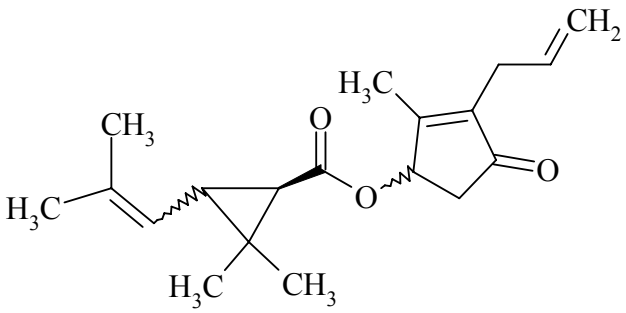
d-ALLETHRIN
742



ISO common name	Not available
Other names	*d*-Allethrin (used by WHO)
Chemical name	(*RS*)-3-Allyl-2-methyl-4-oxocyclopent-2-enyl (*1R*)-*cis, trans*-chrysanthemate (IUPAC); 2-methyl-4-oxo-3- (2-propenyl)-2-cyclopent-1-yl (*1R*)-*cis, trans*-2,2-dimethyl- 3-(2-methyl-1-propenyl) cyclo propanecarboxylate (CA, proposed; *584-79-2*)
Empirical formula	$C_{19}H_{26}O_3$
RMM	302.4
b.p.	281.5 °C
v.p.	1.65×10^{-4} Pa at 21.6 °C
Solubility	In water: 5.0 mg/l at 25 °C (pH 5.9-6.0), soluble in organic solvents

Note: *d*-Allethrin is a mixture of the isomers (1*R-trans, R*), (1*R-trans, S*), (1*R-cis, R*) and (1*R-cis, S*) of allethrin in an approximate ratio of 4:4:1:1. In practice the trans isomer range is 75-85 % and the cis isomer range is 15-25 %.

d-ALLETHRIN TECHNICAL
[*] **742**/TC/M/-

1 Sampling. Take at least 100 g.

2 Identity tests

2.1 GLC. Use the GLC method below. The relative retention time of *d*-allethrin with respect to the internal standard for the sample solution should not deviate by more than 1 % from that for the calibration solution (Fig. 6).

2.2 HPLC. Use the HPLC method below. The retention time of *d*-allethrin for the sample solution should not deviate by more than 5 % from that for the *d*-allethrin working standard solution and the intensities of the *d*-allethrin isomers should give the same pattern as in the working standard solution (Fig. 5).

REAGENTS

Hexane HPLC grade

Ethanol HPLC grade

d-Allethrin working standard technical product of certified purity. Store refrigerated.

Mobile phase hexane–ethanol, 1000 + 1 (v/v). Add by pipette ethanol (1 ml) to hexane (1000 ml); degas before use.

Working standard solution. Weigh 25 mg of *d*-allethrin working standard into a stoppered flask (100 ml). Add by measuring cylinder mobile phase (100 ml) and dissolve.

APPARATUS

High performance liquid chromatograph with a detector suitable for operation at 230 nm and an injector capable of delivering 2 µl

Column stainless steel, 250 × 4 (i.d.) mm, packed with Sumichiral OA-2000I (ionic bond type) (5 µm) obtainable from Sumika Chemical Analysis Service.

Electric integrator or *data system*

[*] CIPAC method 2004. Prepared by the Japanese PAC (JAPAC). Chairman: N.Tamori. Based on a method supplied by Sumitomo Chemical Company, Japan.

PROCEDURE

(a) Liquid chromatographic conditions (typical):

Mobile phase	hexane–ethanol, 1000 + 1 (v/v)
Column	two columns joined, each stainless steel, 250 × 4 (i.d.) mm, packed with Sumichiral OA-2000I, 5 µm
Flow rate	1.0 ml/min
Column temperature	ambient
Injection volume	2 µl
Detector wavelength	230 nm
Retention times	*cis* isomer: about 42 min
	S, 1*R*-*trans* isomer: about 46 min
	R, 1*S*-*trans* isomer: about 48 min
	R, 1*R*-*trans* isomer: about 50 min
	S, 1*S*-*trans* isomer: about 52 min

(b) System equilibration. Inject 2 µl portions of a working standard solution until the retention times obtained for two consecutive injections differ by less than 5 %.

