1.0 INTRODUCTION

This report describes the independent laboratory validation (ILV) of Analytical Method No. AG-677 and modified AG-677 as performed by Ricerca Biosciences, LLC, for the determination of the CGA-64250 (Propiconazole) and metabolites in soil and water using High Performance Liquid Chromatography with Mass Spectrometric Detection [1].

This study was conducted to satisfy guideline requirements described in the US EPA FIFRA Pesticide Assessment Guidelines for Subdivisions N, E, and K, addenda for Data Reporting Guideline for Environmental Methods [2], and as outlined in the harmonized guidelines from the OPPTS, "Public Draft" – Data Reporting for Environmental Chemistry Methods, OPPTS 850.7100 [3]. The protocol for this study is included in Appendix 1 of this report.

2.0 STUDY PERSONNEL

The personnel listed below from Ricerca Biosciences, LLC, participated in the conduct of this study.

Phillip Cassidy	Scientist
James Formanik	Associate Scientist III
Rebecca Killeen	Associate Scientist I

3.0 MATERIALS

3.1 Test and Reference Substances

Standards were shipped from Syngenta on 12/3/03 to Ricerca Biosciences and received on 12/4/03. The following pertain to the standards:

Compound	Reference Number (Ricerca Number)	Weight (mg)	Purity (%)	Expiration Date
CGA-64250	S02-2752 (CS_03370)	240	94.1	6/30/06
CGA-217495	JWP-III-26-3 (CS_03371)	50	96.5	2/28/05
CGA-91305	RW-I-41 (CS_03372)	50	99.3	2/28/05
CGA-118244	CDC-VIII-42-1 (CS_03373)	50	97.6	2/28/05
CGA-118245	CDC-VIII-34-1 (CS_03374)	50	98.7	2/28/05
CGA-136735	JAK-XIX-22-1 (CS_03375)	50	96.5	2/28/05
CGA-71019	WFV-IV-5 (CS_03376)	50	>99.9	2/28/05

Upon arrival, the analytical standards were logged in and stored in a refrigerator. The standards were prepared for calibration and fortification and all solutions were stored in a refrigerator as specified in Method No. AG-677. Characterization and stability data for the analytical reference standards are maintained by Syngenta Crop Protection, Inc.

3.2 Control Soil

The control soil used is described below:

Source of Control:
Madera, California (0-12" sample)

Soil Characterization[1]

Texture	SL[2]
Sand (%)	74
Silt (%)	17
Clay (%)	9
Organic Matter (%)	1.2
pH	7.1
Saturation Paste pH	7.2
Cation Exchange Capacity (meq/100 g)	7.7
%Moisture at 1/3 bar	10.8
%Moisture at 15 bar	5.6
Bulk Density	1.31

1. Ricerca Biosciences Report – 014188-1
2. SL: Sandy Loam

The control surface water used is described below:

Source of Control:
Ten Mile Creek, Florida

Characterization Report[1]

pH	8.0
Sodium	31 ppm
Calcium	49 ppm
Magnesium	13 ppm
Hardness mg equivalent CaCO3/L	177 ppm
Conductivity	0.68 mmhos/cm
Sodium Absorbtion Ratio (SAR)	1.02
Total Dissolved Solids	318 ppm
Turbidity	3.42 NTU
Dissolved Oxygen	9.5 mg/L

1. Ricerca Biosciences Report – 15493-1

The control well water used for method validation was locally obtained:

Source of Control:
Madison, Ohio

Agvise Water Characterization Report[3]

pH	7.3
Phosphate-P	<0.1ppm
Sodium	79 ppm
Calcium	43ppm
Magnesium	9 ppm
Hardness mg equivalent CaCO3/L	142ppm
Conductivity	0.73 mmhos/cm
Sodium Absorbtion Ratio (SAR)	2.87
Total Dissolved Solids	430 ppm
Chloride	100 ppm
Turbidity	3.65 NTU
Sulfate	47 ppm
Nitrate-nitrogen	<0.1 ppm
Total Organic Carbon	1.4 ppm
Alkalinity	118 mg CaCO3/L

3. Agvise Characterization Report – 03-1270

3.3 Equipment and Reagents

The equipment and reagents used for the method validation were as outlined in Method AG-677 (Section II) and modified Method AG-677.

