HPLC DETERMINATION OF THE FUNGICIDES BITERTANOL, IMAZALIL, AND THIABENDAZOLE IN BANANA

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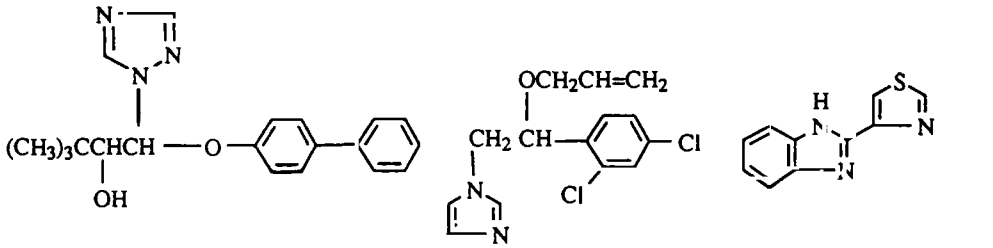
Abstract : The determination of bitertanol, imazalil, and thiabendazole was investigated with isocratic reversed-phase high-performance liquid chromatography. Bitertanol was successfully chromatograghed and quantitated by utilizing a reversed-phase LiChrospher 100 RP-8 column (E. MERCK, Darmstadt, Germany) after extraction with ethyl acetate and clean-up with a Sep-pak plus CN cartridge. An acetonitrile-0.1M H_3PO_4 (60:40) mobile phase was used. Imazalil and thiabendazole were chromatographed by using the same column with a mobile phase of acetonitrile-0.1M H_3PO_4 (90:10) after clean-up with a solvent partition method.

Bitertanol was detected by fluorescence detection. Imazalil was detected by UV and thiabendazole was detected by fluorescence in tandem at typical residue levels on bananas. The practical quantitative limit of bitertanol, imazalil, and thiabendazole was 0.01mg/kg. The recoveries were about 80%.

Introduction



Bitertanol 1 Imazalil 2 Thiabendazole 3

Figure 1: Bitertanol 1, imazalil 2, and thiabendazole 3

The ergosterol biosynthesis inhibitors containing organonitrogen as the basis of agricultural chemicals for plant fungicides were introduced to the commercial markets at the end of the 1960's.

Bitertanol (1, 1,2,4-triazole derivatives) and imazalil (2, imidazole derivative) are two of these types of compounds. Bitertanol 1 gave outstanding fungicidal results with respect to the level of control and dose rate per hectare (Figure 1).

There is a review on the diverse functional groups of ergosterol biosynthesis inhibitors (1). Bitertanol 1 significantly inhibits various pathogens on vegetables and fruits. For bananas, these pathogens include *mycosphaerella musicola, m. fijiensis,* and *m. figensis* var. *diffurmis* (2,3). Recently, bitertanol 1 was found in bananas imported into Japan (4). Both imazalil 2 and thiabendazole 3 have been widely used as post-harvest fungicides of bananas.

Literature references for the determination of bitertanol 1 are generally by gas chromatography (4-14). Additionally, the separation of alcoholic enantiomers (i.e. bitertanol 1) has been performed by gas chromatography (15,16). One HPLC method for the determination of bitertanol 1 was also reported with a reversed-phase LiChrosopher RP-18 column equipped with a fluorescence detector after clean-up by an extraction column filled with diatomaceous earth (17).

The chromatographic determination of imazalil 2 has been reported by gas chromatography (5,11,18-21) as well as HPLC (22-24).

Thiabendazole 3 has been determined by reversed-phase high-performance liquid chromatography (RP-HPLC) using either silica-based C18 (octadecyl silica) column (25-30) or C8 (octyl silica) column (31-35). A sensitive determination of thiabendazole 3 was performed by HPLC with a C18 column after derivatization of the thiabendazole 3 with *p*-nitrobenzyl bromide (36). Additionally, ion-pair HPLC with C18 column separation has been performed for the detection of thiabendazole 3 (37-39).

Finally, the simultaneous determination of imazalil 2 and thiabendazole 3 in citrus fruits was performed by normal phase HPLC with a Sepralyte Diol column after extraction with dichloromethane and clean-up based on a solid phase extraction column (40).

Since permissible residual standards have now been set concerning bitertanol 1, imazalil 2 and thiabendazole 3. the determination of these fungicides in bananas is often required. This report presents an analytical method which is sensitive and robust for the routine analysis of these three fungicides.

Experimental

A. Apparatus

(a) HPLC system (Shimadzu Seisakusho Co. Ltd., Kyoto, Japan)

Pump; LC-10AD. System controller; SCL-10A. Autoinjector; SIL-10A. Oven; CTO-10A. UV-detector; SPD-10AV. Fluorescence detector; RF-535. Integrator: C-R4AX.

Degasser

ERC-3522 (Erma CR. Inc., Saitama, Japan).

Sample injector

Model 7125 with 20 μL loop (Rheodyne Inc., California, U.S.A.).

HPLC conditions for the fungicides are shown in Table 1.

