Introduction of Modifying Solvents to Carbon Dioxide in Supercritical Extractions

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A simple apparatus for adding a modifying solvent to supercritical CO_2 extractant was described. Small, fixed volumes (typically 100 μL) of liquid modifying solvents were delivered during the extraction process by use of an in-line high pressure loop injector and an air pump. Without disconnecting the extraction cell from the supercritical fluid extraction system, the modifying solvent was repeatedly delivered. The solvent modification device was optimized during the extraction of carbaryl and bis(acetylacetonato) copper(II). Extraction recoveries from spiked filter paper and soil samples ranged between 22% and 109%, depending on the analyte and matrix components. The addition of polar modifying solvents were necessary to improve the extractibility of the nonpolar CO_2.

Introduction

Supercritical fluid extraction (SFE) using carbon dioxide as the supercritical fluid has been applied to many environmental matrices. The addition of a more polar solvent can often enhance recovery of the target analyte. The polar co-solvent appears to compete with the analyte of interest for active sorption sites on the surface of the matrix, enhancing desorption of the analyte.[1-3] The desorbed analyte is then solvated by the modified supercritical fluid (SCF) phase, to be eluted and collected for analysis.

Various modifying solvents have been tried over the years,[4] but methanol (MeOH) remains the most popular.[5] In certain cases, however, the addition of MeOH was not sufficient for quantitative extraction of analytes.[2,3] Very small amounts (0.5 vol %) of tributylphosphate showed efficiency comparable to 5% MeOH for the extraction of several pesticides from soil samples.[6] When extracting several PCBs from river sediment, much higher extraction efficiency was obtained when toluene was present than it was not.[7]

In an attempt to evaluate a wider range of solvents, Langenfeld and coworkers[2] performed SFE using various organic modifiers on environmental samples. Known volumes of modifying solvents were added directly to the sample in the extraction cell prior to extraction. A combined static/dynamic mode was used for this study. Acidic and basic modifying solvents (*i.e.*, acetic acid and aniline) greatly enhanced the ability of supercritical CO_2 to recover PCBs from river sediments relative to methanol-modified CO_2. For the SFE of high molecular weight PAHs in air particulates, modifying solvents such as toluene, diethylamine and methylene chloride produced the highest recoveries. Extractability was found to be dependent on a mixture of modifying solvent properties, such as polarizability, acidity/basicity, and dipole moment. It was suggested that a universal modifying solvent would be a solvent (or mixture of solvents) which possesses all of the above characteristics.[2]

Alzaga and co-workers[8] investigated such modifying solvents as toluene, methanol, pyridine, pyrrolidine, and triethylamine for the extraction of the pesticide pirimicarb

from topsoil. Their optimized procedure called for CO_2 modified with triethylamine (5% of the cell volume). Brooks and Uden[9] found 2-methoxyethanol to be the SCF CO_2 modifying solvent of choice for the recovery of abamectin from animal tissues. Methanol and acetonitrile were investigated as modifying solvents, but significantly lower recoveries were found.

The introduction of modifying solvents into the sample matrix is complicated. However, the simplest method for introducing modifying solvent is to inject the modifier into the open extraction cell. This method can be useful for static extractions, but once dynamic extraction begins, the modifying solvent will be rapidly removed from the cell. Should there be insufficient modifying solvent present to fully desorb the target analyte, interact with sorption sites on the matrix or solvate the target analyte, additional injections of solvent will be necessary, requiring disassembly of the extraction cell. Premixed cylinders can be convenient if a single concentration of modifying solvent is desired.[10] The selection of co-solvents available as premixed tanks is limited, however. In addition, a large inventory of tanks is very expensive to maintain particularly when different concentrations of a variety of modifying solvents are required. Another drawback of the use of the premixed tank is that the composition of the solvent mixture can be varied as the tank is emptied, resulting in nonreproducible extractions.[11,12] Lastly, modifying solvents can be added continuously to the extractant stream with a high-pressure pump. While this approach is more flexible than pre-mixed tanks, particularly with respect to varying compositions of the same modifying solvent in CO_2, it still requires flushing of all connecting tubing if a different cosolvent is desired.

