

Comparison of GC-MS and HPLC-UV for Determination of Procymidone in Wine

J. Simal Gándara,[†] P. Paseiro Losada,^{*‡} V. González Rodríguez,[†] and A. Romero Rodríguez[§]

Area de Nutrición y Bromatología, Departamento de Química Pura y Aplicada, Facultad de Ciencia y Tecnología de los Alimentos, Universidad de Vigo, 32004 Orense (Orense), Spain, Area de Nutrición y Bromatología, Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Farmacia, Universidad de Santiago de Compostela, 15706 Santiago de Compostela (La Coruña), Spain, and Area de Tecnología de los Alimentos, Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Veterinaria, Universidad de Santiago de Compostela, 27002 Lugo (Lugo), Spain

Temperature-gradient capillary gas chromatography-mass spectrometry with selected ion monitoring at m/z 124, 187, and 283 and isocratic reversed-phase high-performance liquid chromatography with ultraviolet (UV) detection at 207 nm were compared for the determination of residual levels of procymidone in wine. Previous extraction was carried out using Sep-Pak C₁₈ cartridges. Calibration plots were linear from 1 to 50 ppm of procymidone. Method detection limits for GC-MS and HPLC-UV were 6 and 10 ppb (w/v), respectively, and percent recoveries were $94.7 \pm 5.7\%$ and $96.9 \pm 4.3\%$. The methods do not give statistically different values, but GC-MS has the advantage of confirming the identity of procymidone, thus increasing the reliability of the residual analysis.

INTRODUCTION

The dicarboximide procymidone is a systemic agricultural fungicide that is active against *Botrytis* and *Sclerotinia* (Hisada et al., 1976). Numerous authors have discussed the results of its application to seeds, stems, soil, leaves, and harvested products (Krauthausen and Schietinger, 1989; Enisz, 1990; Creemers et al., 1990; Gullino et al., 1990; Jarowaja and Mackowiak, 1990; Porter et al., 1991; Fullerton and Stewart, 1991; Bryk, 1991; Stewart and Fullerton, 1991; Di Tonno et al., 1991; Scrano et al., 1991). Its mechanism of action has been studied by Pappas and Fisher (1979).

Procymidone is absent from wine made from the grapes of grapevines properly treated with this fungicide. Improper use (harvesting before its elimination) can leave undesirable procymidone residues in the wine produced. Its determination in must and wine allows enforcement of procymidone limits recommended by the OIV (Bertrand and Bertsch, 1990), the U.S. Environmental Protection Agency (1991), or the U.S. Food and Drug Administration (Yess, 1991).

The determination of residual levels of agricultural fungicides has been reviewed by Opfermann (1985), Neuray et al. (1986), Nishijima (1986), and Lemperle (1987). Many, including procymidone, can be determined by gas-liquid chromatography (GLC) or high-performance liquid chromatography (HPLC) (Martindale, 1988), thin-layer chromatography (TLC) (Girenko et al., 1988), differential scanning calorimetry (Donnelly et al., 1990), or NMR spectrometry (Webb, 1990). In the HPLC methods, column switching enhances sensitivity and selectivity and lends itself readily to automation (Hogendoorn et al., 1991a,b). Multiresidue determination of fungicides, including procymidone, has been carried out by capillary gas chromatography (GC) (Taccheo et al., 1985) and HPLC (Ohlin, 1986), both of which have been applied to wine

(Alonso, 1981), and procymidone has been determined by two-dimensional GC (Christall and Stan, 1991) and by dual-column GC (Guyot et al., 1991). Procymidone has also been identified from its degradation products (Pirisi et al., 1986).

Detection devices that have been used for GC determination of procymidone include the electron capture detector (Lemperle et al., 1982), the Hall electrolytic conductivity detector (Ishii et al., 1990), the thermoionic detector (Kobayashi et al., 1989; Huang et al., 1990), the flame ionization detector (Rinderknecht and Wenger, 1983), and the mass spectrometer (Barry et al., 1982); the ECD and the mass spectrometer are the most specific, the latter often being used in SIM mode to avoid interferences and increase sensitivity (Flak et al., 1991; Kadokami et al., 1991). For HPLC, UV detection is widely used (Cabras et al., 1983; Miron and Xirau, 1991), while for TLC (Gardyan and Thier, 1991), microbiological tests using *Penicillium cyclopium* (Zadrozinska et al., 1983) or *Cladosporium cucumerinum* (Gottstein et al., 1984) are often employed.