Table 1: HPLC conditions for bitertanol 1, imazalil 2, and thiabendazole 3

HPLC conditions	Bitertabol 1	Imazalil 2, and Thiabendazole 3
Analytical column	LiChrospher 100 RP-8 (5 μ) 250 x 4 mm i.d.	LiChrospher 100 RP-8 (5 μ) 250 x 4 mm i.d.
Guard column	LiChrospher 100 RP-8 (5 μ) 4 x 4 mm i.d.	LiChrospher 100 RP-8 (5 μ) 4 x 4 mm i.d.
Mobile phase	CH_3CN-0.1M H_3PO_4 (60:40)	CH_3CN-0.1M H_3PO_4 (90:10)
Flow rate	1.0 mL/min	2.0 mL/min
Column temperature	40°C	40°C
Wave length	Fluorescence detection 260 nm (Ex); 325 nm (Em)	UV detection for imazalil 2 203 nm Fluorescence detection for Thiabendazole 3 302 nm (Ex); 350 nm (Em)
Sample size	20 μL	20 μL

(b) Gas chromatooraph-mass spectrometer

Automass 20 (Delsi-Nermag Instruments, Argenteuil, France) and an evaluation unit (JEOL Datum Ltd., Tokyo, Japan).

(c) The following additional equipment was also used:

Food processor; JM-1200 (Mitsubishi electronic Co. Ltd., Tokyo, Japan). Homogenizer; EXCEL autohomogenizer (Nihon Seiki Ltd., Tokyo, Japan). Mechanical shaker; KM shaker V-D (Iwaki Co. Ltd., Tokyo, Japan). Rotary vacuum evaporator; Model N-2 (Tokyo Rikakikai Inc., Tokyo, Japan). Ultrasonic bath; Model FF-12 (Sanko Junyaku Co. Ltd., Chiba, Japan).

B. Reagents

Methanol and acetonitrile of HPLC analytical grade were obtained from Nacalai Tesque Inc., (Kyoto, Japan). Anhydrous disodium hydrogen phosphate (Na_2HPO_4), anhydrous sodium sulphate (Na_2SO_4), sodium hydroxide (NaOH), sodium chloride (NaCl), sulphuric acid (H_2SO_4), *n*-pentane, and phosphoric acid (H_3PO_4) were reagent grade. Ethyl acetate for the residue extraction was obtained from Wako Pure Chemical Industries Ltd., (Osaka, Japan).

Bitertanol 1, imazalil 2, and thiabendazole 3 were obtained from Riedel-de Haen Aktiengesellschaft (Hannover, Germany).

Water was Milli-Q quality.

Sep-pak plus CN cartridge was obtained from Waters Chromatography Division Millipore Corporation (Massachusetts, U. S. A.).

C. Preparation of sample extracts

4-5 Banana fingers were sliced with a knife with skins intact and then homogenized with a food processor.

Another 4-5 banana fingers were peeled and then homogenized with the food processor to obtain the homogenate of the banana pulps.

The extraction procedures for the two prepared banana homogenates were performed by Kitada's method (26). The clean-up procedure for imazalil 2 and thiabendazole 3 was followed by Tonogai's method (24).

Each 10 g of prepared banana homogenate was individually weighed into a 200 mL blender cup. 3 g of anhydrous disodium hydrogen phosphate (Na_2HPO_4), 10 g of anhydrous sodium sulphate (Na_2SO_4), and 80 mL of ethyl acetate were added to each weighed banana homogenate and then extracted by homogenizing for 10 min. at 7000 rpm. The supernatant was filtered through filter paper (No. 5B, Toyo Rosshi Kaisya Ltd., Tokyo, Japan). The remaining precipitate was again homogenized with an additional 80 mL of ethyl acetate and then filtered. The combined filtrate was removed to a separatory funnel. 50 mL of saturated sodium chloride (NaCl) solution and 5 mL of 5*N* NaOH solution were added to the separatory funnel. The filtrate with the two added reagent solutions was mixed on a mechanical shaker. The aqueous layer was discarded and a 50 mL x 2 (Total 100 mL) of 0.1*N* sulphuric acid is added to the organic layer and then shaken. The obtained organic layer was then used to determine bitertanol 1. The aqueous layer (#1) must be saved in another separatory funnel for the determination of imazalil 2 and thiabendazole 3).

For the determination of bitertanol 1, the organic layer was washed with 50 mL of saturated sodium chloride (NaCl) solution, dehydrated with anhydrous sodium sulphate (Na_2SO_4), and evaporated completely to dryness by a vacuum rotary evaporator at 40°C (water bath). The residue was dissolved with 10 mL of *n*-pentane in a ultrasonic bath and then the solution was applied to a Sep-pak plus CN cartridge. The cartridge was rinsed with 10 mL of *n*-pentane and eluted with about 10 mL of methanol. The eluate was made up to a total volume of 10 mL with methanol and then bitertanol 1 was determined by HPLC.

For the determination of imazalil 2 and thiabendazole 3, 20 mL of 5N sodium hydroxide (NaOH) and 50 mL x 2 (total 100 mL) of ethyl acetate were added to the aqueous layer (#1) in the separatory funnel above and then shaken. The combined organic layer was washed with 50 mL of saturated sodium chloride (NaCl) solution, dehydrated with anhydrous sodium sulphate (Na_2SO_4), and evaporated completely to dryness by a vacuum rotary evaporator at 40°C (water bath). The residue was dissolved in 1 mL of methanol by an ultrasonic bath and the determination of imazalil 2 and thiabendazole 3 was completed by HPLC.