4.0 METHOD AND PROCEDURES

Analytical Method No. AG-677 and Modified Method AG-677: "Analytical Method for the Determination of Propiconazole (CGA-64250) and its Degradates CGA-217495, CGA-91305, CGA-118244, CGA-118245, CGA-136735, and CGA-71019 in Soil and Water by High Performance Liquid Chromatography with Mass Spectrometric Detection Including Method Validation Data and Modified Method AG-677, for Water, with a 0.02 ppb Limit of Quantitation" [1]. Method AG-677 has a limit of quantitation (LOQ) in soil of 5 ppb for all analytes and an LOQ of 0.10 ppb in water. Modified Method AG-677 has a limit of quantitation (LOQ) of 0.02 ppb in water. The procedure used by Ricerca Biosciences, to validate this method is described below.

4.1 Sample Preparation, Fortification, and Extraction

Each analytical set consisted of 13 samples: one reagent blank, two matrix blanks, five matrix blanks fortified at the LOQ and five matrix blanks fortified at 10X LOQ.

For the soil sets, a 20 g portion of the control soil was used for each of the samples except the reagent blank. Each sample was placed in separate 250 mL polypropylene bottles and each was fortified at the respective level. Each sample was extracted with 100 mL of 70/30% (v/v) methanol/water and refluxed for one hour. The extracts were transferred back to the polypropylene bottles and centrifuged at 9,000 RPM for 10 minutes. A 50 mL portion of this extract was made basic with the addition of 100 uL of ammonium hydroxide and passed through an SAX SPE cartridge. The extracts were rotary evaporated to remove organic and acidified with 100 uL concentrated acetic acid. The extracts were then passed through ENV and SCX SPE cartridges (piggy-back style) for clean up. All of the compounds were retained on the ENV cartridge except CGA-71019, which was retained on the SCX cartridge. The compounds were eluted from the SPE cartidges into round bottom flasks and were evaporated of organic solvents and re-constituted with sample diluent and analyzed by LC-MS/MS.

For the water sets under Method AG-677, a 100 mL portion of the control water was used for each of the samples. Each sample was made acidic with 100 uL concentrated acetic acid and was passed through an ENV and SCX SPE cartridge (piggy-back style) for clean up. All of the compounds were retained on the ENV cartridge except CGA-71019, which was retained on the SCX cartridge. The compounds were eluted from the SPE cartridges into round bottom flasks and were evaporated of organic solvents and re-constituted with sample diluent and analyzed by LC-MS/MS.

For the modified AG-677 method, lower quantitation limits were possible through the use of 200 mL of water and slightly modified HPLC conditions. Descriptions of LC-MS/MS operating parameters are described in Tables 1 and 2.

4.2 Instrumentation

All samples were analyzed using a PE Sciex API-3000 Triple Quadrupole Mass Spectrometer with TurboIonSpray Interface. LC-MS/MS operating parameters are shown in Table 1 and 2.

4.3 Data Acquisition and Reporting

Peak integration and quantitation were performed by using Analyst, Version 1.1 (PE Sciex Software). Quantitation of all analytes was achieved through the use of external standards. Calibration curves for the analytes were generated by plotting the detector's response in peak area versus the concentrations of the single point calibration standards. A linear regression equation for the fit of the standard curve was derived without forcing the origin, and this equation was used to calculate the concentration of analyte in the samples. Recovery results were computed for each set of samples. Equations used for quantitation are presented in Figure 1.

Statistical treatment of the data included calculation of averages, standard deviations, relative standard deviations and confidence limits. These calculations were performed using Excel. Results were rounded off for reporting purposes but not for calculations.

The first method validation trial failed at Ricerca for each of the three matrices. The reasons for the failure were traced to some analytes being retained on the SPE cartridges and the need for additional solvent to elute them. For the soil, the reason for failure was combined between the elution problem on the SPE cartridges as well as the fact that some solvent had evaporated during the refluxing step and total extract volume was not equal to 100 mL. In the second trial the volume of extract following refluxing was measured and adjusted to 100 mL with extraction solvent. At the SPE clean up additional solvent was used to elute the compounds.

