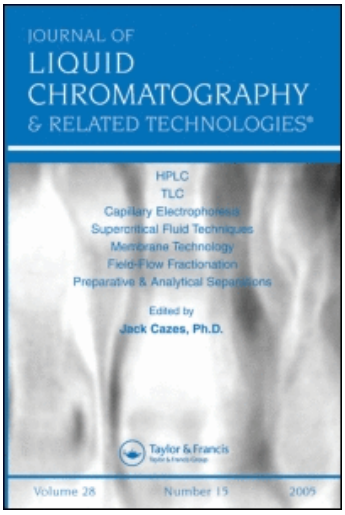

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Determination of Laurocapram in Hypertonic Triazophos Emulsifiable Concentrate by High Performance Liquid Chromatography

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Abstract: A reversed phase high performance liquid chromatographic method has been developed for the determination of laurocapram in hypertonic triazophos emulsifiable concentrates. Analysis was accomplished in a Kromasil C_{18} column with methanol-water (92 : 8, v/v) or acetonitrile-water (90 : 10, v/v) as mobile phase, and detection was performed by UV absorption at a wavelength of 210 nm. The chromatographic behavior and separation performance of samples determined were compared under two elution conditions chosen. The method is rapid, accurate, reliable, and has been successfully applied for the quality control analysis of hypertonic triazophos emulsifiable concentrates in the laboratories of some agricultural chemical plants. Also, this method can be used for laurocapram determination of other pesticide formulations and pharmaceutical preparations.

Keywords: Laurocapram, Hypertonic triazophos emulsifiable concentrate, HPLC, Methanol, Acetonitrile

INTRODUCTION

Laurocapram (1-dodecylazacycloheptan-2-one) patented by Nelson Research in 1983, is one of the most promising permeation promoters.[1] Azone is its

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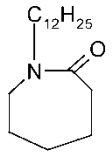
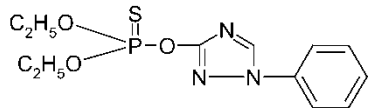
other popular name. This substance was at first used in the fields of medicine and cosmetics and, after several years of application, it was found to have potential in the pesticide area. Recently, permeation studies have suggested that laurocapram acts on the structured lipids of the stratum corneum and enhances the intercellular penetration of drugs by means of the induction of increased fluidity in this region.[2] Therefore, efficient drug components can pass the epidermal layer into pest bodies and plants rapidly. It is well accepted that the best results were achieved when laurocapram concentration in pesticide preparations were 1.0%~1.5%.[3] So, in order to control the optimal laurocapram amount added, it is essential to determine laurocapram in various formulations of pesticides. Gas chromatographic (GC) and thin-layer chromatographic (TLC) methods have been described for the determination of laurocapram since 2000.[4–8] But, such methods all aimed at the assay of laurocapram raw material i.e., technical liquid purity before addition to pesticide preparations. In this paper, a high performance liquid chromatographic (HPLC) method with UV detection for laurocapram analysis is reported. The HPLC-UV method has proven to be applicable to the determination of laurocapram content in hypertonic triazophos [3-(O,O-diethyl)-1-phenyl thiophosphoryl-1,2,4-triazol] emulsifiable concentrate (EC).

Triazophos is a broad-spectrum organophosphate insecticide and acaricide with some nematicidal properties. It is used on various crops, such as okra, cotton, maize, paddy, etc. to control aphids, fruit borer, leaf hopper, cutworms, etc.[9] The product is generally made into an emulsifiable concentrate. Moreover, in order to increase the pesticidal effect, about 1.5% of laurocapram is added to triazophos EC by many manufactures.



Laurocapram



Triazophos

EXPERIMENTAL

Reagents and Chemicals

Reference substances of laurocapram (95%) and hypertonic triazophos EC samples were provided by Jiangpu Agricultural Chemical Plant (Nanjing, PRC). Methanol and acetonitrile were of HPLC grade and were purchased from Hanbang Science and Technology Co. Ltd. (Huaian, PRC) and Merck (Darmstadt, Germany), respectively. Wahaha purified water (Wahaha Group Ltd., Hangzhou, PRC) was used throughout the experiment.

Apparatus and Chromatographic Conditions

Instrumentation for quantitative analysis included a Varian 5060 liquid chromatograph (Varian, Walnut Creek, USA), a Rheodyne 7725i injector valve equipped with a 10-μL loop (Rheodyne, Cotati, USA), and a Waters 486 tunable UV absorbance detector (Waters, Milford, USA) operating at 210 nm. Data acquisition and processing were performed with a JS-3050 chromatographic workstation (Dalian Johnsson Separation Science and Technology Corporation, Dalian, PRC) and a Yokogawa Hokushin Electric Type 3066 pen recorder (Sino-Japanese Sichuan Fourth Meter Factory, Chongqing, PRC).

The optimum UV wavelength of laurocapram was obtained with a 2695 Separations Module equipped with a vacuum degasser, a quaternary pump, an auto-sampler, and a 996 UV-Vis photodiode-array detector (PDA) (Waters, Milford, USA). The separation was controlled and the chromatograms were recorded with a Waters Millinium^{32} chromatography manager system.