For the identification of bitertanol 1, imazalil 2 and thiabendazole 3, the sample solutions were evaporated to dryness, and the residues were then dissolved with 0.5 mL of acetone. The solutions were subject to gas chromatography-mass spectrometry (GC-MS).

Results and Discussion

Figure 2 shows the relationship between capacity factor (k') of bitertanol 1 and the mobile phase solvent. The optimal HPLC condition gave a solvent ratio of 60:40 (acetonitrile-0.1M H_3PO_4). The peaks of banana constituents and that of bitertanol 1 were clearly separated by the mobile solvent. However, when the concentration of acetonitrile was less than 50%, the peak of bitertanol 1 was split into its two diastereomers.

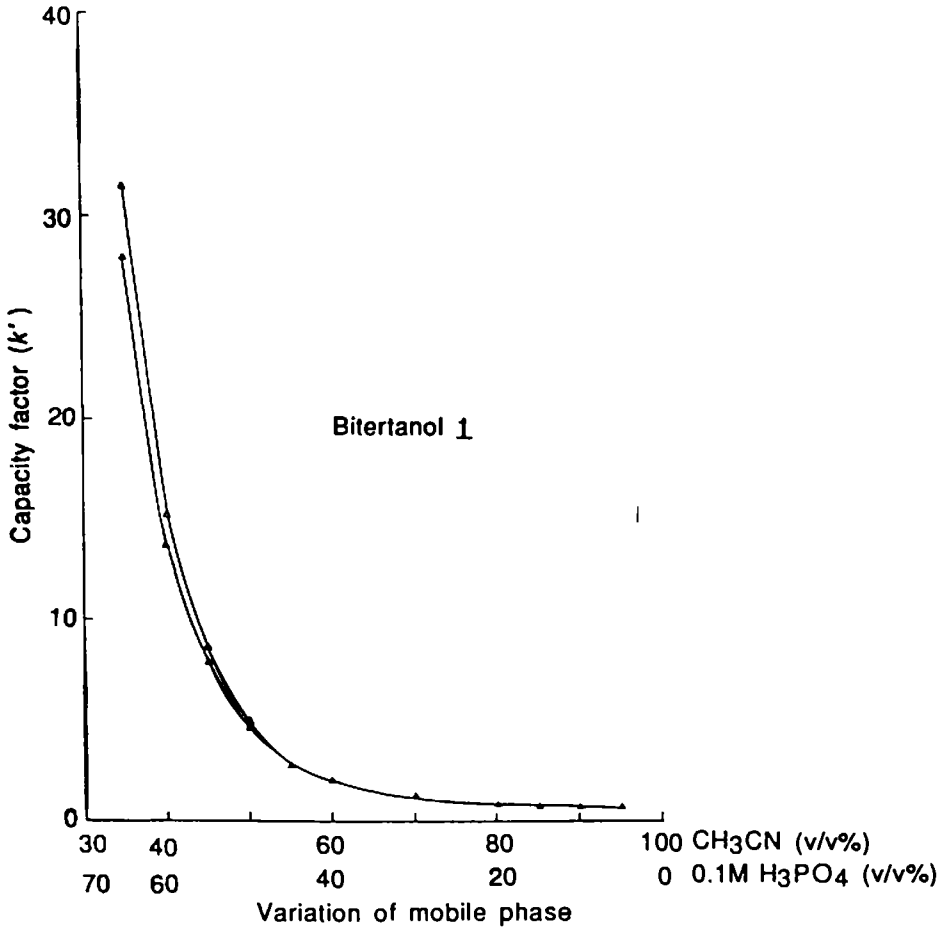


Figure 2: The relationship between capacity factor (k') of bitertanol 1 and the mobile phase solvent

Figure 3 shows the dependence of capacity factor (k') of imazalil 2 and thiabendazole 3 on the ratio of the mobile phase solvents. Here, the best ratio of the eluent solvent was 90:10 (acetonitrile-0.1M H_3PO_4). In the optimal ratio, imazalil 2 and thiabendazole 3 could be completely separated from the peaks of typical banana constituents (Figure 3).