Table 1. LC-MS/MS Operating Parameters – AG-677

A Shimadzu HPLC VP System (Shimadzu Scientific Instruments, Inc. 7102 Riverwood Drive, Columbia, Maryland 21046, USA) was used for connection with a PE Sciex API 3000 LC-MS/MS System (PE Sciex, 71 Four Valley Drive, Concord, Ontario, Canada L4K 4V8) through the Turbo-IonSpray interface. They include:

Shimadzu LC-10_{vp} Pumps
Shimadzu SIL-$10AD_{vp}$ Autosampler
Shimadzu SCL-$10A_{vp}$ System Controller

PE Sciex API 3000 LC-MS/MS System
Turbo-IonSpray Interface

HPLC Parameters (ENV analytes):

HPLC Columns: Inertsil ODS-2, 5 µm, 150 x 4.6 mm, Part No. 0296-150x046

Mobile Phase Flow Rate: 1.5 mL/min, with 0.3 mL/min entering MS
Mobile Phase A: 0.1% (v/v) acetic acid in water
Mobile Phase B: 0.1% (v/v) acetic acid in acetonitrile
Mobile Phase Gradient Program:

Time (min.)	%A	%B
0	70	30
10	25	75
10.5	0	100
13.5	0	100
14	70	30
20	Stop	

Injection Volume: 15 µL (soil); 60 µL (water)

HPLC Parameters (CGA-71019):

HPLC Columns: Zorbax 300-SCX, 5 µm, 150 x 4.6 mm, Part No. 883952-704
Mobile Phase Flow Rate: 1.0 mL/min, with 0.3 mL/min entering MS
Mobile Phase A: 25/75 methanol/water (v/v), with 0.1% acetic acid
Mobile Phase B: 25/75 methanol/water (v/v), with 20 mM ammonium acetate
Isocratic 5 %B
Injection Volume: 5 µL (soil); 20 µL (water)

Table 1. LC-MS/MS Operating Parameters (Continued)

MS/MS Parameters (all analytes):

The samples were analyzed using positive ion detection and MRM scan mode was used for the quantitation.

Analyte	Precursor (Q1, amu)	Product (Q3, amu)
Propiconazole (CGA-64250)	342	159
CGA-91305	258	70
CGA-217495	344	256
Hydroxies	358	256
CGA-71019	70.0	69.9

Typical Acquisition Method Values are listed as follows:

Positive Ion Detection (all compounds):

Gases (N_2)	
NEB	12
CUR	8
CAD	6

Electronic Parameters (ENV analytes):

IS	5000
TEM	500
DP	40
FP	200
EP	-10
CE	25
CXP	15
CEM	2600

Electronic Parameters (CGA-71019):

IS	5000
TEM	500
DP	20
FP	100
EP	-10
CE	30
CXP	15
CEM	2600

Table 2. LC-MS/MS Operating Parameters - Modified AG-677

A Shimadzu HPLC VP System (Shimadzu Scientific Instruments, Inc. 7102 Riverwood Drive, Columbia, Maryland 21046, USA) was used for connection with a PE Sciex API 3000 LC-MS/MS System (PE Sciex, 71 Four Valley Drive, Concord, Ontario, Canada L4K 4V8) through the Turbo-IonSpray interface. They include:

Shimadzu LC-10_{vp} Pumps
Shimadzu SIL-$10AD_{vp}$ Autosampler
Shimadzu SCL-$10A_{vp}$ System Controller

PE Sciex API 3000 LC-MS/MS System
Turbo-IonSpray Interface

HPLC Parameters (ENV analytes):

HPLC Columns: YMC ODS-AQ, 5 µm, 250 x 4.6 mm,
Part No. AQ12S052546WT, with a guard column cartridge

Mobile Phase Flow Rate: 0.8 mL/min
Mobile Phase A: 0.1% (v/v) acetic acid in water
Mobile Phase B: 0.1% (v/v) acetic acid in acetonitrile
Mobile Phase Gradient Program (linear):

Time (min.)	%A	%B
0	60	40
2	60	40
7	15	85
10	15	85
10.5	60	40
14	Stop	

Injection Volume (water): 10 µL

HPLC Parameters (CGA-71019 analytes):

HPLC Columns: Zorbax SB-CN, 5 µm, 150 x 4.6 mm, with guard column cartridge
Part No. 883975-905
Mobile Phase Flow Rate: 0.8 mL/min
Mobile Phase A: 0.1% (v/v) acetic acid in water
Mobile Phase B: 0.1% (v/v) acetic acid in acetonitrile
Isocratic 10%B
Injection Volume (water): 10 µL

Table 2. LC-MS/MS Operating Parameters - Modified AG-677 (Cntd.)