Taylor[10] explained that the best way to introduce modifying solvents depends on the matrix and the analyte. If the interactions between a matrix and an analyte are strong, direct introduction of modifying solvent is preferred to disrupt the interactions. However, if there is a large volume of sample matrix, a single volume addition of the modifying solvent may not be sufficient to wet the entire sample. Also, if the matrix is dried prior to the extraction, a volatile

modifying solvent may disappear before the CO_2 is introduced. In such cases, continuous addition of modifying solvent, either from a premixed cylinder or *via* a high pressure pump, is necessary.

It is clear that investigation of a range of modifying solvents which introduce different solvent/matrix interactions is necessary for the optimization of extraction recoveries in SCF CO_2 based extractions. Furthermore, such optimization appears to be needed on a case-by-case basis for each solute/matrix combination. Investigation of different modifying solvents is difficult because of the requirement either for disassembly of the extraction cell to inject modifying solvent or changeover of the modifying solvent in the co-solvent pump and connecting tubing. In our laboratory, we are modifying the CO_2 extractant with a range of solvents and solvent mixtures in an attempt to better understand the desorption/solvation process and improve extraction efficiency. As part of this research, we have developed a loop injector-based system for adding the modifying solvent. We present here a description of the apparatus. The modification apparatus was applied to the extraction of carbaryl and bis (acetylacetonato) copper(II) to prove its efficiency and to further investigate modifying effects.

Experimental

Chemicals. Technical grade liquid carbon dioxide (Cardox Div., Chemetron Corporation, Countryside, IL) was used as an extraction solvent. Methanol, acetonitrile and chloroform were HPLC grade (Fisher Scientific, Chicago, IL). All other solvents and reagents were A.C.S. grade (Fisher).

Carbaryl (CAS#: 5449-00-3) was purchased locally as a commercial carbaryl insecticide formulation (KGRO Sevin Liquid, K-Mart Inc.). The carbaryl was extracted from the commercial formulation with methylene chloride (MeCl). The MeCl was removed by evaporation and the residual carbaryl was identified by infrared spectroscopy and melting point.

A stock (0.1 M) solution of carbaryl was prepared by weighing an appropriate amount of solid and dissolving it into 100 mL of HPLC grade methanol. Standard dilutions were made in methanol and used to spike solid matrices. These standard solutions were stored in brown bottles at temperatures under 5 °C.

A 1000 ppm copper ion reference solution (Fisher Scientific, Fair Lawn, NJ) was diluted to 100 ppm with deionized water (Mega-Pure water purification system, Corning Science Products, Corning, NY). From this dilution, a series of copper standard solutions (0.25 ppm to 7.50 ppm) was prepared for constructing the calibration curve for atomic absorption analysis. 2,4-pentanedione, 99% (acetyl acetone; Lancaster Synthesis Inc., Windham, NH) was used as a complexing agent for copper ion. The bis(acetyl-acetonato) copper(II), $Cu(acac)_2$, was prepared as follows: 5 mL of the 1000 ppm copper stock solution was transferred to a separation funnel. After adjusting the pH of this solution to pH = 3 with 50% NaOH, 3 mL of neat acetyl acetone was added to the copper solution. The combined solution was shaken manually for about 2 minutes and allowed to separate for 30 minutes. The organic phase
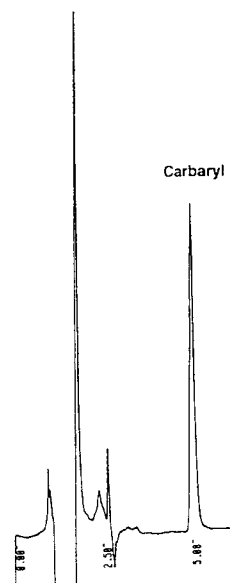

Figure 1. Typical chromatogram of carbaryl. The retention time of carbaryl was 5.1 mimutes. See text for the HPLC conditions.

containing $Cu(acac)_2$ was collected and the process repeated twice more. The combined extracts were diluted to 25 mL with $CHCl_3$. The concentration of this $Cu(acac)_2$ solution (190 ppm) was determined by atomic absorption analysis. This $CHCl_3$ solution was used for spiking filter paper.