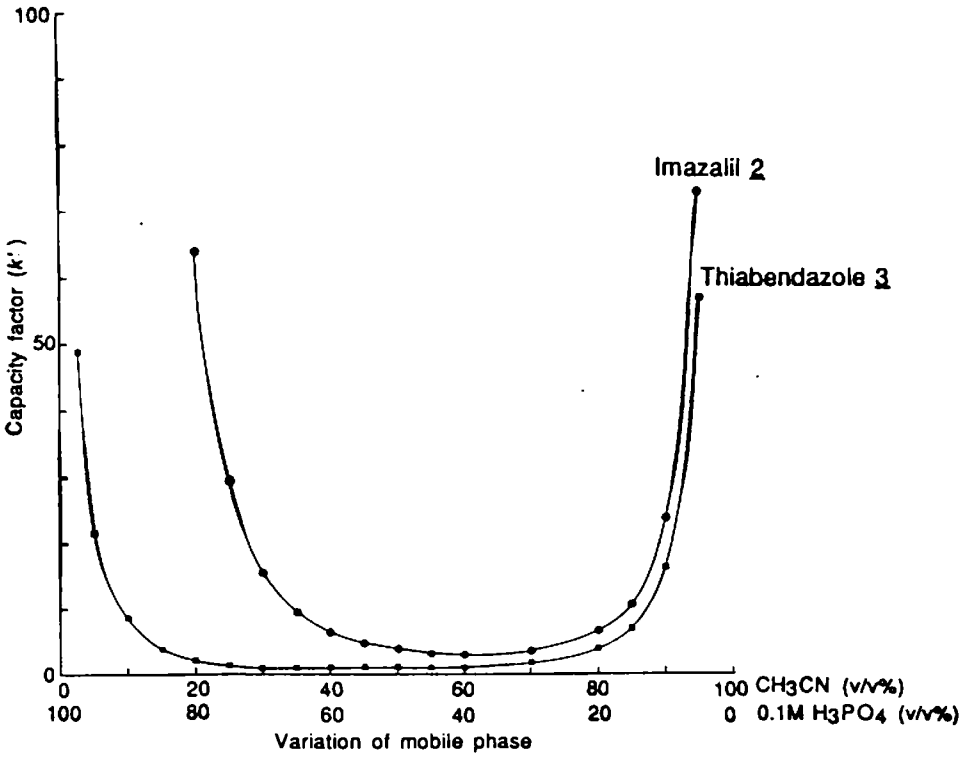


Figure 3: The dependence of capacity factor (k') of imazalil 2 and thiabendazole 3 on the ratio of the mobile phase solvents

Table 2 shows the recovery percentage (%) of bitertanol 1 by Sep-pak cartridges for the clean-up procedure of bitertanol 1. 10 µg of bitertanol 1 (solvent: *n*-pentane) was applied to each Sep-pak cartridge and then rinsed with 10 mL of *n*-pentane. Bitertanol 1 was eluted with methanol from the cartridge. Consequently, the Sep-pak plus CN cartridge was chosen because the recovery percentage (%) of bitertanol 1 with Sep-pak plus CN cartridge was not only superior to 5 other Sep-pak cartridges, but also its interference peak on the chromatogram was less than others for the determination of bitertanol 1 in bananas (Table 2).

The chromatogram of 0.05 µg/mL of bitertanol 1 and the extracted bitertanol 1-free whole banana is shown in Figure 4 (A) and Figure 4 (B), respectively. No interfering peaks were noted on the chromatograms. Figure 4 (C) shows a chromatogram of 0.05 mg/kg of bitertanol 1 added to whole bananas (Figure 4).

The chromatograms of 5 µg/mL imazalil 2 by UV (203 nm) detection and thiabendazole 3 by fluorescence (Ex. 302nm, Em. 350nm) are shown in Figures 5 (A-1) and (A-2), respectively (Figure 5).

Table 2: The recovery percentage (%) of bitertanol 1 by Sep-pak cartridges

Sep-pak cartridge	Recovery (%)
Sep-pak plus CN (Cyanopropyl chemically bonded silica)	99
Sep-pak plus Florisil	99
Sep-pak plus Alumina A	92
Sep-pak plus Alumina B	98
Sep-pak plus Alumina N	96
Sep-pak plus Silica	89

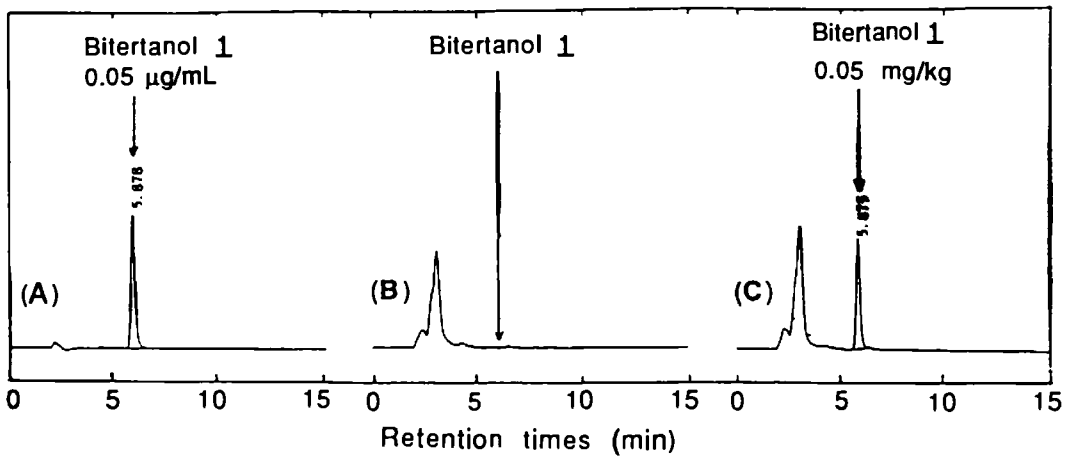


Figure 4: HPLC of bitertanol 1
(A) Chromatogram of 0.05 μg/mL bitertanol 1 standared solution. (B) Chromatogram of the extract of whole banana (bitertanol-free). (C) Chromatogram of the extract of whole banana in which 0.05 mg/kg bitertanol 1 was added.
RP-HPLC condition; Analytical column-LiChrospher 100 RP-8 (5 μ) 250 x 4.0 mm i.d., guard column-LiChrospher 100 RP-8 (5 μ) 4.0 x 4.0 mm i.d., mobile phase-acetonitrile-0.1M H_3PO_4 (60:40), flow rate-1.0 mL/min, column temperature-40°C, detection-fluoresecence, Ex; 260, Em; 325 nm, injection-20 μL.