(c) Preparation of sample solution. Weigh about 25 mg of sample into a stoppered flask (100 ml). Add by measuring cylinder mobile phase (100 ml) and dissolve.

3 *d*-Allethrin

OUTLINE OF METHOD *d*-allethrin is determined by capillary gas chromatography using flame ionisation detection and *m*-terphenyl as internal standard.

REAGENTS

Acetone

d-Allethrin working standard technical product of certified purity. Store refrigerated.

m-Terphenyl internal standard. Must not contain impurities with the same retention time as *d*-allethrin.

Internal standard solution. Dissolve *m*-terphenyl (1.2 g) in acetone (100 ml). Ensure that a sufficient quantity of this solution is prepared for all samples and calibration standards to be analysed.

Calibration solution. Prepare calibration solutions in duplicate. Weigh (to the nearest 0.1 mg) 90 to 110 mg (*s* mg) of *d*-allethrin working standard into a volumetric flask (100 ml). Add by pipette internal standard solution (5.0 ml) and dissolve. Make up to volume with acetone and mix well (Solutions C_A and C_B).

APPARATUS

Gas chromatograph equipped with a split/splitless injection and a flame ionisation detector

Capillary column fused silica, length: 30 m × 0.25 (i.d.) mm, film thickness: 0.25 µm, coated with crosslinked nitroterephthalic acid modified polyethylene glycol (DB-FFAP or equivalent)

Electric integrator or *data system*

PROCEDURE

(a) Gas chromatographic conditions (typical):

Column	fused silica, 30 m × 0.25 (i.d.) mm, film thickness: 0.25 µm, coated with crosslinked nitroterephthalic acid modified polyethylene glycol (DB-FFAP or equivalent)
Injection system	
Injector	split injection
Split flow	approximately 100 ml/min
Injection volume	1 µl
Detector	flame ionisation
Temperatures	
Column oven	240 °C
Injection port	250 °C
Detector	250 °C
Carrier gas	helium, 35 cm/s
Retention times	*d*-allethrin: about: 4.5 min
	m-terphenyl: about: 10.7 min

(b) Linearity check. Check the linearity of the detector response by injecting 1 µl of solutions with *d*-allethrin concentrations 0.5, 1 and 2 times that of the calibration solution before conducting the analysis.

(c) System equilibration. Prepare two calibration solutions. Inject 1 µl portions of the first one until the response factors obtained for two consecutive injections differ by less than 1.0 %. Then inject a 1 µl portion of the second solution. The response factor for this solution should not deviate by more than 1.0 % from that of the first calibration solution, otherwise prepare new calibration solutions.

(d) Preparation of sample solution. Prepare sample solutions in duplicate for each sample. Weigh (to the nearest 0.1 mg) 90 to 110 mg (*w* mg) of sample into a volumetric flask (100 ml). Add by pipette internal standard solution (5.0 ml) and dissolve. Make up to volume with acetone and mix well (Solutions S_A and S_B).

(e) Determination. Inject in duplicate 1 µl portions of each sample solution bracketing them by injections of the calibration solutions as follows:
calibration solution C_A, sample solution S_A, sample solution S_A, calibration solution C_B, sample solution S_B, sample solution S_B, calibration solution C_A, and so on. Measure the relevant peak areas.

(f) Calculation. Calculate the mean value of each pair of response factors bracketing the two injections of a sample and use this value for calculating the *d*-allethrin contents of the bracketed sample injections.

$$f_i = \frac{I_r \times s \times P}{H_s}$$

$$\text{Content of } d\text{-allethrin} = \frac{f \times H_w}{I_q \times w} \text{ g/kg}$$

where:
f_i = individual response factor
f = mean response factor
H_s = peak area of *d*-allethrin in the calibration solution
H_w = peak area of *d*-allethrin in the sample solution
I_r = peak area of the internal standard in the calibration solution
I_q = peak area of the internal standard in the sample solution
s = mass of *d*-allethrin working standard in the calibration solution (mg)
w = mass of sample taken (mg)
P = purity of *d*-allethrin working standard (g/kg)

Repeatability r = 12 g/kg at 953 g/kg active ingredient content
Reproducibility R = 37 g/kg at 953 g/kg active ingredient content

d-ALLETHRIN LIQUID VAPORISER
[*] **742**/LV/M/-

1 Sampling. Take at least 500 ml.

2 Identity tests
2.1 GLC. As for **742**/TC/M/2.
2.2 HPLC. As for **742**/TC/M/2 except:

(c) Preparation of sample solution. Weigh sufficient sample to contain 25 mg of *d*-allethrin into a volumetric flask (100 ml). Make up to volume with mobile phase and mix well.