HPLC Instrumentation. HPLC was used for carbaryl analysis. The HPLC system consisted of a Waters Model 590 pump (Waters Corp., Milford, MA), a Rheodyne Model 7125 injection valve (Rheodyne, Inc., Cotati, CA) with a 100 μL sample loop and a Waters Model 481 LC Spectrophotometer detector. Chromatograms were printed on a Waters Model 740 Data Module. The column was a Spherisorb C-18 (25 cm × 4.6 mm i.d., Phase Separations Inc., Norwalk, CT). Chromatographic elutions were performed isocratically with MeOH-H_2O-acetonitrile (40 : 45 : 15, v/v/v) at a flow rate of 1 mL/min. The detection wavelength and sensitivity were 220 nm and 0.05 absorbance units full scale (a.u.f.s), respectively. A typical chromatogram of carbaryl is shown in Figure 1.

Atomic Absorption Spectrophotometer. A Perkin-Elmer Model 305 atomic absorption spectrophotometer (Perkin-Elmer Corporation, Norwalk, CT) was used for the determination of extracted copper. The detection wavelength was 324.7 nm with a spectral bandwidth of 0.7 nm.

SFE Apparatus. The SFE apparatus was constructed with an Isco Model 260 D syringe pump (Isco. Inc., Lincoln, NE) as the pressure generator. A gas chromatographic oven was used to elevate the CO_2 extractant to the required temperature (Figure 2). The SFE cell was preceded by a 10-m coil of 1/16-in. o.d. stainless steel tubing to provide temperature equilibration for the supercritical CO_2. A high pressure switching valve (Model 7010, Rheodyne) was used either to direct CO_2 flow to the extraction cell or bypass the cell. Use of the switching valve allowed the exchange of the extraction cells without depressurizing the SFE system. This valve also makes it possible to perform supercritical fluid extractions in the static mode. The extraction cells consisted of empty 5-cm or 8-cm × 4.6 mm i.d. HPLC columns (Alltech Associates, Deerfield, IL), with 1/4-in. diameter × 1/
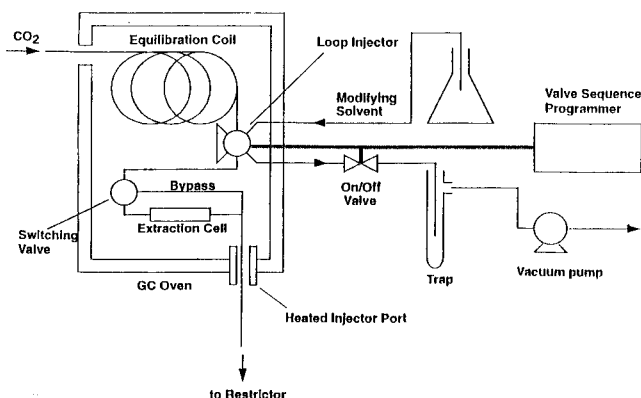
Figure 2. Solvent modification system. See text for description.

32-in. thick 2 μm stainless steel frits in both the inlet and outlet ends. Knurl-Lok plastic fingertight fittings (Upchurch Scientific Inc., Oak Harbor, WA) were used to secure the extraction cell in line. The use of these fittings limited the maximum system pressure to 5000 psi.

The pressure restrictor was a 34-cm length of 1/16-in. o.d. by 0.020-in. i.d. stainless steel tubing crimped at the very end. The flow rate of expanded gas was monitored by a soap film flow-meter connected to the upper exit end of the trapping system.

Collection of the analyte extract was performed by placing the tip of the restrictor in a 1.0-cm o.d.× 10-cm Pyrex culture tube, which contained 5 mL of trapping solution. In order to keep the depressurized gaseous CO_2 from freezing, the culture tube and trapping solution were kept in a warm water bath (30-40 °C) throughout the extraction.

Solvent Modification System. In order to deliver known quantities of modifying solvents on-line to the SFE extraction cell, a standard HPLC loop injector (Model 7010, Rheodyne) was installed in-line before the extraction cell (Figure 2). Repetitive delivery of modifying solvent was facilitated by the addition of a pneumatic actuator controlled by a digital valve sequence programmer (Valco Inc., Houston, TX). In this manner, 100 μL of the modifying solvent could be repetitively injected into the SFE cell at operator-prescribed intervals.