The chromatograms of fungicide-free whole banana by UV (203 nm) detector and fluorescence detector (Ex. 302nm, Em. 350nm) are shown in Figures 5 (B-1) and (B-2), respectively. No interfering peaks were observed in the chromatograms.

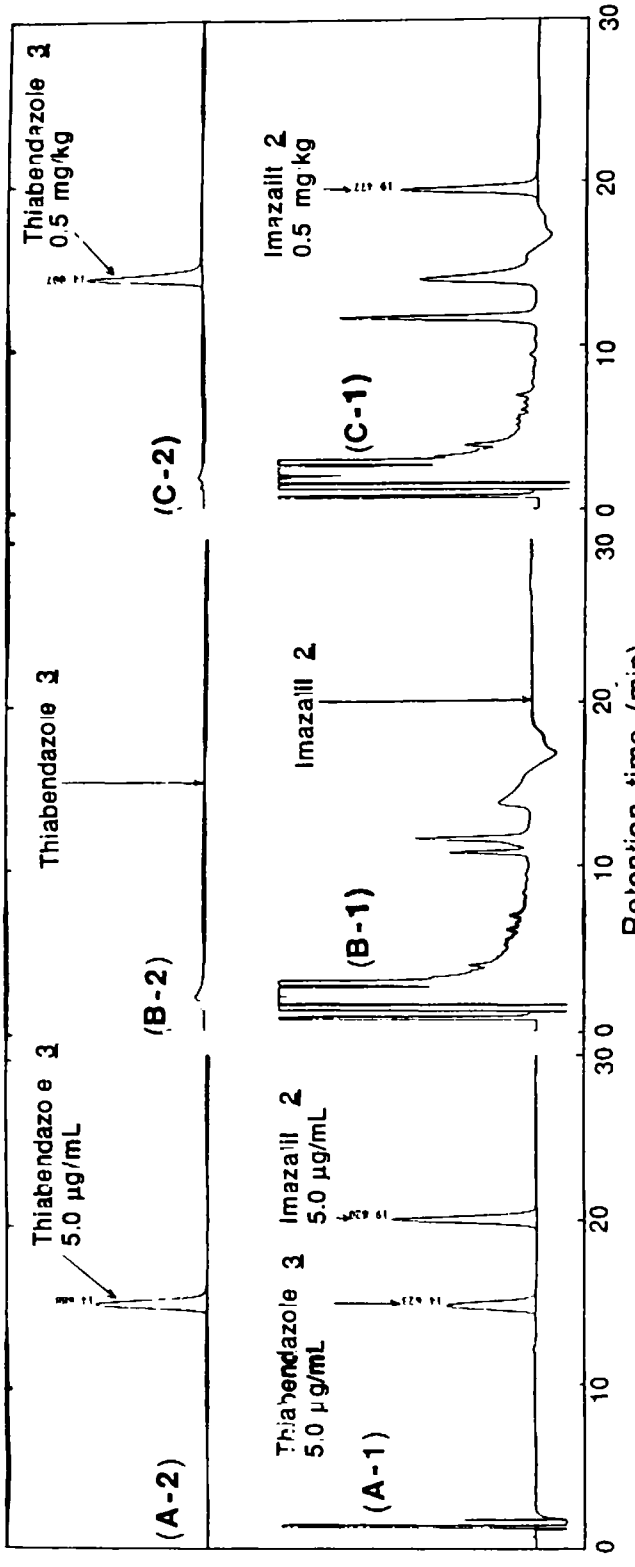


Figure 5. HPLC of imazalil 2 and thiabendazole 3
(A-1, A-2) Chromatogram of 5.0 µg/mL imazalil 2 and thiabendazole 3 standard solution. A-1: UV chromatogram. A-2: fluorescence chromatogram
(B-1, B-2) Chromatogram of the extract of whole banana (fungicide-free). B-1: UV chromatogram. B-2: fluorescence chromatogram.
(C-1, C-2) Chromatogram of the extract of whole banana in which 0.5 mg/kg imazalil 2 and thiabendazole 3 were added. C-1: UV chromatogram C-2: fluorescence chromatogram.
RP-HPLC condition. Analytical column-LiChrospher 100 RP-8 (5 µ) 250 x 4.0 mm i.d., guard column-LiChraspher 100 RP-8 (5 µ, 4.0 x 4.0 mm i.d., mobile phase-acetonitrile-0.1M H_3PO_4 (90:10), flow rate-2.0 mL/min, column temperature-40°C, detection-UV, 203 nm, fluorescence, Ex; 302, Em, 350 nm, injection-20 µL.

The chromatograms of 0.5 mg/kg of imazalil 2 added to whole banana by UV (203nm) detector and thiabendazole 3 by fluorescence detector (Ex. 302nm, Em. 350nm) are shown in Figures 5 (C-1) and (C-2), respectively (Figure 5).

The chromatograms of 1.0 μg/mL of thiabendazole 3 and the extracted fungicide-free banana pulp are shown in Figures 6 (A) and (B), respectively. Apparently, there are no interferences for the determination of thiabendazole 3 in banana pulp.

Figure 6 (C) shows a chromatogram of 0.05 mg/kg of thiabendazole 3 extracted from banana pulp.