MS/MS Parameters (all analytes):

The samples were analyzed using positive ion detection and MRM scan mode was used for the quantitation.

Analyte	Precursor (Q1, amu)	Product (Q3, amu)
Propiconazole (CGA-64250)	342	159
CGA-91305	258	70
CGA-217495	344	256
CGA-118244/118245	358	256
CGA-136735	358	256
CGA-71019	70.1	69.9

Typical Acquisition Method Values are listed as follows:

Positive Ion Detection

Gases (N_2)

NEB	12
CUR	8
CAD	6

Electronic Parameters

IS	5000
TEM	500
DP	40
FP	200
EP	-10
CE	25
CXP	15
CEM	2600

Figure 1. Calculations for the LC-MS/MS Quantitations

As per Method AG-677, external calibration was used for all of the analysis. The Analyst Software (version 1.1) was used to calculate a best-fit, weighted line of the standards. Recovery results were calculated from the concentration found as it appeared on this line. From the concentration found and the sample volumes, the analyte concentration could be calculated for the original sample volume. Percent recovery can be obtained by the comparison between the residue found and amount added (fortified level).

a) Concentration Found:

Concentration found (µg/mL) = (Peak Area)/Slope

Peak Area and Slope are obtained from Analyst (version 1.1)

b) Sample calculated concentration (soil):

$$\text{Sample concentration (ppb)} = \frac{\text{Conc. Found (ng/mL)* Final Volume (mL)}}{\text{Sample Weight (20 g)}}$$

c) Sample calculated concentration (water):

$$\text{Sample concentration (ppb)} = \frac{\text{Conc. Found (ng/mL)* Final Volume (mL)}}{\text{Sample Weight (200 mL)}}$$

d) Percent Recovery:

Percent Recovery = (Residue Found / Amount Added) X 100

e) Confidence Limit:

$$\text{Confidence Limit} = \pm (t \times SD) / n^{0.5}$$

t = t-distribution value for n-1 degree of freedom
SD = Standard Deviation
n = number of samples

The Calculation of confidence limit was performed in Excel with a confidence limit of 95%.

The percent recoveries shown on Table 2 through 7 may not exactly match the corresponding recoveries on the Analyst result tables in Appendix 3. This is because Analyst uses a large string of unrounded numbers to calculate the percent recoveries.

Summary of Modified AG-677 for Water

8.1 Analytical Methodology

The method follows AG-677 except that the LC column and mobile phase conditions were modified to improve peak resolution, simplify the mobile phase composition, and improve signal to noise (especially for CGA-71019). In addition, the final solvent for the CGA-71019 sample fraction was changed from methanol:water to an acetonitrile:water mixture for consistency with the LC mobile phase change. The details of the modified water method are described below.

8.2 Method Synopsis

Method AG-677 was written for the determination of propiconazole (parent) and six degradation products in soil and water. The following propiconazole degradates were included in the method: CGA-91305, CGA-217495, CGA-118244, CGA-118245, CGA-136735 and CGA-71019. To briefly summarize, water samples were made acidic then passed through a Varian ENV SPE column attached in series with a Varian SCX SPE column. The ENV SPE retains propiconazole, CGA-91305, CGA-217495, CGA-118244, CGA-118245 and CGA-136735, while CGA-71019 passes through the first column before being retained on the SCX SPE. The two SPE columns were then separated. The ENV analytes were eluted using acetonitrile while CGA-71019 was eluted from the SCX SPE using 2.5% ammonium hydroxide in 70:30 (v/v) methanol:water. The organic content was removed by rotary evaporation. The samples were adjusted to the appropriate final volume and organic content and transferred into an autosampler vial in preparation for analysis by LC/MS/MS.

The modifications to this method included increasing the water extraction volume from 100mL to 200mL, decreasing injection volumes that resulted in introducing less sample matrix into the LC/MS/MS, the mobile phases for the two columns/analyses were changed to be comprised of the same organic and aqueous components, resulting in shorter analysis times and fewer mobile phases to maintain, the final dilution solvent for CGA-71019 was changed to 30:70 ACN: H_2O to be compatible with the modified mobile phase which enhanced the signal to noise ratio for this analyte, and the modified mobile phase also resolved the CGA-136735 analyte from the other two hydroxy metabolites, CGA-118244 and CGA-118245.