HPLC separation and measurement were carried out on a 5-μm Kromasil C_{18} column with the dimensions of 150 × 4.6-mm (Hanbang Science and Technology Co. Ltd., Huaian, PRC) at 30°C. Two mobile phase systems were selected and compared: methanol-water (92 : 8, v/v) and acetonitrile-water (90 : 10, v/v). The flow rate was set at 1.0 mL/min.

Procedure

50.00 mg of laurocapram reference substance was accurately weighed into a 25-mL volumetric flask and methanol was added to the volume. All other standard solutions of laurocapram were prepared from this stock solution by serial dilution with methanol in the further stages of the experiment.

About 38 μL hypertonic triazophos EC was accurately weighed and transferred into a 25-mL volumetric flask. After being dissolved with methanol, methanol was added to the mark.

RESULTS AND DISCUSSION

Chromatograms

Typical chromatograms of laurocapram standard solution and hypertonic triazophos EC sample solution, under two elution conditions, are shown in Figure 1. The retention times for laurocapram are 6.8 min and 8.7 min, respectively, with methanol-water (92 : 8, v/v) and acetonitrile-water (90 : 10, v/v) as the mobile phases. There are several large peaks in the chromatograms of hypertonic triazophos EC sample (Figures 1c and 1d), and even in those of laurocapram standard (Figure 1a and 1b). On one hand, the sample contains triazophos, emulsifier, solvent, etc., as the composition of triazophos EC. On the other hand, the short

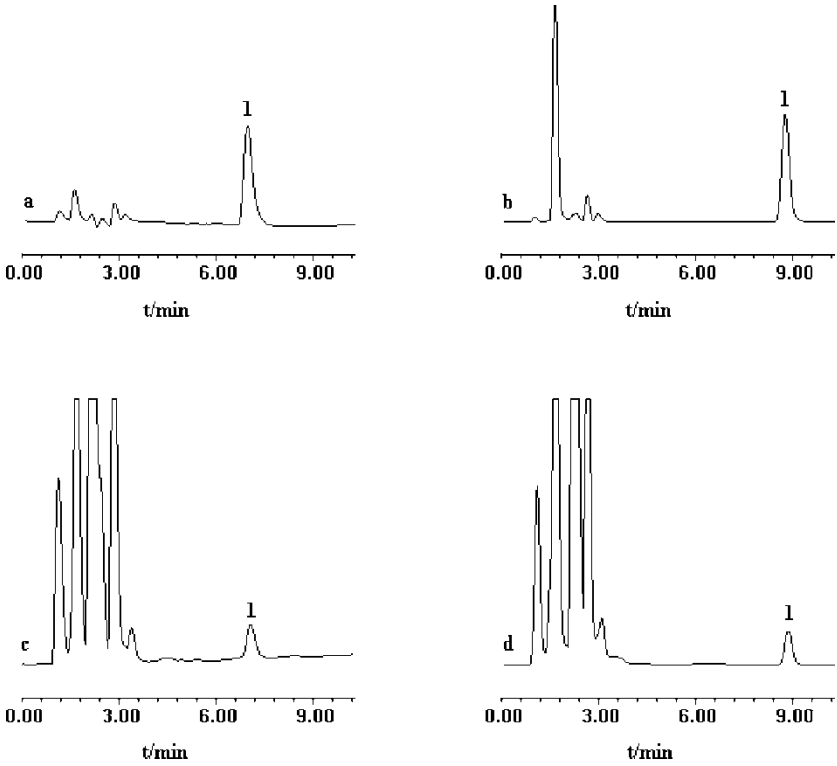


Figure 1. Chromatograms of laurocapram standard solution and hypertonic triazophos EC sample solution. Column: Kromasil C_{18}, 5 μm, 150 × 4.6 mm (I.D.). Column temperature: 30°C. Mobile phase: methanol-water (92 : 8, v/v) (a, c); acetonitrile-water (90 : 10, v/v) (b, d). Flow rate: 1.0 mL/min. Injection volume: 10 μL. Wavelength used for UV detection: 210 nm. a, b. Laurocapram standard solution; c, d. Hypertonic triazophos EC sample solution. Sensitivity: a, c. S/N = 1000; b, d. S/N = 4500. Peak: 1. laurocapram.

detection wavelength (210 nm) used yields stronger absorption of those ingredients, as well as the trace impurities in laurocapram standard. Even so, laurocapram is distinctly separated, which is the basis of quantitative determination.

Linear Range and Detection Limit

Linearity between peak areas versus amounts of laurocapram was obtained in the concentration range of 0.001∼0.1 mg/mL and 0.00005∼0.1 mg/mL, respectively, with methanol-water (92 : 8, v/v) and acetonitrile-water (90 : 10, v/v) as the mobile phases. The linear equations and correlation coefficients, as well as detection limits calculated at signal-to-noise ratio of 3 (S/N = 3), are shown in Table 1.