The addition-recovery percentages (%) of bitertanol 1, imazalil 2 and thiabendazole 3 in whole banana and banana pulp were determined. Fungicide-free bananas were used as a control. The spiked levels of bitertanol 1 in whole banana were 0.05, 0.10, 0.50 and 1.00 mg/kg. For imazalil 2 and thiabendazole 3, the spiked levels in whole banana were 0.50, 1.00 and 5.00 mg/kg. For thiabendazole 3 in banana pulp, the spiked level were 0.05, 0.10, 0.50 and 1.00 mg/kg. Their recovery percentages (%) ranged from 75.8 to 82.7% (Table 3).

Table 3: Recovery and coefficient of variation (c.v.) of bitertanol 1, Imazalil 2, and thiabendazole 3

Spiked (mg/kg)	Bitertanol 1 (whole banana)		Imazalil 2 (whole banana)		Thiabendazole 3 (whole banana)		Thiabendazole 3 (banana pulp)	
	Recovery (%)	c.v. (%)	Recovery (%)	c.v. (%)	Recovery (%)	c.v. (%)	Recovery (%)	c.v. (%)
0.05	79.2	2.6					75.8	2.6
0.10	79.5	2.2					77.9	2.7
0.50	82.7	2.3	77.9	1.0	81.1	1.1	76.2	2.1
1.00	80.7	2.2	79.1	2.7	81.3	2.9	76.7	2.2
5.00			77.7	0.4	79.9	1.0		

a) Every value of the recovery is the average of five trials.

Figure 7 shows the HPLC chromatogram of bitertanol 1, imazalil 2 and thiabendazole 3 found in bananas at a commercial market in Tokyo. Figures 7 (A), 7 (B-1, B-2) and 7 (C-1, C-2) show the chromatograms of bitertanol 1 in whole banana, imazalil 2 and thiabendazole 3 in whole banana, and imazalil 2 and thiabendazole 3 in banana pulp, respectively.

The detected residues of bitertanol 1, imazalil 2, and thiabendazole 3 in bananas at a commercial market are shown in Table 4. All residues were found to be within acceptable levels (Table 4).

Figures 8 (A-1), 8 (A-2), and 8 (A-3) show the mass spectra of bitertanol 1, imazalil 2, and thiabendazole 3 in whole bananas. Figures 8 (B-1) and 8 (B-2) show mass chromatograms and total ion chromatograms (TIC) of 100 μg/mL of bitertanol 1, and 50 μg/mL each imazalil 2 and thiabendazole 3, respectively (Figure 8).

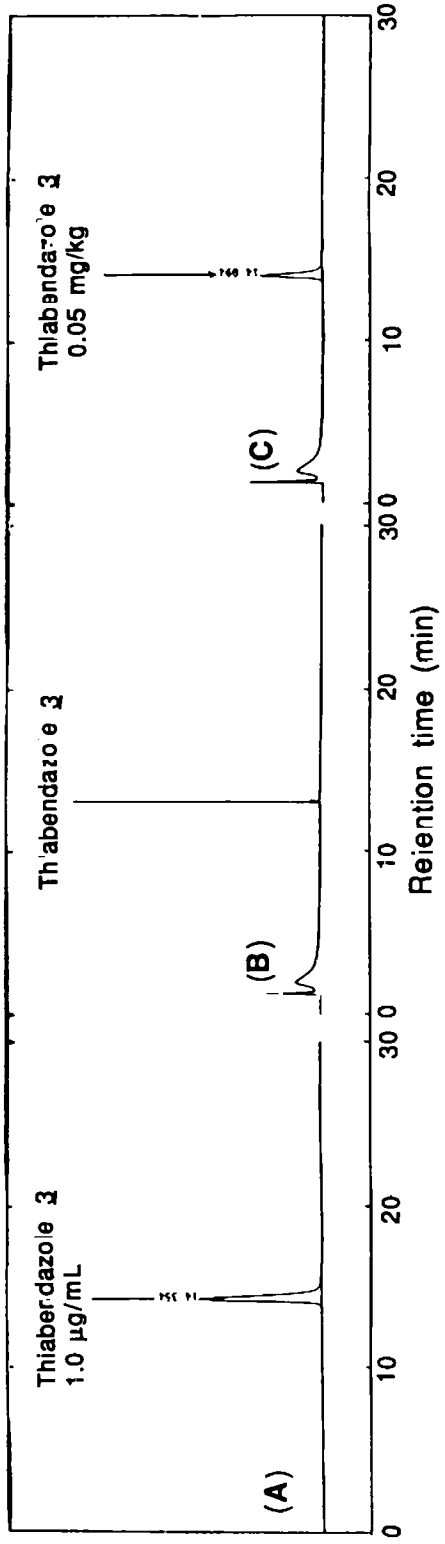


Figure 6: HPLC of thiabendazole 3
(A) Chromatogram of 1.0 µg/mL thiabendazole 3 standard solution.
(B) Chromatogram of the extract of banana pulp (thiabendazole-free).
(C) Chromatogram of the extract of banana pulp in which 0.05 mg/kg thiabendazole 3 was added.
RP-HPLC condition: Analytical column-LiChrospher 100 RP-8 (5 µ) 250 x 4.0 mm i.d., guard column-LiChrospher 100 RP-8 (5 µ) 4.0 x 4.0 mm i.d., mobile phase-acetonitrile-0.1M H_3PO_4 (90:10), flow rate-2.0 mL/min, column temperature-40°C, detection-fluorescence, Ex, 302, Em; 350 nm, injection-20 µL.