Baldi et al. (1990) have discussed gel permeation procedures for the extraction and cleanup of xenobiotics, including procymidone, and Andersson and Paelsheden (1991) have compared the efficiencies of acetone and ethyl acetate extraction methods for multiresidue determination in fruits and vegetables. For GC, a short Florisil column has been used (Valverde et al., 1991), while a Carbo-pack cartridge is suitable for liquid chromatography (Di Corcia and Marchetti, 1992).

In this work we compared two chromatographic techniques for determination of procymidone in wine: HPLC-UV and GC-MS [using a faster method than Flak et al.'s (1991)]. For both, procymidone was extracted from the sample by a Sep-Pak C₁₈ column.

EXPERIMENTAL PROCEDURES

1. **Apparatus** used included the following: Hewlett-Packard HP5890 Series II gas chromatograph with split-splitless injector; Hewlett-Packard HP5988-A standard mass range mass spectrometer; Hewlett-Packard HP9153-C Chemstation; Spectra-Physics SP8700 XR extended-range LC pump; Spectra-Physics

* Author to whom correspondence should be addressed.

[†] Universidad de Vigo.

[‡] Universidad de Santiago de Compostela (La Coruña).

[§] Universidad de Santiago de Compostela (Lugo).

SP8750 organizer; Spectra-Physics SP8440 UV-vis detector; Spectra-Physics SP4290 integrator and SP WINNER software V. 4.00; BRANSON ultrasonic bath, Model 2200; AFORA glassware.

2. Reagents used included the following: helium N-50 and N-52 (Sociedad Española de Oxígeno, SEO), used to degass the mobile phases in HPLC and as the carrier gas in GC, respectively [nitrogen N-52 (SEO) was also used to evaporate solutions to dryness]; water, demineralized Milli-Q quality (Millipore Corp.); acetonitrile, gradient grade, LiChrosolv(R) (Merck Ref 30); methanol, gradient grade, LiChrosolv(R) (Merck Ref 6007); polyester membrane (47 mm × 0.4 μm) (Nucleopore Corp.); Sep-Pak C₁₈ cartridges [Waters Art. 5190 (Millipore Corp.)]; procymidone (CAS Registry No. 32809-16-8; RIEDEL Ref 36640) [stock solution: 100 mg of procymidone in 200 mL of acetonitrile (500 μg/mL)].

3. Calibration. A working solution with a concentration of 50 μg/mL was prepared by diluting 10 mL of the stock solution of procymidone in 100 mL of acetonitrile. Aliquots of 1, 5, 10, 25, and 40 mL of this working solution were pipetted into separate 50-mL volumetric flasks and made up to the mark with acetonitrile. These five solutions and a sample of the working solution, giving concentrations ranging from 1 to 50 μg/mL, were used to construct the calibration graphs for the two chromatographic methods. The regression between area and concentration was represented by $y = 12029 + 838488x$ ($r = 0.9986$) for GC-MS analysis and $y = 1786 + 13566x$ ($r = 0.9998$) for HPLC-UV analysis.

4. Extraction. Sep-Pak C₁₈ cartridges were prepared for use by elution with methanol (5 mL) and deionized double-distilled water (5 mL). Only new cartridges were used. Samples of wine (50 mL) were passed through a prepared cartridge using a 50-mL Luer-lock glass syringe; the flow rate was controlled at about 3 mL/min by hand. The cartridge was then eluted with methanol (3 mL) at a hand-controlled flow rate of about 1 mL/min. The methanol eluate was concentrated to dryness under a stream of nitrogen, and the resulting residue was dissolved in 1 mL of acetonitrile and analyzed chromatographically.

5. Analysis. **5.1. GC-MS Analysis. GC Conditions.** Two-microliter portions of standard and sample solutions were injected under the following conditions: carrier gas, He N-52; pressure, 100 kPa (15 psi); column material, fused silica; stationary phase, HP-1 (cross-linked methyl silicone gum); dimensions, 12 m × 0.2 mm × 0.33 μm film thickness; splitless injection, split valve flow rate 15 mL/min, purge valve flow rate 2 mL/min, splitless valve on after 1 min; injection temperature, 300 °C; temperature gradient, initial column temperature of 50 °C held for 0.5 min, programmed heating at 50 °C/min from 50 to 250 °C and at 10 °C/min from 250 to 300 °C.

MS Conditions: solvent delay, 2 min; transfer line temperature, 300 °C; ion source temperature, 200 °C; pressure in ionization chamber, 3×10^{-6} Torr; electron ionization mode at 70 eV; multiplier voltage, 1000 V; acquisition mode, selected ion monitoring (SIM) at m/z 124, 187, and 283, dwell time for each ion 60 ms. Procymidone mass spectra and TIC, from m/z 60 to 290, and SIM chromatograms are shown in Figures 1 and 2, respectively.

