considerable effort made to report this information through presentations (3,4) and by the publishing of less comprehensive reports (5,6).

Recently there have been reports of Methiocarb residues in wines that are considerably higher than those reported in our study. This raises the question as to whether this is due to differences in a) analytical technique, b) field application practices or 3) other factors.

The OSU results reviewed in this paper have been substantiated by other workers. For instance, similar field application rates in California resulted in Mesurol residues of less than 7 ppm in wines, there being no effect of these residues on the sensory properties of the wines (7). However, other factors that may influence subsequent residue levels in wines include climatic conditions (temperature and sunshine may affect degradation of Methiocarb; rain would reduce residues on grapes). For instance Australian workers have reported a more rapid reduction (degradation?) in Methiocarb residues remaining on

grapes under their warm, dry conditions (8) than was observed in our study (1). Therefore, the higher residues reported in some Oregon wines from recent vintages may have been influenced by seasonal climatic effects.

In response to a request from WAB, OSU is initiating a Mesurol study financially supported by WAB. On Nov. 20, WAB approved expenditure of \$5,000 to assist in initiation of studies which will include the following objectives: 1) evaluation of analytical methodologies for Mesurol (Methiocarb) in wine, and 2) determination of Methiocarb in Oregon wines. An expanded proposal to develop procedures for possible removal of Methiocarb will be considered separately.

Conclusions - Recommendations

1. At this time it is not legal to use Mesurol on grapes in the U.S. Whether Mobay will petition for registration is under review.
2. No Mesurol (Methiocarb) residues (zero tolerance) are permitted in 1985 vintage wines in the U.S. Wines produced prior to the 1985 vintage may contain Mesurol (Methiocarb) residues as long as total residues are less than the temporary tolerances set by EPA for the given year (refer previously).
3. Avoid blending/"topping" of '85 wines with '84 wines that may contain Mesurol (Methiocarb) residues.
4. The current status of Mesurol is a marketing as well as a research issue: Oregon wines that are known to contain Mesurol (Methiocarb) residues should not be marketed in regions that have zero or lower tolerances for Mesurol than the U.S.

References

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*No tolerance was specified for wine at this time, however, EPA specifies that the tolerance set for the agricultural raw commodity (grapes) would apply.