An air pump is used to pull a partial vacuum on the solvent trap. This pump is operated on a continuous basis. A pneumatically actuated ON/OFF valve is located between the trap and the loop injector. This valve is in the OFF position except when the injector loop requires filling, which prevents the modifying solvent from being pulled continuously through the loop. A subsequent modification employs a reciprocating piston pump to recycle the modifying solvent continually through the injection loop. The only disadvantage to this is the time involved in changing modifying solvents (typically 2-3 minutes). Note that unlike pump delivery of the modifying solvent to the high pressure connecting tubing, the extraction system does not have to be depressurized to flush the solvent lines. On command of the programmer, the pneumatic actuator turns the loop injector and opens the ON/OFF valve, causing solvent to be pulled through the sample loop by the applied partial vacuum. After a set period of time (typically 5 seconds) the programmer sequences the pneumatic actuator back to the original

position, injecting the modifying solvent contained in the loop injector. At the same time, the ON/OFF valve is closed. This process can be repeated as often as desired; we typically inject modifying solvent every two to five minutes.

Filter Paper Spikes. Filter paper (Whatman #44, 5.5 cm) was used for preliminary evaluations of SFE recovery. A half disk of filter paper was rolled up tightly and placed into the extraction cell. One hundred microliters of the standard solution was spiked into the filter paper contained in the extraction cell by using a 100 μL microsyringe (Hamilton Co., Reno, Nevada). The solvent was allowed to dry for at least one hour and the cell was put on-line for extraction.

Carbaryl-Spiked Soil Samples. The soil sample for carbaryl analysis was collected from the Michigan Technological University campus. The soil was allowed to dry at 110 °C and sieved through a 0.6 mm screen to remove debris before spiking with carbaryl. A 50.0 g portion of the soil was placed in a 1 L round-bottom flask and spiked with a MeCl solution of carbaryl to produce a level of 10 ppm (w/w) carbaryl in the soil. The container of soil was then placed in a water bath at 40 °C and the MeCl was slowly evaporated over a period of approximately 24 hours in a hood using a rotary evaporator. After the MeCl was completely evaporated, the soil was tumbled in the rotary evaporator to ensure homogeneity. Weighed samples were washed with liquid methanol and the eluates analyzed for carbaryl. A 99.8% recovery was achieved ($n = 10$, 1.7% r.s. d.) indicating that the carbaryl spiking was sufficiently homogeneous for subsequent SFE determinations.

SFE Conditions. The SFE conditions employed for carbaryl were 3000 psi, 40 °C, and 300 cc/min of gaseous CO_2 flow rate (measured with a bubble flow meter). For the extraction of the $Cu(acac)_2$ complex, the conditions were similar: 3000 psi, 37 °C, and a flow rate of 0.3-0.6 mL/min (as liquid CO_2). Extractions were carried out for 30 minutes, except for the soil spiked with carbaryl, for which the extraction time was 60 minutes. Methanol was used as the solvent modifier for the extraction of carbaryl. Both methanol and a mixture of MeOH/acetyl acetone (90 : 10, v/ v) were evaluated as modifiers for the extraction of the Cu (acac)$_2$ complex. The trapping solution was 50% methanol (in water) for the carbaryl extractions. The trapping solution was an acidic (pH = 0.6) aqueous solution for the copper extractions. Trapping in such an aqueous phase produced dissociation of the $Cu(acac)_2$ complex and allowed direct analysis of the extract by atomic absorption spectroscopy. In all cases, the trapped SFE eluate was diluted to 10.0 mL volumetrically, producing solution concentrations of 4.0 ppm carbaryl and 1.9 ppm copper for analysis, assuming 100 percent recovery.

Results and Discussion

SFE Recoveries of Carbaryl from Filter Paper.

With our solvent modification device, 100 μL of liquid methanol was successfully added to the extraction cell every 5 minutes. The addition of methanol improved the extraction recovery dramatically to 97.6% with 8.5% r.s.d. (Table 1). Only 50.0% (20% r.s.d.) of the carbaryl was extracted from spiked filter paper with unmodified CO_2. These results are

Table 1. SFE recoveries of carbaryl from filter paper

Modifier	% recovery (% r.s.d.)
None	50.0 (20)
MeOH	97.6 (8.5)