[*] CIPAC method 2004. Prepared by the Japanese PAC (JAPAC). Chairman: N.Tamori. Based on a method supplied by Sumitomo Chemical Company, Japan.

3 *d-allethrin*. As for **742**/TC/M/3 except:

(d) Preparation of sample solution. Weigh (to the nearest 0.1 mg) sufficient sample to contain 90 to 110 mg (*w* mg) of *d*-allethrin into a volumetric flask (100 ml). Add by pipette internal standard solution (5.0 ml) and dissolve. Make up to volume with acetone and mix well (Solutions S_A and S_B).

Repeatability r = 0.4 g/kg at 33.8 g/kg active ingredient content
Reproducibility R = 0.77 g/kg at 33.8 g/kg active ingredient content

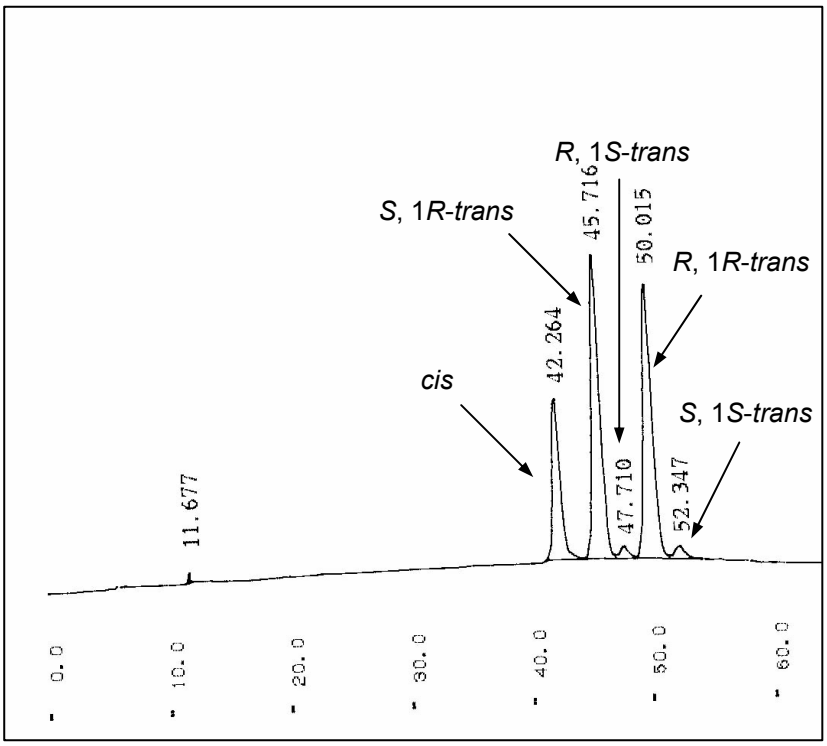


Fig. 5 HPLC chromatogram of *d*-allethrin working standard

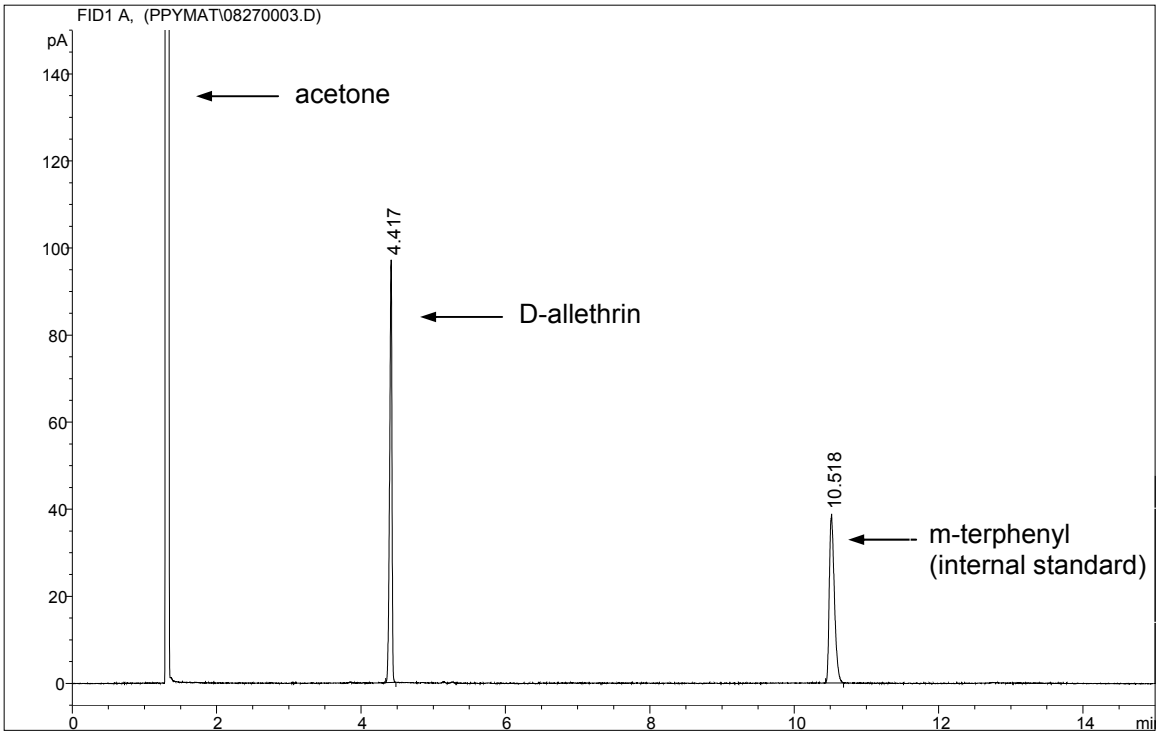


Fig. 6 Gas chromatogram of *d*-allethrin TC

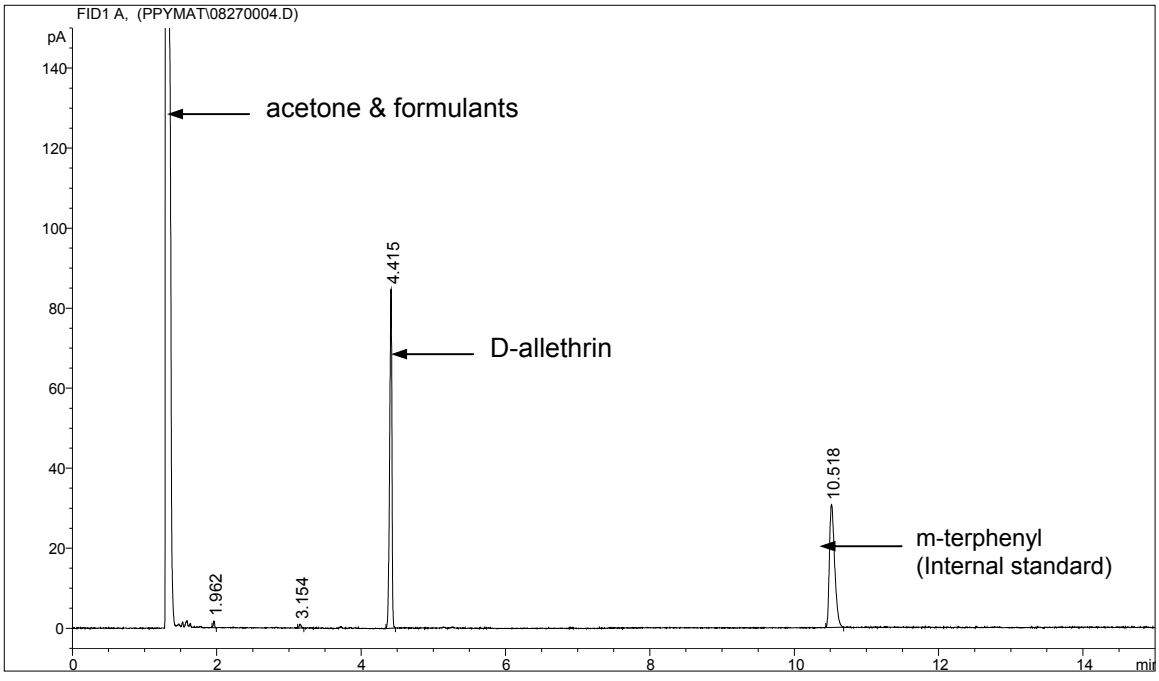


Fig. 7 Gas chromatogram of *d*-allethrin LV