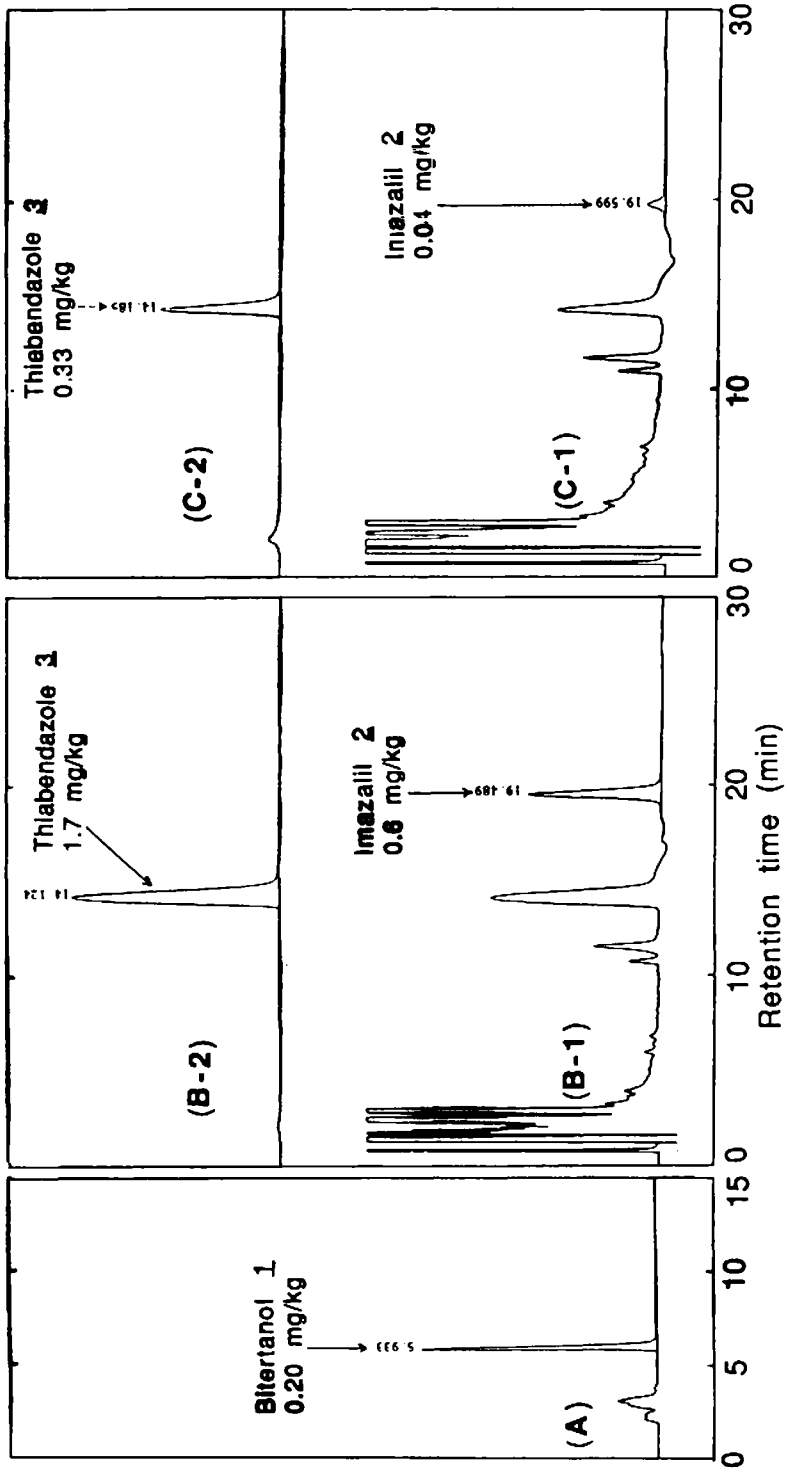


Figure 7: HPLCs of bitertanol 1, imazalil 2, and thiabendazole 3 in bananas at a commercial market
(A) Chromatogram of bitertanol 1 extracted from whole banana.
(B-1, B-2) Chromatograms of imazalil 2, and thiabendazole 3 extracted from whole banana. B-1: UV chromatogram.
B-2: fluorescence chromatogram.
(C-1, C-2) Chromatograms of imazalil 2, and thiabendazole 3 extracted from banana pulp. C-1: UV chromatogram. C-2: fluorescence chromatogram.