Extraction conditions: P = 3000 psi; T = 40 °C; flow rate = 300 mL/min.; time = 30 min. Trapping solution: 50% MeOH; 100 μL of modifier was injected every 5 min. Sample mass: 0.5 g; n = 3-4. Spike level: 400 ppm

not unexpected. Carbaryl is adsorbed on filter paper, a matrix composed of almost pure cellulose, $(C_6H_{10}O_5)_n$. Hydrogen bonds are likely formed between carbaryl and the cellulose matrix, preventing quantitative recovery with non-polar CO_2 alone. The added methanol appears to compete with carbaryl for the sorption sites on the matrix surface, as had been postulated in other studies.[2,13]

SFE Recoveries of Cu(acac)₂ from Filter Paper. Neither unmodified nor MeOH-modified CO_2 was able to quantitatively extract the Cu(acac)₂ complex, giving 67.8 and 69.1% recoveries, respectively (Table 2). However, the addition of acetyl acetone to the modifying methanol resulted in quantitative recovery (109%). It is suspected that there is a competition for copper ion between the acetyl acetone complexing agent and Lewis base sites on the cellulose matrix which are capable of complexing copper ion. Repetitive addition of acetyl acetone as a modifying solvent component (10:90 acetyl acetone:MeOH, v/v) proved necessary to ensure quantitative recovery of the spiked copper. Several compositions of co-solvents were evaluated before the optimum composition was determined. Such flexibility in changing the modifying solvent is a key advantage of this solvent modification system.

SFE of Carbaryl from Soil. Only 21.9% of the spiked carbaryl was recovered from soil samples by SFE with unmodified CO_2. The recovery improved dramatically (82.3%) with the addition of MeOH every five minutes (Table 3). In an attempt to improve on the MeOH recovery, a series of organic solvents was chosen as supercritical fluid modifiers. Each modifying solvent exhibited solvent/matrix interactions (acid/base, hydrogen bonding and dipole-dipole) to a different degree. The solvents selected were MeOH, toluene, pyrrole, propylene carbonate, and dimethyl form-amide (DMF). The resulting SFE recoveries of carbaryl from soil samples with various modifiers are shown in Table 3.

Toluene was chosen because it was not likely to have any specific polar interactions with the sorption sites on the matrix. Indeed, the extraction efficiency found with toluene was only moderately better than unmodified CO_2 (31.5%

Table 2. SFE recoveries of Cu(acac)₂ from filter paper

Modifier	% recovery (% r.s.d.)
None	67.8 (16)
MeOH	69.1 (7.6)
MeOH/acetyl acetone	109 (12)

Extraction conditions: P = 3000 psi; T = 37 °C; flow rate = 0.3-0.6 mL/min.; time = 30 min. Trapping solvent: aqueous, pH = 0.6; 100 μL of modifier was injected every 3 min. n = 6-8. Spike level: 200 ppm

Table 3. SFE recoveries of carbaryl from soil

Modifier	% recovery (% r.s.d.)
none	21.9 (11)
Methanol	82.3 (7.0)
Toluene	31.5 (16)
Pyrrole	38.5 (28)
Propylene carbonate	54.0 (6.4)
Dimethyl formamide	73.8 (9.8)

Extraction conditions: P = 3000 psi; T = 40 °C; flow rate = 300 mL/min.; time = 60 min. Trapping solution: 50% MeOH; 100 μL of modifier was injected every 5 min. Sample mass: 0.5 g; n = 3-5. Spike level: 100 ppm

recovery). Pyrrole and DMF are weak bases and were investigated to see how efficiently they could displace analytes from the matrix surface. Pyrrole showed only a small improvement compared to unmodified CO_2 (38.5% recovery, 28% r.s.d.). With DMF, however, the extraction efficiency improved to 73.8% (9.8% r.s.d.). This enhancement in recovery may result from differences of the degree of specific solvent/matrix interactions between pyrrole and DMF or may simply reflect a difference in the solvation characteristics of the modified SCF solution. Propylene carbonate has been suggested for use as a modifying solvent,[4] however only 54.0% carbaryl was recovered from the spiked soil using this modifying solvent. It is clear that none of the chosen solvents alone possesses the proper combination of solvation/desorption properties to produce quantitative recoveries. Different modifying solvents or mixtures of modifying solvents warrant investigation if improved extraction recovery is required. Our solvent modification system is well suited for this approach.