8.3 Step-wise Procedure

1. Condition the SPE columns by passing 5 mL of methanol followed by 5 mL 0.2% acetic acid through each column.
2. Measure 200 mL ± 0.5 mL water into a graduated cylinder. Fortify if necessary.
3. Add 400 µL concentrated acetic acid to the water samples; mix.
4. Add 2-3 mL of 0.2% acetic acid to the lower SCX column prior to the ENV column (1 gram/6 mL Varian ENV SPE part number 1225-5012 and 1 gram/6 mL Varian SCX SPE part number 1225-6011). Pass the sample through the piggybacked

columns. Do not permit the SCX column to go dry while the top ENV column still contains sample. Add 0.2% acetic acid to the lower SCX column, as needed, to prevent it from going dry. Discard the eluate.

5. As the sample finishes passing through the ENV SPE, add an additional ca. 5 mL 0.2% acetic acid to rinse the graduated cylinders and pass through the corresponding SPE columns. Discard the wash.
6. Rinse the SPE column assembly with approximately 5 mL purified water. Discard the wash.
7. Disconnect the two SPE columns. Rinse the SCX column with approximately 5 mL of 70% methanol/water. Discard the wash.
8. Collection of ENV Analytes. Place a pre-calibrated 50 mL concentration tube containing approximately 2 mL of purified water beneath the ENV SPE column. Elute the analytes (propiconazole, CGA-91305, CGA-217495, CGA-118244, CGA-118245 and CGA-136735) with 15 mL acetonitrile.
9. Remove the organic solvent via rotary evaporation using a water bath temperature of approximately 40°C until <1 mL of water remains. Add 600 µL acetonitrile and dilute to the 2 mL calibrated mark with purified water. Mix well. (Samples may be further diluted using 30% acetonitrile/water, if needed.) Store under refrigeration (<5°C) until the time of analysis.
10. Collection of SCX Analyte (CGA-71019). Place a pre-calibrated 50 mL concentration tube beneath the SCX SPE column. Elute CGA-71019 with 10 mL of 2.5% ammonium hydroxide in 70% methanol/water.
11. Remove the organic solvent via rotary evaporation using a water bath temperature of approximately 40°C until <1 mL of water remains. Add 600 µL acetonitrile and dilute to the 2 mL calibrated mark with purified water. Mix well. (Samples may be further diluted using 30% acetonitrile/water, if needed.) Store under refrigeration (<5°C) until the time of analysis.

The limit of detection defined as the smallest standard amount injected during the chromatographic analysis, ranged from 0.04 ng to 0.05 ng depending upon instrument sensitivity and injection volume. The ENV analyses were analyzed with LC injection volumes of 40 µL or 50 µL, which yielded a limit of detection range of 0.04 ng to 0.05 ng. The SCX analyses were analyzed with LC injection volumes of 40 µL or 50 µL, which yielded the same limit of detection as the ENV analytes. In all cases, the lowest standard concentration was 0.001 ng/µL. The limit of quantitation, LOQ, defined as the lowest fortification specified by the method that gives adequate recovery according to EPA guidelines, was 0.02 ppb for all analytes.

In-house purified water (Hydro Picotech 2) or pure water purchased from Merck or Fisher Scientific was used for control and procedural recovery samples to verify method performance for each sample set. Tables 1 and 2 represent typical instrument settings for the LC and mass spectrometer system.

8.4 Quantitation and Calculations

Within an analytical set, all extracts (samples, controls, and procedural recovery spikes) were bracketed with four to five calibration standards. Instrument control and data collection were

accomplished using the Sciex RAD™ program. The data were analyzed and raw nanogram amounts found were calculated using the Sciex computer MacQuan™ quantitation software. These calculated amounts were then transferred into the Multichrom™ software package for final residue calculations. Calculations are as shown below and in method AG - 677[2]. Calculations were preferentially performed by computer program or manually as shown below.

Calculate the analyte concentration (in ppb) for field-incurred residues using the equation:

$$RES(ppb) = \frac{\text{Analyte found (ng)}}{\text{SWI (mg)}} \times 1000$$

where RES was the residue value in ppb, analyte found (ng) was calculated from the standard calibration curve, and SWI was the sample weight injected (mg).

The amount, in milligrams, of sample weight injected (SWI) can be calculated using the equation:

$$SWI(mg) = \frac{FW(g) \times IV(\mu L)}{FV(mL)}$$

where FW was the final sample weight (g) [Note: for a 200 mL water sample, FW = 200 g], IV was the LC injection volume (µL) and FV was the final volume in which sample was dissolved (mL).