5.2. HPLC-UV Analysis. HPLC Conditions: column, 15 cm × 5 mm i.d., stainless steel; packing, 5 μm of Pecosphere CRT C₁₈ RC, C₁₈ guard columns; injection, 20-μL loop in a Rheodyne valve, filled with a Hamilton syringe; flow, 0.5 mL/min; isocratic elution, 70:30 acetonitrile-water.

UV Conditions: wavelength, 207 nm; response, 1; range, 0.64.

RESULTS AND DISCUSSION

1. Detection Limits for Calibration Procedure and Method. The lowest concentrations of procymidone detectable at a signal-to-noise ratio of 3 were 0.3 μg/mL using GC-MS and 0.5 μg/mL using HPLC-UV. These results were verified by spiking a blank (wine made from grapevines not treated with procymidone; see Figures 3 and 5) with these levels of procymidone. If concentration by Sep-Pak is considered, the limits of detection of both

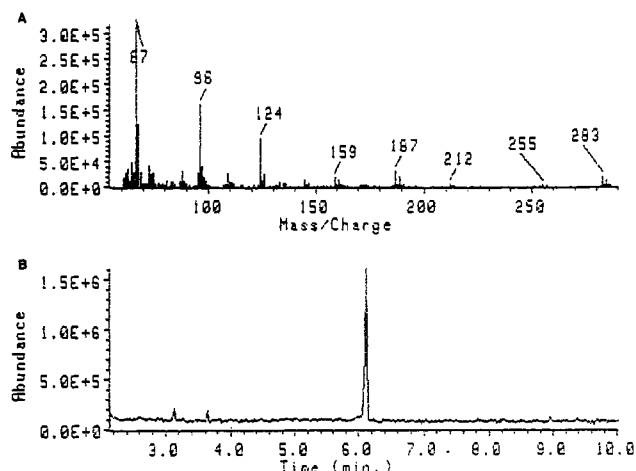


Figure 1. (A) Mass spectrum and (B) total ion chromatogram (TIC) of procymidone standard.

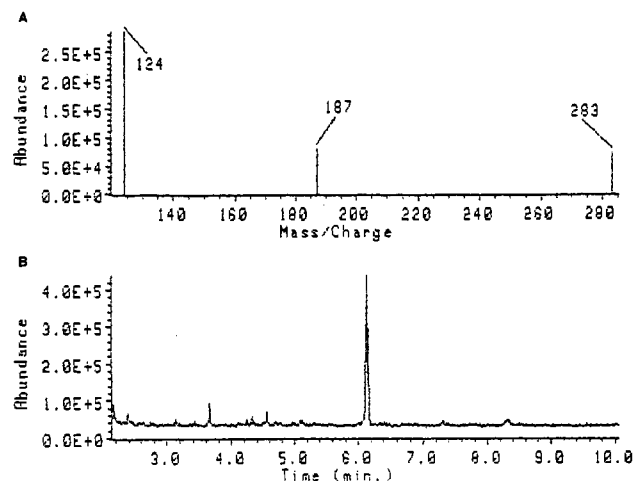


Figure 2. (A) Mass spectrum and (B) single ion monitoring (SIM) chromatogram at m/z 124, 187, and 283 of procymidone standard.

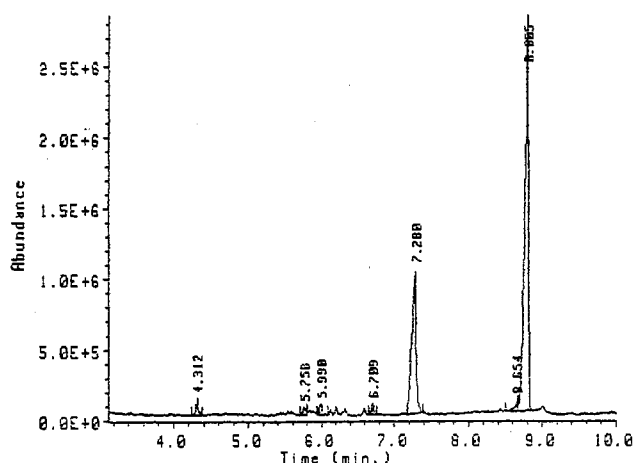


Figure 3. SIM chromatogram of control wine from untreated grapevines.

methods are 50 times smaller, i.e., 6 and 10 ppb (w/v) or ng/mL, respectively.