Table 1. Regression equations and detection limits of laurocapram

Mobile Phase	Regression equation	r	Detection limit, mg/mL
Methanol-water (92 : 8, v/v)	$A = -2344.7500 + 9.8956E7C$	0.9998	2.50×10^{-4}
Acetonitrile-water (90 : 10, v/v)	$A = -4117.3892 + 8.7162E7C$	0.9998	1.25×10^{-5}

Result of Sample Analysis

One sample of hypertonic triazophos EC commercial product was analyzed for laurocapram content under two elution conditions (Figure 1c and 1d). The quantitation was based on the standard curve (peak areas). The contents of laurocapram obtained, intra-day and inter-day, shown in Table 2, were obtained from the triplicate analyses.

The recovery was evaluated by adding known amounts of laurocapram to sample solution and analyzing by the same HPLC method. It can be seen from Table 3 that the recovery data were 100.7∼102.2% and 99.5∼101.6%, respectively, with methanol-water (92 : 8, v/v) and acetonitrile-water (90 : 10, v/v) as the mobile phases. The quantitation of laurocapram had no interferences, due to the good separation from other components in hypertonic triazophos EC.

Optimization of Chromatographic Conditions

Organic Modifier in Mobile Phase

Various methanol or acetonitrile concentrations in the mobile phase were varied to search for optimum separation conditions. The retention time of laurocapram was increased rapidly with a decrease of methanol content and, in contrast, slowly with the decrease of acetonitrile content. The two

Table 2. Determination of laurocapram in real sample (%, n = 3)

	Intra-day			Inter-day		
Mobile phase	Content	Average	RSD	Content	Average	RSD
Methanol-water (92 : 8, v/v)	1.78, 1.78, 1.77	1.78	0.32	1.78, 1.76, 1.77	1.77	0.57
Acetonitrile-water (90 : 10, v/v)	1.72, 1.72, 1.73	1.72	0.34	1.72, 1.71, 1.74	1.73	0.89

Table 3. Recovery of laurocapram in hypertonic triazophos EC (n = 5)

Mobile phase	Original (mg/L)	Added (mg/L)	Found (mg/L)	Recovery (%)	RSD (%)
Methanol-water	20.43	10.00	30.56	100.6	0.14
(92 : 8, v/v)	20.57	20.00	40.75	100.9	0.19
	20.28	30.00	60.76	102.4	0.09
Acetonitrile-water	19.80	10.00	29.85	100.3	0.13
(90 : 10, v/v)	19.94	20.00	39.83	99.5	0.03
	19.65	30.00	60.20	102.8	0.53

lines intersect where the concentration of the two organic modifiers in the mobile phase was approximately 90% (v/v) (Figure 2). When 92% methanol was employed, a satisfactory separation was obtained. If 92% acetonitrile was used, there was a peak of impurity in the hypertonic triazophos EC sample near the peak of laurocapram. So, 90% acetonitrile was selected.

Detection Wavelength

The strongest absorption peak can be found at 202.6 nm from the PDA spectrum of laurocapram. The wavelength of 210 nm was chosen because of the optimum signal-to-noise ratio.

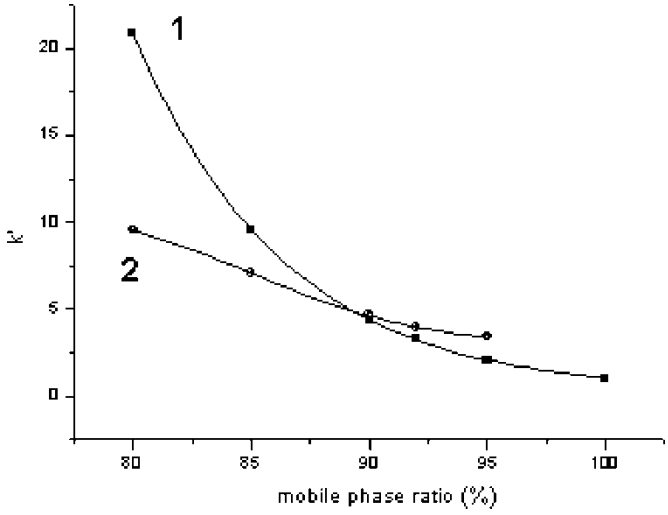


Figure 2. Influence of organic modifier contents in mobile phase on retention of laurocapram. Other chromatographic conditions as in Figure 1. 1) methanol-water; 2) acetonitrile-water.

CONCLUSIONS

The content of laurocapram in hypertonic triazophos EC was determined by reversed phase high performance liquid chromatography with two elution systems. Detection was performed at 210 nm. There are lower background absorbance, smoother baseline, lower detection limit and shorter equilibrium time with the mobile phase of acetonitrile-water. However, the price of acetonitrile is much higher than that of methanol. So, it is economical to use methanol as the organic modifier. Moreover, the result with methanol as the organic modifier is satisfactory for the Department of Quality Inspection of a factory.

ACKNOWLEDGMENT

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