The present configuration of our solvent modification system is such that 100 microliters of modifying solvent is valved into the extraction cell on a recurring basis. The extraction cell volumes vary, but were nominally 2-3 mL in volume. The volumes of the injector, switching valve and connecting tubing were negligible. On the basis of extraction cell volume, therefore, we subject sample matrices to a modifier level of about 5%. According to Langenfeld,[2] this level of co-solvent is greater than that which serves principally to effect desorption from the matrix (1%, v/v) but less than the level required for significant solubility enhancement (10%, v/v).

The concentration profile of the modifying solvent as it enters the cell is likely to exhibit a rather abrupt increase. According to the data presented by Zeigler and co-workers,[14] the pressure and temperature conditions we employed are above the critical-mixture curves for all combinations of SCF CO_2 and the modifying solvents methanol and toluene. Therefore, when a plug of modifying solvent is introduced into the extraction cell, no phase boundary should exist, and the modified SCF CO_2 should behave as a single-phase system. However, this is a function of the amount of liquid solvent injected. Given the injection volume in our solvent modification system, it is likely that the co-solvent enters the extraction cell still in the liquid state, since the volume of co-solvent exceeds that of the tubing connecting the loop

injector and the extraction cell. Upon dispersal of the co-solvent into the sample matrix, however, the co-solvent/CO_2 ratio is decreased to the point where a single-phase system is formed. Upon the next addition of liquid co-solvent, the process repeats itself. Therefore, the extraction process is very similar to that process when liquid modifying solvent is added directly to the sample matrix in the open extraction cell prior to SFE.

Conclusions

The solvent modification apparatus developed in this work for the SFE system introduced the modifying solvents repeatedly and consistently to the sample matrix. Unlike a high-pressure pump, the extraction system did not have to be depressurized to flush the solvent lines when there were changes of the modifying solvents. With the aid of this modification apparatus, it was possible to investigate a range of modifying co-solvents with repetitive delivery of the modifying solvent at desired intervals.

The addition of polar organic modifying solvents to supercritical CO_2 enhanced the recoveries of the target analytes, carbaryl and the $Cu(acac)_2$ complex. The most critical factor in the SFE process is to decrease the matrix/analyte interaction and increase the partition ratio to the supercritical fluid. The action of the modifying solvent appears to be competition with the analyte for sorption sites on the matrix. Work is under way to investigate means of identifying the optimum solvent or mixture of solvents for any analyte/matrix combination encountered.

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The Synthesis of Trifluoromethylated 1,2-Diphenylvinyl Sulfone and It's Synthetic Utilities

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The treatment of 1,1-bis(phenylthio)-2,2,3,3,3-pentafluoropropylbenzene (**1**) with 2 equiv. of phenyllithium in THF at -78 °C resulted in the formation of isomeric mixture (70 : 30) of trifluoromethylated 1,2-diphenylvinyl sulfide **2** in 87% yield. The further oxidation of **2** with *m*-chloroperbenzoic acid in methylene chloride afforded isomeric mixture (70 : 30) of trifluoromethylated 1,2-diphenylvinyl sulfone **3** in 87% yield. When **3** was reacted with carbon nucleophiles such as methyllithium, *n*-butyllithium, phenyllithium and lithium octylide, the corresponding addition-elimination adducts **4, 5, 6** and **7** were obtained in moderate to good yields. The reaction of **3** with 4 equiv. of tributyltin hydride in benzene at reflux temperature provided isomeric mixture (90 : 10) of trifluoromethylated 1,2-diphenylvinyl stannane **8** in 41% yield. The reaction of **8** with methyllithium in the presence of trimethylsilyl chloride gave isomeric mixtures (90 : 10) of trifluoromethylated 1,2-diphenylvinyl silane **9** in 88% yield. Finally, the treatment of **8** with Br_2 and I_2 resulted in the formation of isomeric mixtures (90 : 10) of trifluoromethylated 1,2-diphenylvinyl bromide **10** and iodide **11** in 72% and 90% yields, respectively.

Introduction

Recently, considerable effort has been paid to the development of fluorine-containing synthetic building blocks[1-7]

because of their potential to give new synthetic routes to a variety of fluoroorganic compounds, some of which exhibit unique biological properties in the areas of agrochemicals, pharmaceuticals and material science.[8-10] Of particular inter-