2. Recovery and Precision of Method. A procymidone-spiked wine blank (500 ng/mL) was prepared by making 1 mL of the 25 μg/mL standard procymidone solution up to 50 mL with wine from grapevines not treated with procymidone. This solution was assayed 10 times. Average recoveries ± standard deviation were $94.7 \pm 5.7\%$ for GC-MS and $96.9 \pm 4.3\%$ for HPLC-UV.

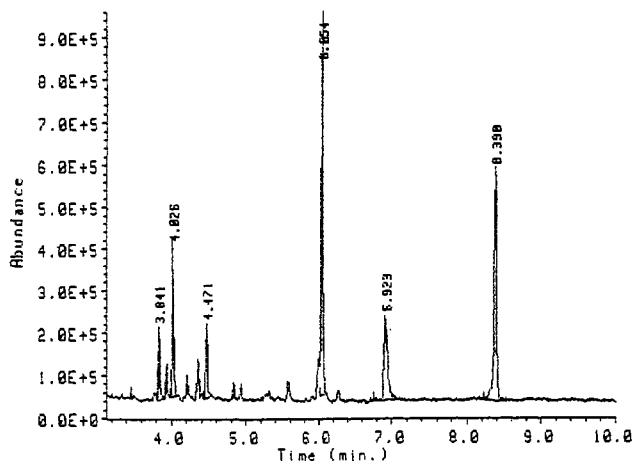


Figure 4. SIM chromatogram of wine with procymidone residues from improperly procymidone-treated grapevines.

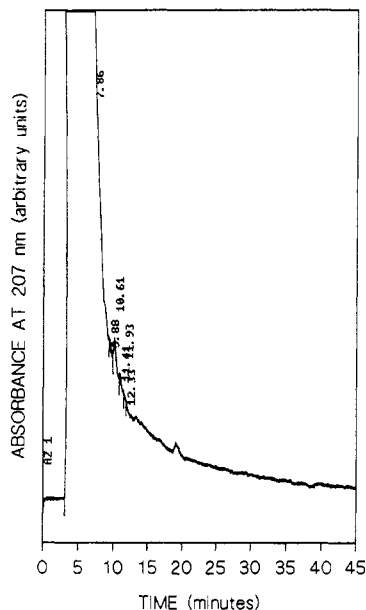


Figure 5. HPLC-UV chromatogram of control wine from untreated grapevines.

3. Comparison of Results. The two methods were compared by studying test samples (Figures 4 and 6) containing different amounts of analyte (Miller and Miller, 1988) and looking at the difference between each pair of results using the two-tailed paired *t*-test. Adopting the null hypothesis that there is no significant difference in the mean concentrations given by the two methods, we can test whether the mean of the differences differs significantly from zero.

The equation for calculating *t* is

$$t = \bar{x}_d(n)^{1/2}/s_d$$

where *t* has (*n* - 1) degrees of freedom. The critical value of $|t|$ is 3.182 (*P* = 0.05), and since the calculated value of $|t|$ (Table I) is less than this, the null hypothesis is retained; i.e., the methods do not give significantly different values for the mean concentration of procymidone.

CONCLUSIONS

Two chromatography-spectrometry techniques (GC-MS and HPLC-UV) are proposed for the determination of procymidone in wine. Both quantify procymidone at low parts per billion levels in wine with excellent precision and accuracy and also give statistically similar results.

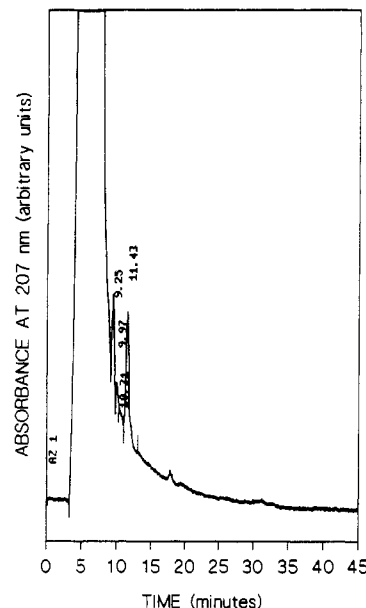


Figure 6. HPLC chromatogram of wine with procymidone residues from improperly procymidone-treated grapevines.

Table I. Two-Tailed Paired *t*-Test To Compare the Two Methods for the Determination of Procymidone in Wine

sample (<i>n</i> = 4)	concn by GC-MS method, ppb	concn by HPLC-UV method, ppb	difference
1	164	183	-19
2	88	64	+24
3	414	394	+20
4	502	436	+66
\bar{x}_d			+22.75
s_d			±34.75
<i>t</i>			1.309

GC-MS has the advantage that the identification of procymidone based on retention times is backed up by the mass spectrum.

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