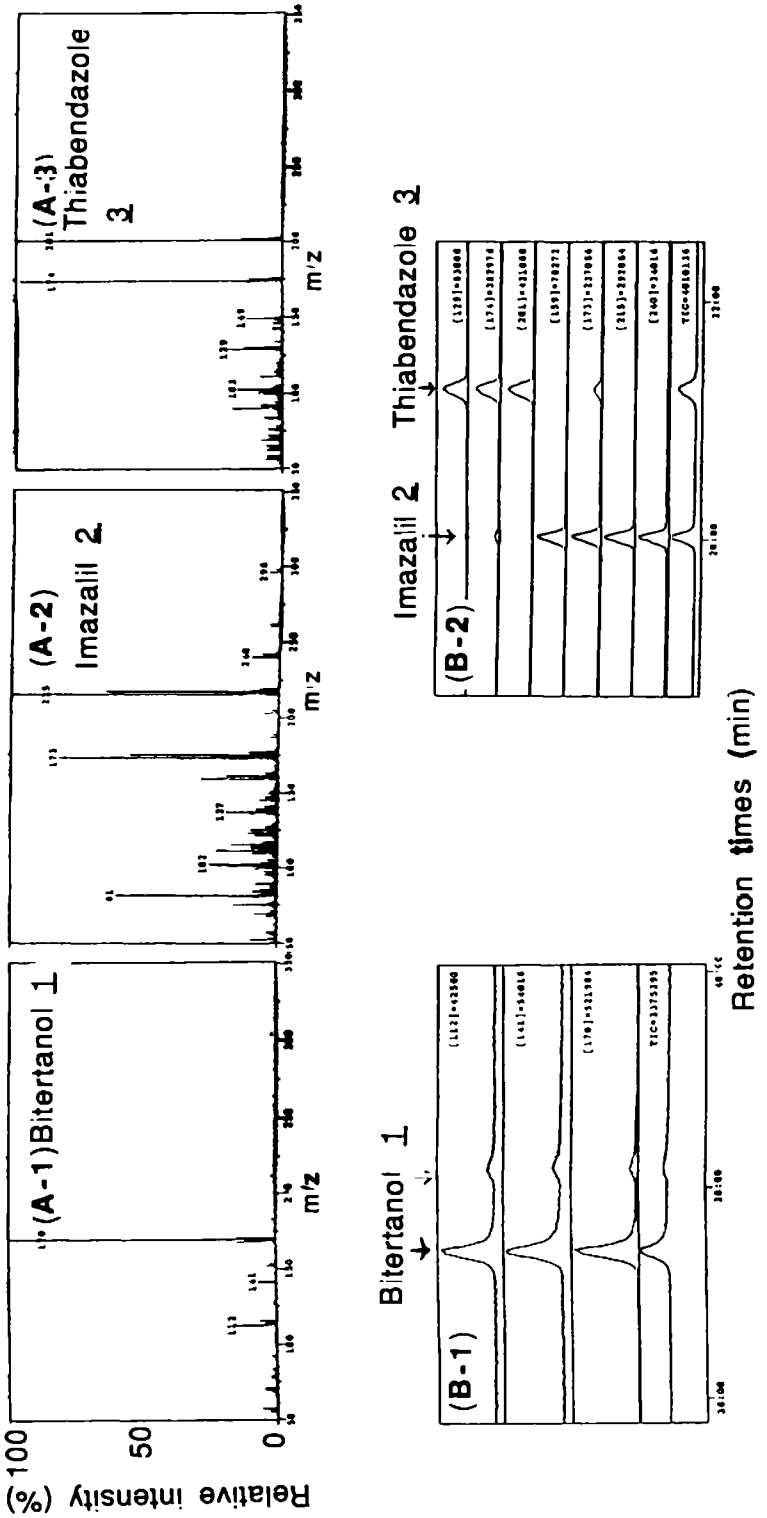


Figure 8: Mass spectra, mass chromatograms, and total ion chromatograms (TIC) of bitertanol 1, imazalil 2, and thiabendazole 3.
(A-1) Mass spectrum of bitertanol 1 (0.08 mg/kg). (A-2) Mass spectrum of imazalil 2 (0.6 mg/kg). (A-3) Mass spectrum of thiabendazole 3 (1.7 mg/kg). These compounds were extracted from whole banana.
(B-1) Mass chromatogram and total ion chromatogram of bitertanol 1 standard solution (100 µg/mL). (B-2) Mass chromatogram and total ion chromatogram of imazalil 2 and thiabendazole 3 standard solution (50 µg/mL).
Parameters for GC-MS: column-DB-17, 0.25 mm i.d. x 30 m, 0.25 µ film (J & W Scientific Inc.), inlet-splitless capillary (250°C), oven temperature 50°C (3 min)-20°C/min-250°C (20 min)-30°C/min-270°C (10 min), carrier-He at 3 psi, injection-2 µL, mode-EI, interface temperature-230°C, ion source temperature-130°C ionization energy-70eV, emission current-300 µA.

Table 4: The detected residues of bitertanol 1, imazalil 2, and thiabendazole 3 in bananas at a commercial market

No.	Bitertanol 1 (whole banana) (mg/kg)	Imazalil 2 (whole banana) (mg/kg)	Thiabendazole 3	
			(whole banana) (mg/kg)	(banana pulp) (mg/kg)
1	- a)	-	-	-
2	0.08	-	-	-
3	0.29	-	-	-
4	-	-	-	-
5	0.01	0.6	1.7	0.33
6	-	-	-	-
7	0.20	-	-	-
8	-(trace)	-	-	-

a) -: less than 0.01 mg/kg.

Summary

For the determination of bitertanol 1, after a clean-up procedure by a solid phase extraction with Sep-pak plus CN, HPLC with a fluorescence detection was demonstrated. For the simultaneous determination for imazalil 2 and thiabendazole 3, a reverse-phase HPLC (RP-HPLC) with a LiChrospher 100 RP-8 column was performed. Satisfactory detection limits (sensitivity) of each compound were obtained by the technically simple procedure. Positive identification *via* gas-chromatography-mass spectrometry was accomplished for the three fungicides. The above proposed analysis procedures for fungicide residues in bananas is simple and sensitive.

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