Corrections may be made to the residue value (RES) calculated above. At the discretion of the study director, this value may be corrected to account for the average recovery and/or sample moisture.

The recovery factor, expressed as a percentage (R%), was calculated using the following equation.

$$R\% = \frac{\text{RES fortified (ppb)} - \text{RES control (ppb)}}{\text{ppb analyte added}} \times 100$$

NOTE: The residues reported in this study were not corrected for procedural recovery values.

The mass spectral analyses of degradate CGA-71019 were initially established to monitor two transitions, T1 and T2. The T1 transition monitored 70.1 => 69.9 m/z, while the T2 transition monitored 70.1 => 43.0 m/z. Due to the low sensitivity of the T2 transition, this data was not integrated nor reported, and was observed as a confirmation transition only. Refer to Figure 2 for an example set of extracted ion chromatograms for CGA-71019.

TABLE 1. TYPICAL LC SYSTEM OPERATING CONDITIONS

LC Instrumentation:

Perkin-Elmer Series 200 LC Pump
Perkin-Elmer Series 200 Autosampler
Peltier Cooling Tray for Autosampler
Eppendorf Model CH-30 Column Heater with TC-50 controller

Operating Conditions (ENV analytes, i.e., all but CGA-71019):

Column Temp.: ca. 30°C Injection Volume: 40 µL -50 µL
Sample Tray Temperature: 6-10°C
Mobile Phase Flow Rate: 0.8 mL/min
Column: YMC ODS-AQ, 5 µm, 120 Å, 150 x 4.6 mm, Part No. AQ12S051546WT
Mobile Phase 1: 0.1% acetic acid in purified water
Mobile Phase 2: 0.1% acetic acid in acetonitrile

LC Mobile Phase Program (gradient):

Step	Time, min.	1,%	2,%
0 (equil)	3.5	60	40
1	2.0	60	40
2	5.0	15	85
3	3.0	15	85
4	0.5	60	40

Linear gradients used. Total LC run time of ca. 14 minutes.

Operating Conditions (CGA-71019):

Column Temperature: ca. 30°C Injection Volume: 40 µL -50 µL
Sample Tray Temperature: 6 - 10°C
Mobile Phase Flow Rate: 0.8 mL/min
Column: Zorbax SB-CN, 150 x 4.6 mm, Part No. 883975-905
Mobile Phase 1: 0.1% acetic acid in purified water
Mobile Phase 2: 0.1% acetic acid in acetonitrile

LC Mobile Phase Program (isocratic):

Step	Time, min.	1,%	2,%
0 (equil)	0.2	90	10
1	4.0	90	10

TABLE 2. MASS SPECTROMETER SYSTEM DESCRIPTION AND TYPICAL OPERATING CONDITIONS

Mass Spectrometer System (see AG - 677 for additional details)

PE Sciex API III+ Mass Spectrometer with Sciex Turbo IonSpray™ Liquid Introduction Interface
Instrument Control and Data Collection: Apple MacIntosh Quadra 950 Computer

Parameter	ENV Analytes	CGA-71019
Turbo IonSpray Temp. (°C)	ca. 450	ca. 450
Dwell Time (msec)	220-250	250
Ionization Mode	positive	positive
ISV	4700	4700
OR	55.0	55.0
R1	27.00	27.0
L7	22.00	22.00
R2	15.00	15.00
RX	5.00	5.00
R3	13.00	13.00
L9	-250.00	-250.00
FP	-250.00	-250.00
MU	-3700.00	-3700.00
CGT	280-300	280-300
Scan Type	MRM	MRM
Mode	profile	profile

Monitoring Ions

Analyte	Exact Molecular Weight	Q1 Molecular Ion	Q3 Product Ion
Propiconazole	341.07	342.0	159.0
CGA-91305	257.01	258.0	70.0
CGA-217495	343.01	344.0	256.0
CGA-118244	357.06	358.0	256.0
CGA-118245	357.06	358.0	256.0
CGA-136735	357.06	358.0	256.0
CGA-71019*	69.03	70.1	69.9

*Note: CGA-71019 does not form an abundant product ion in MS/MS. However, some improvement in signal-to-noise can be gained by MS/MS using the molecular ion only.